CHAPTER 13

ELASTIC DUMBBELL MODELS

This chapter is intended to provide an overview of the kinetic theory of polymers by using an ultrasimplified model for a polymer molecule, namely an elastic dumbbell. In equilibrium systems one can write down a formal expression for the configurational distribution function directly by means of equilibrium statistical mechanics. For nonequilibrium systems, on the other hand, the situation is much more complicated; the best we can do, in general, is to derive a second-order partial differential equation (called the "diffusion equation") for the configurational distribution function. Only for particularly simple macromolecular models has this equation been solved analytically.

Once the configurational distribution function has been obtained (usually by means of perturbation theory or by numerical methods), one then needs an expression for the stress tensor in order to make the connection with rheological behavior and fluid dynamics. This stress tensor expression accounts for the various mechanisms by which forces are transmitted through the fluid.

In §13.1 we describe in some detail the way in which a flowing polymer solution is to be modeled and the assumptions that are made in setting up the kinetic theory. Then in §13.2 and §13.3 we give the two main parts of the kinetic theory: (1) the establishment of the "diffusion equation" for the configurational distribution function, and (2) the development of an expression for the stress tensor. All of this is done for any kind of elastic dumbbell, that is, the force law for the spring is not specified. The kinetic theories discussed in later chapters also consist of the same two main parts.

In §13.4 we take the spring to be "Hookean," the tension in the spring being proportional to the bead separation; we then show that the equations for this particularly simple model can be solved exactly. In fact, we are able to get a complete constitutive equation and then all of the rheological properties for the model system. By contrast, in §13.5 we take the spring to be nonlinear; for this slightly more complicated model we obtain only a perturbation solution for steady, homogeneous flows and a numerical solution for steady shear flow.

In §13.6 we take up the subject of "hydrodynamic interaction," which accounts for the fact that the beads of the dumbbell perturb the flow field in the neighborhood of the dumbbell. Inclusion of hydrodynamic interaction makes the theory somewhat more involved, but several approximate procedures are available to take this effect into account. Finally in §13.7 we examine some of the consequences of allowing the hydrodynamic drag and Brownian motion to be anisotropic; such effects would be expected to be important in the modeling of concentrated systems and melts.

Much of what we do in this chapter is used directly in Chapter 15, where we deal with bead-spring chains. In that chapter it is found that chains with Hookean springs have a rheological response equivalent to a set of Hookean dumbbells with a spectrum of time

constants. In addition the notation, physical ideas, and general procedures will carry over directly into this later development.

§13.1 MODELING OF SOLUTIONS OF FLEXIBLE POLYMERS

We are concerned here with a dilute solution of a polymer, with n polymer molecules per unit volume. The solvent is taken to be a Newtonian fluid[1] with viscosity η_s. Throughout most of the chapter it is assumed that the solution is sufficiently dilute that the polymer molecules do not interact with one another.

In this chapter we idealize the polymer molecule as an elastic dumbbell—two beads, each of mass m, joined by a nonbendable spring. The beads are labeled "1" and "2" and their instantaneous locations in space are called $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The "connector vector," $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, describes the overall orientation and the internal configuration of the polymer molecule. We may thus describe the configuration either by specifying $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ or by giving $\boldsymbol{r}_c$ and $\boldsymbol{Q}$. Further comments on this model are given in §11.5.

The flow field of the polymer solution is taken to be homogeneous, in the sense that the rate-of-strain tensor is the same at all points in the flow field. Therefore we can always write the mass-average velocity of the solution as $\boldsymbol{v} = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}]$ where $\boldsymbol{v}_0$ is a vector independent of position, $\boldsymbol{r}$ is the position vector, and $\boldsymbol{\kappa}$ is a traceless tensor that is independent of position but that may depend on the time t; the requirement that $\text{tr}\,\boldsymbol{\kappa} = 0$ is needed because the fluid is assumed to be incompressible. Table 13.1-1 gives several examples of homogeneous velocity fields that are used in the kinetic theory discussions in this volume. The assumption of a homogeneous velocity field is normally not a serious one; it is only when the velocity gradient changes appreciably over a distance comparable to the size of the polymer molecule that this assumption has to be avoided.

It has been customary in most kinetic theories to assume that the phase-space distribution function can be written as the product of a configuration-space distribution function and a velocity-space distribution function; it is then assumed further that the velocity-space distribution function is Maxwellian about the solution velocity at the center of mass of the dumbbell, and that the configuration-space distribution function is independent of the location of the center of mass of the polymer molecule. Although we will use these conventional assumptions throughout most of this chapter, we start by being somewhat more general.

We begin by replacing the distribution function $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{p}_1, \boldsymbol{p}_2, t)$ in the phase space by $F(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, t)$, the corresponding distribution function in position-velocity space. We then define the configuration-space distribution function $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$ by

$$F(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, t) = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)\Xi(\dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, \boldsymbol{r}_1, \boldsymbol{r}_2, t) \tag{13.1-1}$$

where the velocity-space distribution function Ξ satisfies the normalization condition $\iint \Xi\, d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2 = 1$. Then we assume that the configuration-space distribution functon Ψ can be factored

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = n\psi(\boldsymbol{Q}, t) \tag{13.1-2}$$

to indicate that the distribution of configurations is independent of the location of the dumbbells in space; the distribution function $\psi(\boldsymbol{Q}, t)$ satisfies the normalization condition $\int \psi(\boldsymbol{Q}, t) d\boldsymbol{Q} = 1$. If we wish to make the assumption that the velocity distribution is

[1] The use of a viscoelastic solvent has been considered by S. Hayashi, *J. Phys. Soc. Japan*, **19**, 2306 2312 (1964).

TABLE 13.1-1

Homogeneous Velocity Fields with $v_0 = 0$

Examples of the flow:

$$v_x = \kappa_{xx}x + \kappa_{xy}y + \kappa_{xz}z$$

$$v_y = \kappa_{yx}x + \kappa_{yy}y + \kappa_{yz}z$$

$$v_z = \kappa_{zx}x + \kappa_{zy}y + \kappa_{zz}z$$

where the κ_{ij} are possibly functions of time; it is required that $\sum_i \kappa_{ii} = 0$ because the fluid is incompressible.

Type of Flow	Velocity Components		Standard Abbreviations[a]	Reference to Chapter 3
Simple shear flows	$v_x = \kappa_{xy}y$ $v_y = 0$ $v_z = 0$	(A)	$\kappa_{xy} = \dot{\gamma}$	§3.1
Shearfree flows ($0 \le b \le 1$)	$v_x = -\frac{1}{2}\kappa_{zz}(1+b)x$ $v_y = -\frac{1}{2}\kappa_{zz}(1-b)y$ $v_z = \kappa_{zz}z$	(B)	$\kappa_{zz} = \dot{\varepsilon}$	§3.1
Eccentric disk (or orthogonal rheometer) flow	$v_x = -W\left(y - \frac{a}{b}z\right)$ $v_y = Wx$ $v_z = 0$	(C)	—	Problem 3B.1
Homogeneous, potential flows	$\boldsymbol{v} = -\nabla\Phi$, with $\Phi = -\frac{1}{2}(\boldsymbol{\kappa}:\boldsymbol{rr})$ and $\boldsymbol{\kappa} = \boldsymbol{\kappa}^\dagger$.	(D)	—	—

[a] The quantity $\dot{\gamma}$, called the "shear rate," is defined as $\dot{\gamma} = \sqrt{\frac{1}{2}(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}})}$ and is always positive. Hence for steady shear flows we can write $v_x = \dot{\gamma}y$, whereas for unsteady shear flows we use the more general notation $v_x(t) = \dot{\gamma}_{yx}(t)y$. The quantity $\dot{\varepsilon}$, on the other hand, may be positive or negative.

Maxwellian[2] about the mass-average velocity of the solution $\boldsymbol{v}$ at the center of mass of the dumbbell,[3] then we write

$$\Xi_{eq}(\dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2) = \frac{\exp\{-[\frac{1}{2}m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})^2 + \frac{1}{2}m(\dot{\boldsymbol{r}}_2 - \boldsymbol{v})^2]/kT\}}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp\{-[\frac{1}{2}m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})^2 + \frac{1}{2}m(\dot{\boldsymbol{r}}_2 - \boldsymbol{v})^2]/kT\} d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2} \tag{13.1-3}$$

This assumption is tantamount to saying that the velocity distribution in a flow system is the same as that in a solution at equilibrium; it is sometimes called the assumption of "equilibration in momentum space" (see §18.3(a)). It is essential that this assumption be

[2] This is consistent with Eq. 12.3-1 from which we get in general

$$\Xi_{eq} = \frac{e^{-\mathscr{H}/kT}}{\iint e^{-\mathscr{H}/kT}\, d\boldsymbol{p}_c\, dP} \tag{13.1-3a}$$

[3] One could assume a velocity distribution Maxwellian about $\boldsymbol{v}_v$, the solution velocity at bead v; it has been shown that, for chains with Hookean springs, the rheological properties are negligibly different from those calculated with Eq. 13.1-3 [R. B. Bird, X. J. Fan, and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **15**, 85 92 (1984)].

used only when absolutely necessary, and that turns out to be only in the Brownian motion term in the equation of motion and in the bead-momentum flux contribution to the stress tensor.

In this chapter we use the same notation for average values that we introduced in Chapter 12. A velocity-space average of a time-independent function $B(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2)$ is given by:

$$[\![B]\!] = \iint B\Xi \, d\dot{\boldsymbol{r}}_1 \, d\dot{\boldsymbol{r}}_2 \tag{13.1-4}$$

and this average is in general a function of $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, and t. The phase-space average of $B(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2)$ is then

$$\langle B \rangle = \frac{1}{nV} \iint [\![B]\!] \Psi \, d\boldsymbol{r}_1 \, d\boldsymbol{r}_2 \tag{13.1-5}$$

and this average is in general a function of the time t. These equations should be compared with Eqs. 12.4-2 and 12.4-3, respectively. Note that if B depends only on $\boldsymbol{Q}$, then $\langle B \rangle = \int B\psi \, d\boldsymbol{Q}$.

In the next section we write an equation of motion for each of the beads of the dumbbell. In so doing, it is assumed that the inertial term (that is, "mass × acceleration") can be neglected, because of the small mass and the sluggish motion of the beads as they move through the viscous medium. This neglect of inertia terms in the equation of motion is a standard assumption in the kinetic theories of polymers. Each bead is presumed to experience four kinds of forces:

a. *A hydrodynamic drag force* $\boldsymbol{F}_\nu^{(h)}$. This is the force of resistance experienced by a bead as it moves through the solution. A simple expression that we can use for this force is one that is reminiscent of Stokes' law; specifically, we take the drag force to be proportional to the difference between the (appropriately averaged) bead velocity and the mass-average velocity of the solution. More complicated expressions can be used that take into account hydrodynamic interaction (see §13.6) or that allow for anisotropy of the hydrodynamic drag (see §13.7). All these expressions are empiricisms that purport to account approximately for the very complex intermolecular forces between the polymer and solvent molecules.

b. *A Brownian force* $\boldsymbol{F}_\nu^{(b)}$. Because of thermal fluctuations in the liquid, the beads are jostled about in an irregular manner. The average of this rapidly fluctuating force can, however, be described by an expression that involves the configurational distribution function. The origin of this expression is far from obvious; in Chapter 18 it is derived from first principles, but in this chapter we accept it as a suitable way to describe the "time smoothed" Brownian force.

c. *An intramolecular force* $\boldsymbol{F}_\nu^{(\phi)}$. This is the force on one bead resulting from the "spring" in the dumbbell. This is given as the negative of the gradient of the spring potential energy ϕ. The various kinds of springs used in molecular models are summarized in Table 11.5-1.

d. *An external force* $\boldsymbol{F}_\nu^{(e)}$. Examples of external forces are gravitational and electrical forces. Artificial gravitational forces, such as those produced in an ultracentrifuge, are of particular interest in polymeric systems.

Explicit formulas for these forces are given in subsequent sections. Suffice it to say at this point that, roughly speaking, the hydrodynamic forces (and in some instances the external forces) tend to orient and distort the polymer molecule, the intramolecular forces tend to restore the molecule to its original shape, and Brownian forces tend to randomize the orientations of the molecules.

In this section we have described, mostly in words, the kind of modeling that is done in the kinetic theory that follows. It is evident that several assumptions are inherent in the theoretical development. At the very outset there is the choice of the molecular model used to represent the polymer molecule. Then there are the assumptions for the velocity distribution function and the expression for the hydrodynamic drag. All of these elements of the theory can be and are being challenged. Attempts to improve the modeling add considerably to the complexity of the theory and calculations, but the basic framework of the theory remains unchanged.

§13.2 THE "DIFFUSION EQUATION" FOR THE CONFIGURATIONAL DISTRIBUTION FUNCTION

As mentioned in the introduction to this chapter, the kinetic theory consists of two main parts, one of which is the development of an equation for the configurational distribution function. This second-order partial differential equation is called the "diffusion equation," since it describes how the system points "diffuse" in the multidimensional configuration space appropriate for the molecular model. It has nothing to do with the spatial movement of the centers of mass of the polymer molecules in three-dimensional space. This diffusion equation is obtained by combining the equations of motion of the beads with an equation of continuity that describes the conservation of system points in the configuration space.

a. The Equations of Motion for the Beads of the Dumbbell

We can write an equation of motion for each bead of the dumbbell indicating that the mass of the bead times its acceleration is equal to the sum of all forces acting on the bead. When we neglect the inertial terms containing the bead masses, we get a "force balance" among the four forces described qualitatively in the foregoing section:

$$\boldsymbol{F}_v^{(h)} + \boldsymbol{F}_v^{(b)} + \boldsymbol{F}_v^{(\phi)} + \boldsymbol{F}_v^{(e)} = \boldsymbol{0} \qquad (v = 1, 2) \tag{13.2-1}$$

in which

$$\boldsymbol{F}_v^{(h)} = -\zeta \cdot [[\dot{\boldsymbol{r}}_v]] - (\boldsymbol{v}_v + \boldsymbol{v}'_v)] \tag{13.2-2}$$

$$\boldsymbol{F}_v^{(b)} = -\frac{1}{\Psi}\frac{\partial}{\partial \boldsymbol{r}_v} \cdot [[m(\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v})]\Psi] \tag{13.2-3}$$

$$\boldsymbol{F}_v^{(\phi)} = -\frac{\partial}{\partial \boldsymbol{r}_v}\phi \tag{13.2-4}$$

We now discuss each of the contributions to the force balance.

Equation 13.2-2 describes the hydrodynamic force acting on bead v. According to this expression the force is proportional to the difference between the bead velocity $\dot{\boldsymbol{r}}_v$ (appropriately averaged with respect to the velocity distribution) and the velocity $(\boldsymbol{v}_v + \boldsymbol{v}'_v)$ of the solution at bead v. The velocity $\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_v]$ is the imposed homogeneous flow field at bead v, and $\boldsymbol{v}'_v$ is the perturbation of the flow field at bead v resulting from the motion of the other bead; this perturbation is referred to as "hydrodynamic interaction." Throughout most of this chapter we neglect hydrodynamic interaction and $\boldsymbol{v}'_v$. We note further that,

according to Eq. 13.2-2, the hydrodynamic drag force is not necessarily collinear with the velocity difference, since the coefficient of proportionality is a symmetric second-order tensor $\boldsymbol{\zeta}$, called the "friction tensor." In most of this chapter we take this tensor to be isotropic, so that $\boldsymbol{\zeta} = \boldsymbol{\delta}\zeta$, where the scalar ζ is called the "friction coefficient." The beads actually execute very tortuous paths as they move about in the solvent, but by using the velocity average of $\dot{\boldsymbol{r}}_\nu$ we obtain a kind of "smoothed out" drag force. It must be emphasized that we do not evaluate this velocity-averaged quantity $[\![\dot{\boldsymbol{r}}_\nu]\!]$ by using the Maxwell velocity distribution, since this would give the fluid velocity $\boldsymbol{v}$; it turns out that it is not necessary to evaluate this average explicitly inasmuch as this quantity is substituted later into the equation of continuity.

Equation 13.2-3 represents the force associated with Brownian motion (see §18.3b). The true Brownian motion force would be a rapidly and irregularly fluctuating function. Instead of the latter we use a statistically averaged force, the origin of which can be understood from the complete phase-space kinetic theory given in Chapter 18. It should be noted that the expression for the Brownian force has the form of the divergence of a momentum flux with respect to the solution velocity $\boldsymbol{v}$ at the center of mass of the dumbbell. In almost all kinetic theories published so far, equilibration in momentum space has been tacitly assumed; that is, Eq. 13.1-3 is used to evaluate the velocity space average in Eq. 13.2-3. When this is done the Brownian force contribution assumes the much simpler form $\boldsymbol{F}_\nu^{(b)} = -kT(\partial \ln \Psi/\partial \boldsymbol{r}_\nu)$. It is this standard expression that we use in this chapter, except in the last section.

Equation 13.2-4 gives the force $\boldsymbol{F}_\nu^{(\phi)}$ on the νth bead resulting from the intramolecular potential energy. For the simple model under consideration this is just the force acting through the spring in the dumbbell. Expressions for the intramolecular potentials of dumbbells are given in Table 11.5-1. For the dumbbell models the forces on the two beads are equal and opposite, so that it is useful to define a "connector force" $\boldsymbol{F}^{(c)}$ *by* $\boldsymbol{F}^{(c)} = \boldsymbol{F}_1^{(\phi)} = -\boldsymbol{F}_2^{(\phi)}$.

If we now assume that the friction tensor is a multiple of the unit tensor, and if the Maxwellian velocity distribution is used in the Brownian motion term, then the equation of motion becomes

$$-\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu]) - kT\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln \Psi + \boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)} = \boldsymbol{0} \qquad (\nu = 1, 2) \qquad (13.2\text{-}5)$$

When these two equations are added together[1] and then divided by 2, we get the equation of motion for the center of mass $\boldsymbol{r}_c = \frac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$; when they are subtracted,[1] we get the equation of motion for the dumbbell connector vector $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$:

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_c] + \frac{1}{2\zeta}\sum_\nu \boldsymbol{F}_\nu^{(e)} \qquad (13.2\text{-}6)$$

$$[\![\dot{\boldsymbol{Q}}]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{Q}] - \frac{2kT}{\zeta}\frac{\partial}{\partial \boldsymbol{Q}}\ln\psi - \frac{2}{\zeta}\boldsymbol{F}^{(c)} + \frac{1}{\zeta}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}] \qquad (13.2\text{-}7)$$

[1] In doing these operations we need to use Eq. 13.1-2 and the chain rule of partial differentiation (see §E.1):

$$\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi = \left(\frac{\partial}{\partial \boldsymbol{r}_\nu}\boldsymbol{r}_c\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_c}\ln n\psi + \left(\frac{\partial}{\partial \boldsymbol{r}_\nu}\boldsymbol{Q}\right)\cdot\frac{\partial}{\partial \boldsymbol{Q}}\ln n\psi \qquad (13.2\text{-}5a)$$

Then $(\partial/\partial \boldsymbol{r}_c)\ln n\psi = \boldsymbol{0}$ since n is assumed to be constant (i.e., no concentration gradients) and $\psi = \psi(\boldsymbol{Q}, t)$; furthermore $(\partial/\partial \boldsymbol{r}_1)\boldsymbol{Q} = -\boldsymbol{\delta}$ and $(\partial/\partial \boldsymbol{r}_2)\boldsymbol{Q} = +\boldsymbol{\delta}$.

The first of these equations shows that, in the absence of external forces, the center of mass of the dumbbell moves on the average with the solution velocity at the location of the center of mass. The second equation is used presently to obtain the diffusion equation for $\psi(\boldsymbol{Q}, t)$. For the remainder of this discussion it is assumed that the external forces $\boldsymbol{F}_v^{(c)}$ are independent of $\boldsymbol{r}_c$.

b. The Equation of Continuity for $\psi(\boldsymbol{Q}, t)$

The location and orientation of a single dumbbell is given by specifying x_1, y_1, z_1 and x_2, y_2, z_2 for the locations of the beads. This set of six coordinates can be represented as a single "system point" in a six-dimensional configuration space. For a solution containing a large number of dumbbells, the time rate of change of system points within a six-dimensional hypercube of volume $\Delta x_1\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2$ is

$$\frac{\partial}{\partial t} \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) \Delta x_1\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2 \tag{13.2-8}$$

The rate at which system points enter the hypercube is

$$\begin{aligned}(\llbracket \dot{x}_1 \rrbracket \Psi)|_{x_1}\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2 - (\llbracket \dot{x}_1 \rrbracket \Psi)|_{x_1 + \Delta x_1}\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2 \\ + \text{10 additional terms describing motion in the other five coordinate directions}\end{aligned} \tag{13.2-9}$$

These two expressions can now be equated and then divided by $\Delta x_1\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2$; when Δx_1, Δy_1, and so on, are allowed to approach zero, we then get

$$\frac{\partial \Psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{r}_1} \cdot \llbracket \dot{\boldsymbol{r}}_1 \rrbracket \Psi\right) - \left(\frac{\partial}{\partial \boldsymbol{r}_2} \cdot \llbracket \dot{\boldsymbol{r}}_2 \rrbracket \Psi\right) \tag{13.2-10}$$

which is called the *equation of continuity* for Ψ, because of its similarity with the equation of continuity in hydrodynamics. This equation can be rewritten in terms of $\boldsymbol{r}_c$ and $\boldsymbol{Q}$:

$$\frac{\partial \Psi}{\partial t} = -\underline{\left(\frac{\partial}{\partial \boldsymbol{r}_c} \cdot \llbracket \dot{\boldsymbol{r}}_c \rrbracket \Psi\right)} - \left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \llbracket \dot{\boldsymbol{Q}} \rrbracket \Psi\right) \tag{13.2-11}$$

When Eqs. 13.2-6 and 13.1-2 are used, it is found that the dashed-underlined term is zero, so that we finally obtain

$$\frac{\partial \psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \llbracket \dot{\boldsymbol{Q}} \rrbracket \psi\right) \tag{13.2-12}$$

It is this form of the equation of continuity that we need presently.

c. The "Diffusion Equation" for $\psi(\boldsymbol{Q}, t)$

Substitution of $[\![\dot{\boldsymbol{Q}}]\!]$ from Eq. 13.2.7 into Eq. 13.2-12 gives the *diffusion equation*:[2]

$$\boxed{\frac{\partial \psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \left\{[\boldsymbol{\kappa} \cdot \boldsymbol{Q}]\psi - \frac{2kT}{\zeta}\frac{\partial}{\partial \boldsymbol{Q}}\psi - \frac{2}{\zeta}\boldsymbol{F}^{(c)}\psi + \frac{1}{\zeta}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\psi\right\}\right)} \tag{13.2-13}$$

This is the second-order partial differential equation that describes the way in which the distribution of configurations changes with time when the time-dependent homogeneous velocity field is specified by $\boldsymbol{\kappa}(t)$.

Before leaving the diffusion equation for ψ, which was the principal goal of this section, we point out that two important results may be obtained from Eq. 13.2-13 without specifying the nature of the spring force. First, for the steady-state, homogeneous, potential flow of a dilute solution of dumbbells with any physically reasonable spring force law and with no external forces, the diffusion equation has the solution[3,4]

$$\begin{aligned}\psi(\boldsymbol{Q}) &= \left[\frac{1}{J_{eq}} e^{-\phi^{(c)}/kT}\right]\left[\frac{J_{eq}}{J} e^{(\zeta/4kT)(\boldsymbol{\kappa}:\boldsymbol{Q}\boldsymbol{Q})}\right] \\ &\equiv \psi_{eq}\phi_{fl}\end{aligned} \tag{13.2-14}$$

Here J_{eq} is the normalization constant for the equilibrium distribution function ψ_{eq}, and J is that for the nonequilibrium distribution function; J depends on the parameters appearing in the spring connector force $\boldsymbol{F}^{(c)} = +\partial\phi^{(c)}/\partial\boldsymbol{Q}$ as well as on the constants describing the flow field through the tensor $\boldsymbol{\kappa}$. The potential-flow distribution is the product of the equilibrium distribution function ψ_{eq} and a dimensionless factor ϕ_{fl} that contains information about the flow pattern.

Second, we can multiply Eq. 13.2-13 by any function of the connector vector, $B(\boldsymbol{Q})$, and then integrate over all the configuration space. This gives the *equation of change* for $\langle B \rangle$:

$$\begin{aligned}\frac{d}{dt}\langle B\rangle = &\left(\boldsymbol{\kappa}:\left\langle \boldsymbol{Q}\frac{\partial}{\partial \boldsymbol{Q}}B\right\rangle\right) + \frac{2kT}{\zeta}\left\langle\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)\right\rangle - \frac{2}{\zeta}\left\langle\left(\boldsymbol{F}^{(c)}\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)\right\rangle \\ &+ \frac{1}{\zeta}\left\langle\left([\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)\right\rangle\end{aligned} \tag{13.2-15}$$

[2] Note that Eq. 13.2-13 (with no external forces) can be rearranged as

$$\frac{\partial \psi}{\partial t} + \left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\frac{\partial}{\partial \boldsymbol{Q}}\psi\right) = \frac{2kT}{\zeta}\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\frac{\partial}{\partial \boldsymbol{Q}}\psi\right) + \frac{2}{\zeta}\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\boldsymbol{F}^{(c)}\psi\right) \tag{13.2-13a}$$

This is similar in form to a diffusion equation with the "convective" terms on the left, and the "diffusive" and "source" terms on the right; in the diffusive term the *rotatory diffusivity* is given by

$$D_{rot} = \frac{2kT}{\zeta} \tag{13.2-13b}$$

with dimensions (length)^2/time. It is thus clear why Eq. 13.2-13 is called the *diffusion equation for* ψ. The D_{rot} in Eq. 13.2-13b is *not* the (translational) diffusivity for the diffusion of dumbbells through the solvent, which is $D_{tr} = kT/2\zeta$. For a discussion of translational diffusivity see Example 13.6-2 and §18.4; see also H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), pp. 271–272, 279–280.

[3] R. B. Bird, M. W. Johnson, Jr., and C. F. Curtiss, *J. Chem. Phys.*, **51**, 3023–3026 (1969).

[4] J. F. Stevenson and R. B. Bird, *Trans. Soc. Rheol.*, **15**, 135–145 (1971).

The details of the integration are given in Example 13.2-1. In obtaining this equation, use is made of the fact that ψ approaches zero rapidly enough as $\boldsymbol{Q}$ goes to infinity that surface integrals can be discarded. A similar relation holds for a tensor function $\mathbf{B}(\boldsymbol{Q})$ of any order. We shall be particularly interested in the case where $\mathbf{B}$ is the second-order tensor $\boldsymbol{QQ}$:

$$\frac{d}{dt}\langle \boldsymbol{QQ}\rangle - \{\boldsymbol{\kappa}\cdot\langle \boldsymbol{QQ}\rangle\} - \{\langle \boldsymbol{QQ}\rangle\cdot\boldsymbol{\kappa}^{\dagger}\} = \frac{4kT}{\zeta}\,\boldsymbol{\delta} - \frac{4}{\zeta}\langle \boldsymbol{QF}^{(c)}\rangle + \frac{1}{\zeta}\langle[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\boldsymbol{Q} + \boldsymbol{Q}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\rangle \quad (13.2\text{-}16)$$

or

$$\langle \boldsymbol{QQ}\rangle_{(1)} = \frac{4kT}{\zeta}\,\boldsymbol{\delta} - \frac{4}{\zeta}\langle \boldsymbol{QF}^{(c)}\rangle + \frac{1}{\zeta}\langle(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\boldsymbol{Q} + \boldsymbol{Q}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\rangle \quad (13.2\text{-}17)$$

That is, we designate the left side of Eq. 13.2-16 by the abbreviation $\langle \boldsymbol{QQ}\rangle_{(1)}$ given in Appendix D, Eq. D.2-4a; this is consistent with the notation for "convected time derivatives" introduced in Chapter 9, although no use of the theory of such derivatives will be needed here. To understand the connection with the notation of Chapter 9, note that the term $\{\boldsymbol{v}\cdot\nabla\langle \boldsymbol{QQ}\rangle\}$ is identically zero for homogeneous flows, and that $\nabla\boldsymbol{v} = \boldsymbol{\kappa}^{\dagger}$ and $(\nabla\boldsymbol{v})^{\dagger} = \boldsymbol{\kappa}$. Finally we note that, in a system at equilibrium (that is, $\boldsymbol{\kappa} = \mathbf{0}$ and $\boldsymbol{F}_v^{(e)} = \mathbf{0}$), Eq. 13.2-17 gives

$$\langle \boldsymbol{QF}^{(c)}\rangle_{\text{eq}} = kT\,\boldsymbol{\delta} \quad (13.2\text{-}18)$$

a result we need in the next section.

EXAMPLE 13.2-1 Time Rate of Change of Average Values

Derive Eq. 13.2-15 for the "equation of change for $\langle B\rangle$" in the absence of external forces.

SOLUTION First, we multiply Eq. 13.2-12 by B and integrate over the entire configuration space:

$$\int B\frac{\partial\psi}{\partial t}\,d\boldsymbol{Q} = -\int\left(\frac{\partial}{\partial\boldsymbol{Q}}\cdot[\![\dot{\boldsymbol{Q}}]\!]\psi\right)B\,d\boldsymbol{Q} \quad (13.2\text{-}19)$$

Because B is independent of t, the time derivative can be taken outside the integral on the left side. The integral on the right side can be rearranged:

$$\frac{d}{dt}\int B\psi\,d\boldsymbol{Q} = -\int\left(\frac{\partial}{\partial\boldsymbol{Q}}\cdot[\![\dot{\boldsymbol{Q}}]\!]\psi B\right)d\boldsymbol{Q} + \int\left([\![\dot{\boldsymbol{Q}}]\!]\psi\cdot\frac{\partial}{\partial\boldsymbol{Q}}B\right)d\boldsymbol{Q} \quad (13.2\text{-}20)$$

The first integral on the right side can be transformed into a surface integral by the use of the Gauss divergence theorem (see Appendix A), and the distribution function is zero on this infinitely large surface. Hence Eq. 13.2-20 becomes

$$\frac{d}{dt}\langle B\rangle = \left\langle\left([\![\dot{\boldsymbol{Q}}]\!]\cdot\frac{\partial}{\partial\boldsymbol{Q}}B\right)\right\rangle \quad (13.2\text{-}21)$$

Next we insert $[\![\dot{Q}]\!]$ from Eq. 13.2-7:

$$\frac{d}{dt}\langle B\rangle = \left\langle\left([\boldsymbol{\kappa}\cdot Q]\cdot\frac{\partial}{\partial Q}B\right)\right\rangle - \frac{2kT}{\zeta}\left\langle\left(\frac{\partial}{\partial Q}\ln\psi\cdot\frac{\partial}{\partial Q}B\right)\right\rangle - \frac{2}{\zeta}\left\langle\left(F^{(c)}\cdot\frac{\partial}{\partial Q}B\right)\right\rangle \tag{13.2-22}$$

The average value in the second term on the right side can be rewritten as

$$\begin{aligned}\int\left(\frac{\partial}{\partial Q}\ln\psi\cdot\frac{\partial}{\partial Q}B\right)\psi\,dQ &= \int\left(\frac{\partial}{\partial Q}\psi\cdot\frac{\partial}{\partial Q}B\right)dQ \\ &= \int\left(\frac{\partial}{\partial Q}\cdot\psi\frac{\partial B}{\partial Q}\right)dQ - \int\psi\left(\frac{\partial}{\partial Q}\cdot\frac{\partial B}{\partial Q}\right)dQ \\ &= \int_{\substack{\text{surface}\\ \text{at } Q=\infty}}\left(\boldsymbol{n}\cdot\psi\frac{\partial B}{\partial Q}\right)dS - \left\langle\left(\frac{\partial}{\partial Q}\cdot\frac{\partial}{\partial Q}B\right)\right\rangle\end{aligned} \tag{13.2-23}$$

Here again the Gauss divergence theorem has been used, and the surface integral is zero. When this result is inserted into Eq. 13.2-22 and the term containing $\boldsymbol{\kappa}$ rearranged slightly, Eq. 13.2-15 (with no external force terms) is finally obtained.

§13.3 EXPRESSIONS FOR THE STRESS TENSOR

The total stress tensor $\boldsymbol{\pi}$ (as defined in Chapter 1) in a polymer solution is presumed to be the sum of a contribution from the solvent, $\boldsymbol{\pi}_s$, and another, $\boldsymbol{\pi}_p$, resulting from the presence of the polymer molecules (here idealized as elastic dumbbells):

$$\begin{aligned}\boldsymbol{\pi} &= \boldsymbol{\pi}_s + \boldsymbol{\pi}_p \\ &= (p_s\boldsymbol{\delta} + \boldsymbol{\tau}_s) + (p_p\boldsymbol{\delta} + \boldsymbol{\tau}_p) \\ &= p\boldsymbol{\delta} + \boldsymbol{\tau}\end{aligned} \tag{13.3-1}$$

where $p = p_s + p_p$ and $\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p = -\eta_s\dot{\boldsymbol{\gamma}} + \boldsymbol{\tau}_p$; here η_s is the solvent viscosity, $\dot{\boldsymbol{\gamma}} = \nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^\dagger$ is the rate-of-strain tensor and $\boldsymbol{\delta}$ is the unit tensor. The stress tensor $\boldsymbol{\tau}$ is zero at equilibrium. For additional comments see §D.6.

In order to obtain a kinetic theory expression for $\boldsymbol{\pi}_p$, we follow the elementary physical derivation provided by Kramers,[1] which we know from more elaborate and complete kinetic theory developments[2,3] accounts for the most important effects. The dumbbells will contribute to the stress in the suspension for three principal reasons: (1) an arbitrary plane in the suspension may at any moment be straddled by the two beads of the dumbbell, and there will in general be a force of tension or compression transmitted through the connector; (2) a similar contribution arises from the effects of different external forces acting on the two beads of the dumbbell straddling the plane; and (3) the beads themselves may cross the arbitrary plane and bring with them a certain amount of momentum. The resulting connector, external force, and bead contributions to the stress

[1] H. A. Kramers, *Physica*, **11**, 1–19 (1944); *J. Chem. Phys.*, **14**, 415–424 (1946); see also R. B. Bird, H. R. Warner, Jr. and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971).

[2] See Chapters 17 and 18, which are an updated version of C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (1976).

[3] C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191–204 (1983); R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983).

tensor will be labeled $\pi_p^{(c)}$, $\pi_p^{(e)}$, and $\pi_p^{(b)}$. There may be still other mechanisms by which the polymer molecule contributes to the stress tensor, but these can be discovered only by taking a more fundamental approach to the subject.[2]

a. Contribution from the Intramolecular Potential, $\pi_p^{(c)}$

Consider an arbitrary plane of area S in the solution moving with the local solution velocity v; the orientation of the plane is given by a unit vector n. See Fig. 13.3-1*a* for the specification of the nomenclature and sign convention. First we ask the question: how many dumbbells with connector vector Q will be straddling the plane, with bead "1" on the negative side and bead "2" on the positive side? This quantity is given by the product of

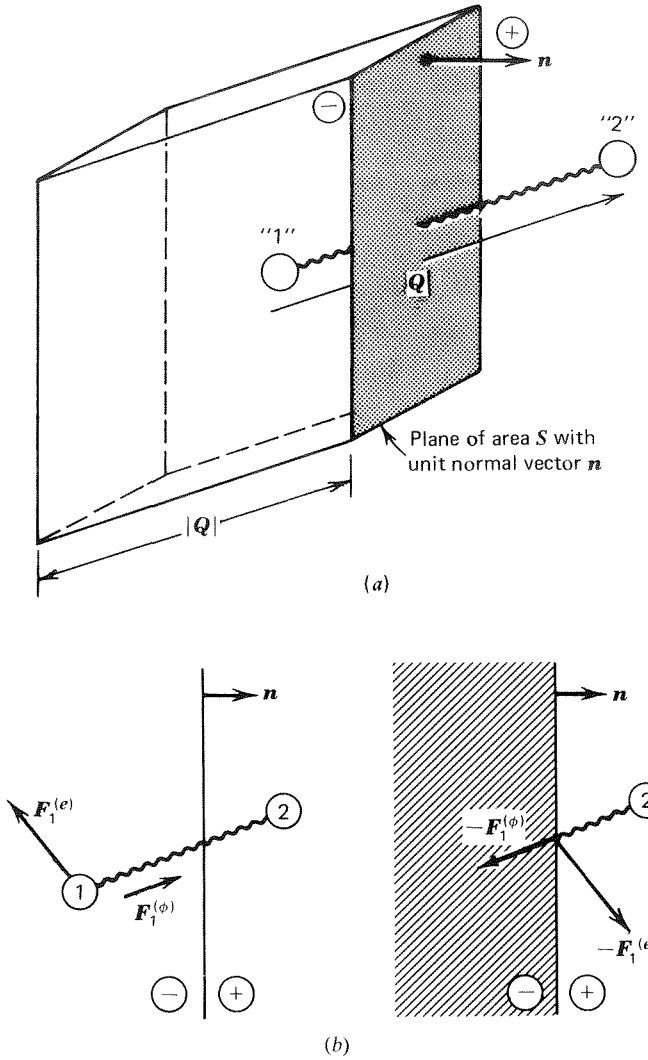


FIGURE 13.3-1. In (*a*) is shown the volume that may be occupied by bead "1" when the connector vector is Q and the dumbbell intersects the shaded plane. In (*b*) it is shown how the "negative material" can be replaced by the forces $-F_1^{(\phi)}$ and $-F_1^{(e)}$.

three factors: the number of dumbbells per unit volume, n; the volume in which bead "1" must be, namely $(\boldsymbol{n}\cdot\boldsymbol{Q})S$; and the probability $\psi(\boldsymbol{Q},t)d\boldsymbol{Q}$ that the dumbbell is in the configuration range $d\boldsymbol{Q}$ about $\boldsymbol{Q}$. Because of these dumbbells there will be a contribution to the force of the "negative material" on the "positive material" in the amount of $-\boldsymbol{F}_1^{(\phi)}$. This can be seen in the following way: There is a force $\boldsymbol{F}_1^{(\phi)}$ exerted on bead "1" through the connector. When all the negative material is replaced by an equivalent continuum, this force must be replaced by a force $\boldsymbol{F}_1^{(\phi)}$ exerted by the positive material on the negative continuum. Thus the force of the negative continuum on the positive material is $-\boldsymbol{F}_1^{(\phi)}$ (see Fig. 13.3-1*b*.) The contribution of dumbbells of all orientations, with bead "1" in the negative region and bead "2" in the positive region, to the stress (force per unit area) is then

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is positive}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_1^{(\phi)})d\boldsymbol{Q} \tag{13.3-2}$$

Similarly the stress contribution of the dumbbells of all orientations with bead "2" in the negative region and bead "1" in the positive region is

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is negative}}} n(-\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_2^{(\phi)})d\boldsymbol{Q} \tag{13.3-3}$$

We next introduce the "connector tension" $\boldsymbol{F}^{(c)}$, defined to be equal to $\boldsymbol{F}_1^{(\phi)}$ and $-\boldsymbol{F}_2^{(\phi)}$. Then the two integrals can be combined to give

$$-\int_{\substack{\text{Integral}\\ \text{over all } \boldsymbol{Q}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)\boldsymbol{F}^{(c)}\,d\boldsymbol{Q} = -\left[\boldsymbol{n}\cdot n\int \boldsymbol{Q}\boldsymbol{F}^{(c)}\psi(\boldsymbol{Q},t)d\boldsymbol{Q}\right] \tag{13.3-4}$$

But this average is to be identified with $[\boldsymbol{n}\cdot\boldsymbol{\pi}_p^{(c)}]$; hence the contribution of the dumbbell spring connectors to the stress in the solution is

$$\boldsymbol{\pi}_p^{(c)} = -n\int \boldsymbol{Q}\boldsymbol{F}^{(c)}\,\psi(\boldsymbol{Q},t)d\boldsymbol{Q} = -n\langle\boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle \tag{13.3-5}$$

Since $\boldsymbol{F}^{(c)}$ is directed along the line connecting the two beads, the force $\boldsymbol{F}^{(c)}$ can be replaced by $F^{(c)}\boldsymbol{Q}/Q$, where $F^{(c)}$ is the magnitude of the force. It is thus clear that we may write either $\langle\boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle$ or $\langle\boldsymbol{F}^{(c)}\boldsymbol{Q}\rangle$ in Eq. 13.3-5, and that $\boldsymbol{\pi}_p^{(c)}$ is a symmetric tensor.

b. Contribution from the External Forces, $\boldsymbol{\pi}_p^{(e)}$

Suppose that beads of type "1" may be subjected to an external force $\boldsymbol{F}_1^{(e)}$ and that beads of type "2" may be acted on by a force $\boldsymbol{F}_2^{(e)}$. These may be, for example, electrical forces resulting from an electric field acting on the charges on the beads. For the moment we let these forces be arbitrary, and we inquire as to the contribution to the stress tensor from dumbbells that straddle an arbitrary fluid plane (as depicted in Fig. 13.3-1*a*).

By arguments similar to those in §13.3 (a) we find that the contributions to the stress tensor corresponding to those in Eqs. 13.3-2 and 3 are

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is positive}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_1^{(e)})d\boldsymbol{Q} + \int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is negative}}} n(-\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_2^{(e)})d\boldsymbol{Q} \quad (13.3\text{-}6)$$

To get this result we use the picture provided in Fig. 13.3-1*b*. We could, however, just as well have calculated the force exerted by the "positive material" on the "negative material." This would lead to the expression:

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is positive}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_2^{(e)})d\boldsymbol{Q} + \int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is negative}}} n(-\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_1^{(e)})d\boldsymbol{Q} \quad (13.3\text{-}7)$$

But this quantity has to be the negative of that in Eq. 13.3-6. Therefore one-half of the difference of these last two expressions can be identified as $[\boldsymbol{n}\cdot\boldsymbol{\pi}_p^{(e)}]$, so that

$$\boldsymbol{\pi}_p^{(e)} = \tfrac{1}{2}n\langle\boldsymbol{Q}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\rangle \quad (13.3\text{-}8)$$

This contribution to the stress tensor is not necessarily symmetric: if the same force acts on each bead, the external force contribution to the stress tensor is zero, although such forces lead to the external force term in the equation of motion (see Eq. 17.4-25).

c. Contribution from Bead Motion, $\boldsymbol{\pi}_p^{(b)}$

We know that the motion of the beads across an arbitrary plane will contribute to the stress tensor because of the momentum transported by the beads. In order to get the contribution associated with this mechanism, we must first ask: how many "1" beads with velocity $\dot{\boldsymbol{r}}_1$ will cross an arbitrary surface in time Δt? This will be given by the volume of the parallelepiped in Fig. 13.3-2, multiplied by the number of dumbbells per unit volume:

$$n((\dot{\boldsymbol{r}}_1 - \boldsymbol{v})\cdot\boldsymbol{S}\boldsymbol{n})\Delta t \quad (13.3\text{-}9)$$

The amount of momentum transported across the plane is then

$$n((\dot{\boldsymbol{r}}_1 - \boldsymbol{v})\cdot\boldsymbol{S}\boldsymbol{n})m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})\Delta t \quad (13.3\text{-}10)$$

Hence the average value of the momentum flux (momentum per unit time per unit area) resulting from beads "1" of all possible velocities and dumbbells of all possible configurations will be

$$n\boldsymbol{n}\cdot\int[\![m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})]\!]\psi(\boldsymbol{Q},t)d\boldsymbol{Q} \quad (13.3\text{-}11)$$

Then the average value of the momentum flux resulting from both beads is obtained by adding to the above a similar contribution for beads of type "2." This average value must

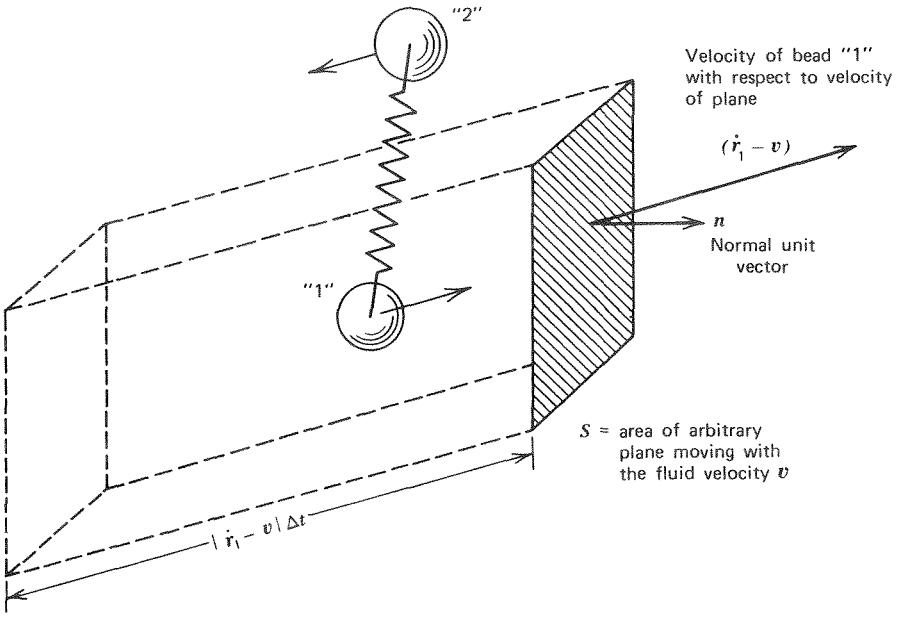


FIGURE 13.3-2. A bead of a dumbbell crossing an arbitrary surface and contributing to the stress tensor π.

then be identified with $[\boldsymbol{n} \cdot \boldsymbol{\pi}_p^{(b)}]$ and, hence, the contribution of the bead motion to the stress will be

$$\boldsymbol{\pi}_p^{(b)} = n \int \left[\!\!\left[\sum_{v=1}^{2} m(\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}) \right]\!\!\right] \psi(\boldsymbol{Q}, t) d\boldsymbol{Q} \tag{13.3-12}$$

This is then the contribution due to the bead motion; we sometimes refer to this as the "Brownian motion contribution" (note the appearance here of the momentum flux $m(\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v})$ which also appears in Eq. 13.2-3). When the integrations implied by $[\![\ ]\!]$ are performed using the Maxwellian distribution in Eq. 13.1-3 we get finally

$$\boldsymbol{\pi}_p^{(b)} = 2nkT\boldsymbol{\delta} \quad \text{(Maxwellian)} \tag{13.3-13}$$

Since the expression in Eq. 13.3-13 is isotropic, this contribution will not normally be of rheological interest. The fact that each bead gives a contribution of $nkT\boldsymbol{\delta}$ is a direct consequence of the "equilibration in momentum space."

When the contributions from the solvent and polymer are finally combined, we obtain for the stress tensor of a dilute solution of dumbbells without the Maxwellian velocity distribution function assumption:

$$\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\langle \boldsymbol{Q}\boldsymbol{F}^{(c)} \rangle + \tfrac{1}{2}n\langle \boldsymbol{Q}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}] \rangle + nm \sum_{v=1}^{2} \langle (\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}) \rangle \tag{13.3-14}$$

Solvent contribution	Contribution of intramolecular forces	Contribution of external forces	Contribution of the bead motion

This expression can be slightly modified by writing the intramolecular force contribution in terms of the forces on the individual beads ($\boldsymbol{F}_\nu^{(\phi)} = -\partial\phi/\partial\boldsymbol{r}_\nu$) and the location of the beads relative to the dumbbell center of mass ($\boldsymbol{R}_\nu = \boldsymbol{r}_\nu - \boldsymbol{r}_c$):

$$\pi = \pi_s + n\sum_{\nu=1}^{2}\langle \boldsymbol{R}_\nu(\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)})\rangle + nm\sum_{\nu=1}^{2}\langle(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})\rangle \tag{13.3-15}$$

Next one can use Eq. 13.2-1 to replace $\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)}$ by $-\boldsymbol{F}_\nu^{(h)} - \boldsymbol{F}_\nu^{(b)}$. When the Brownian force given by Eq. 13.2-3 is inserted into $\sum_\nu\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(b)}\rangle$ an integration by parts and other manipulations can be performed to get[3]

$$\boxed{\pi = \pi_s - n\sum_\nu\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)}\rangle + 2nm\langle(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})\rangle} \tag{13.3-16}$$

In going from Eq. 13.3-15 to Eq. 13.3-16 the only assumption is that Ξ is an even function of $\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}$ (see Example 13.3-1). Equations 13.3-14 to 13.3-16 are valid whether or not hydrodynamic interaction is included and whether or not the friction tensor is isotropic.

In most kinetic theory publications, it is assumed that the velocity distribution is Maxwellian; in this chapter we adopt the same assumption except in the final section. Then the last term in Eqs. 13.3-14 and 13.3-15 becomes $2nkT\boldsymbol{\delta}$, and the last term of Eq. 13.3-16 becomes $nkT\boldsymbol{\delta}$.

Finally we may express the stress tensor in terms of $\boldsymbol{\tau}$ (see Eq. 13.3-1) by subtracting from Eq. 13.3-14 the corresponding expression at equilibrium, [i.e., with $\boldsymbol{\kappa} = \boldsymbol{0}$ and $\boldsymbol{F}_\nu^{(e)} = \boldsymbol{0}$], namely, $p\boldsymbol{\delta} = p_s\boldsymbol{\delta} - n\langle \boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle_{\text{eq}} + 2nkT\boldsymbol{\delta} = p_s\boldsymbol{\delta} + nkT\boldsymbol{\delta}$ (where Eq. 13.2-18 has been used). When, in addition, we insert the explicit expression for the Newtonian solvent contribution to the stress tensor, we get finally Eq. A of Table 13.3-1, which we henceforth refer to as the *Kramers form for the stress tensor.*[1] Equations B and C correspond to Eqs. 13.3-15 and 13.3-16. The latter we call the *Kramers–Kirkwood form of the stress tensor*, since this also appears in Kramers' landmark publication,[1] but was exploited by Kirkwood in his

TABLE 13.3-1

Expressions for the Stress Tensor for Elastic Dumbbells[a] (Maxwellian Velocity Distribution Assumed)

Kramers:[b]	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\langle \boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle + \frac{1}{2}n\langle \boldsymbol{Q}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\rangle + nkT\boldsymbol{\delta}$	(A)
Modified-Kramers:	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + n\sum_\nu\langle \boldsymbol{R}_\nu[\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)}]\rangle + nkT\boldsymbol{\delta}$	(B)
Kramers–Kirkwood:[c]	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\sum_\nu\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)}\rangle$	(C)
Giesekus:[d]	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + \frac{1}{4}n\zeta\langle \boldsymbol{Q}\boldsymbol{Q}\rangle_{(1)} + \frac{1}{4}n\langle \boldsymbol{Q}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}) - (\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\boldsymbol{Q}\rangle$	(D)

[a] R. B. Bird and C. F. Curtiss, *J. Polym. Sci.: Polym. Symp.*, **73**, 187–199 (1985).

[b] H. A. Kramers, *Physica*, **11**, 1–19 (1944).

[c] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).

[d] H. Giesekus, *Rheol. Acta*, **2**, 50–62 (1962); this expression is less general than Eqs. A–C, in that the friction tensor must be isotropic and hydrodynamic interaction is neglected. For a discussion of hydrodynamic interaction, see §13.6 and Problem 13B.8.

impressive series of papers on kinetic theory.[4] Equation D, the *Giesekus form of the stress tensor*,[5] in Table 13.3-1 is obtained by eliminating $\langle \boldsymbol{Q}\boldsymbol{F}^{(c)} \rangle$ from Eq. A by using Eq. 13.2-17. Each of the entries in this table has been used in the kinetic theory literature. The table should be helpful in keeping track of which forces are being used [$\boldsymbol{F}^{(c)}$, $\boldsymbol{F}_\nu^{(\phi)}$, $\boldsymbol{F}_\nu^{(e)}$, or $\boldsymbol{F}_\nu^{(h)}$], which sign precedes the force term, and whether or not $nkT\boldsymbol{\delta}$ appears in the expression.

In most of the rest of this chapter the external forces are left out of consideration. They are included in the discussion of the equations of motion for the beads in §13.6, where hydrodynamic interaction is incorporated into the theory. The external force terms are needed there for the discussion of translational diffusivity in Example 13.6-2. Furthermore, external forces are included in the phase-space kinetic theory in Chapters 17 and 18.

EXAMPLE 13.3-1 Alternative Form for the Stress Tensor

Show how to go from Eq. 13.3-15 to Eq. 13.3-16.

SOLUTION When $\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)}$ is replaced by $-\boldsymbol{F}_\nu^{(h)} - \boldsymbol{F}_\nu^{(b)}$ in Eq. 13.3-15 we are confronted with:

$$-n\sum_\nu \langle \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(b)} \rangle = nm\sum_\nu \int \boldsymbol{R}_\nu \frac{\partial}{\partial \boldsymbol{r}_\nu} \cdot ([\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!]\psi) d\boldsymbol{Q} \tag{13.3-17}$$

Then use of the chain rule enables us to replace $\partial/\partial \boldsymbol{r}_\nu$ by derivatives with respect to $\boldsymbol{r}_c$ and $\boldsymbol{Q}$. Since $[\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!]\psi$ does not depend on $\boldsymbol{r}_c$, the right side of Eq. 13.3-17 becomes:

$$nm\sum_\nu \int \boldsymbol{R}_\nu (-1)^\nu \frac{\partial}{\partial \boldsymbol{Q}} \cdot ([\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!]\psi) d\boldsymbol{Q} = -\tfrac{1}{2}nm \int \sum_\nu [\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!]\psi \, d\boldsymbol{Q} \tag{13.3-18}$$

where integration by parts has been performed. We now consider the expression

$$\begin{aligned}\sum_\nu [\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!] &= \sum_\nu [\![(\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v}))(\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v}))]\!] \\ &= \sum_\nu [\![\dot{\boldsymbol{R}}_\nu \dot{\boldsymbol{R}}_\nu]\!] + 2[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!]\end{aligned} \tag{13.3-19}$$

But if it is assumed that the velocity distribution is even in $\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}$, we may equally well write the expression in Eq. 13.3-19 as

$$\begin{aligned}\sum_\nu \sum_\mu [\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\mu - \boldsymbol{v})]\!] &= \sum_\nu \sum_\mu [\![(\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v}))(\dot{\boldsymbol{R}}_\mu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v}))]\!] \\ &= \left[\!\!\left[\left(\sum_\nu (\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v})) \right) \left(\sum_\mu (\dot{\boldsymbol{R}}_\mu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v})) \right) \right]\!\!\right] \\ &= 4[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!]\end{aligned} \tag{13.3-20}$$

Twice Eq. 13.3-19 minus Eq. 13.3-20 then yields

$$\sum_\nu [\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!] = 2\sum_\nu [\![\dot{\boldsymbol{R}}_\nu \dot{\boldsymbol{R}}_\nu]\!] \tag{13.3-21}$$

[4] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).

[5] H. Giesekus, *Rheol. Acta*, **5**, 29–35 (1966); see also A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539–553 (1971).

so that

$$-n\sum_{\nu}\langle \boldsymbol{R}_{\nu}\boldsymbol{F}_{\nu}^{(b)}\rangle = -nm\sum_{\nu}\langle \dot{\boldsymbol{R}}_{\nu}\dot{\boldsymbol{R}}_{\nu}\rangle \tag{13.3-22}$$

When this is used in Eq. 13.3-15, after some additional rearrangement, Eq. 13.3-16 results.

§13.4 HOOKEAN DUMBBELLS

Up to this point the theory has been developed for dumbbells with any kind of elastic connector, linear or nonlinear. In this section we specialize to the Hookean spring connector for which

$$\boldsymbol{F}^{(c)} = H\boldsymbol{Q} \tag{13.4-1}$$

where H is the spring constant. For this model the polymer contribution to the stress tensor $\boldsymbol{\tau}_p$ is then given by Eqs. A and D of Table 13.3-1 as

$$\text{Kramers:} \qquad \boldsymbol{\tau}_p = -nH\langle \boldsymbol{QQ}\rangle + nkT\boldsymbol{\delta} \tag{13.4-2}$$

$$\text{Giesekus:} \qquad \boldsymbol{\tau}_p = +\frac{n\zeta}{4}\langle \boldsymbol{QQ}\rangle_{(1)} \tag{13.4-3}$$

In order to use either of these expressions, one would have to know the distribution function $\psi(\boldsymbol{Q}, t)$ for evaluating the average values. However, for the Hookean dumbbells one can simply eliminate $\langle \boldsymbol{QQ}\rangle$ between these two equations and obtain a rheological equation of state directly.[1,2] This is done by subtracting $nkT\boldsymbol{\delta}$ from both sides of Eq. 13.4-2, then multiplying by $\lambda_H = \zeta/4H$ (which is the time constant for the Hookean dumbbells), and then performing the operation of convected differentiation given in Eq. D.2-4a (indicated by the subscript $_{(1)}$); in doing this we note that $\boldsymbol{\delta}_{(1)} = -\boldsymbol{\gamma}_{(1)}$. Then the resulting equation is added to Eq. 13.4-3 to obtain:

$$\boldsymbol{\tau}_p + \lambda_H\boldsymbol{\tau}_{p(1)} = -nkT\lambda_H\boldsymbol{\gamma}_{(1)} \tag{13.4-4}$$

When written in terms of $\boldsymbol{\tau}$ this equation becomes

$$\boxed{\boldsymbol{\tau} + \lambda_1\boldsymbol{\tau}_{(1)} = -\eta_0(\boldsymbol{\gamma}_{(1)} + \lambda_2\boldsymbol{\gamma}_{(2)})} \tag{13.4-5}$$

in which $\boldsymbol{\gamma}_{(1)}$ and $\boldsymbol{\gamma}_{(2)}$ are kinematic tensors defined in §D.3 and

$$\eta_0 = \eta_s + nkT\lambda_H \tag{13.4-6}$$

$$\lambda_1 = \lambda_H \tag{13.4-7}$$

$$\lambda_2 = \left(\frac{\eta_s}{\eta_s + nkT\lambda_H}\right)\lambda_H \tag{13.4-8}$$

[1] H. Giesekus, *Rheol. Acta*, **1**, 2-20 (1958); **5**, 29-35 (1966).
[2] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539-553 (1971); P. H. van Wiechen and H. C. Booij, *J. Eng. Math.*, **5**, 89-98 (1971).

Equation 13.4-5 is then the *constitutive equation* for a dilute solution of polymer molecules modeled as Hookean dumbbells; it is exactly of the form of a "convected Jeffreys model" (called the "Oldroyd-B model") discussed in §7.2. Therefore many results from continuum mechanics can be taken over directly. For example, it was shown in Example 9.4-1 how differential constitutive equations can be transformed into integral constitutive equations. The Hookean-dumbbell-solution constitutive equation may be put into the form[2]

$$\boxed{\tau = -\eta_s\dot{\gamma} + \int_{-\infty}^{t} \left\{\frac{nkT}{\lambda_H} e^{-(t-t')/\lambda_H}\right\}\gamma_{[0]}(t, t')dt'} \tag{13.4-9}$$

in which $\gamma_{[0]}$ is the finite strain tensor defined in Eq. D.3-4; the quantity in braces plus $2\eta_s(\partial/\partial t')\delta(t-t')$ is called the "memory function" (see Eq. D.4-2).

Since the complete constitutive equation is known for this molecular model, the derivation of expressions for the material functions is straightforward (see Examples 13.4-1 and 2). In addition the average value of the square of the end-to-end distance is easily obtained by taking the trace of Eq. 13.4-2

$$\langle Q^2\rangle = \frac{3kT}{H} - \frac{\text{tr}\,\tau_p}{nH} \tag{13.4-10}$$

Then, using Eq. 13.4-9 we can get the ratio of $\langle Q^2\rangle$ to its value at equilibrium:

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{\text{eq}}} = 1 - \frac{\text{tr}\,\tau_p}{3nkT}$$

$$= 1 - \frac{1}{3\lambda_H}\int_{-\infty}^{t} e^{-(t-t')/\lambda_H}\,\text{tr}\,\gamma_{[0]}(t, t')dt' \tag{13.4-11}$$

This result gives us a measure of the molecular stretching in any flow situation, either in terms of the stresses or in terms of the finite strain tensor $\gamma_{[0]}(t, t')$. The ratio $\langle Q^2\rangle/\langle Q^2\rangle_{\text{eq}}$ can be measured by means of light scattering.[3]

All the results thus far were obtained without solving the diffusion equation to get the configurational distribution function $\psi(\boldsymbol{Q}, t)$. If one wishes to have the distribution of dumbbell orientations, the distribution of the end-to-end distance, or other more detailed information, then it is necessary to have the configurational distribution function. For Hookean dumbbell solutions this has been found to be:[2]

$$\boxed{\psi(\boldsymbol{Q}, t) = \frac{(H/2\pi kT)^{3/2}}{\sqrt{\det\boldsymbol{\alpha}}} e^{-(H/2kT)(\boldsymbol{\alpha}^{-1}:\boldsymbol{QQ})}} \tag{13.4-12}$$

$$\boxed{\boldsymbol{\alpha}(t) = \boldsymbol{\delta} - \frac{1}{\lambda_H}\int_{-\infty}^{t} e^{-(t-t')/\lambda_H}\boldsymbol{\gamma}_{[0]}(t, t')dt'} \tag{13.4-13}$$

[3] F. R. Cottrell, E. W. Merrill, and K. A. Smith, *J. Polymer Sci.*, Part A-2, 7, 1415-1434 (1969). See also *Light Scattering from Polymer Solutions*, M. B. Huglin ed., Academic Press, New York (1972). Equation 13.4-11 has been used for classification of flow fields as "strong" or "weak" [R. I. Tanner, *Engineering Rheology*, Oxford University Press, London (1985), pp. 185-193].

The combination $\mathbf{B} = \boldsymbol{\delta} - \boldsymbol{\gamma}_{[0]}$, a weighted average of which is α, is shown in Chapter 9 to be positive definite. For any given flow field (described by $\boldsymbol{\kappa}(t)$ in Eq. 13.2-13), one can obtain the finite strain tensor $\boldsymbol{\gamma}_{[0]}(t, t')$ and hence the distribution function $\psi(\boldsymbol{Q}, t)$. For a system at rest, the finite strain tensor is zero and the equilibrium distribution function in Table 11.5-1 is obtained. The Hookean dumbbell is the only dumbbell model for which $\psi(\boldsymbol{Q}, t)$ has been found for arbitrary time-dependent flow patterns.

EXAMPLE 13.4-1 Shear Flow Material Functions and Molecular Stretching

Use the results of this section to find **(a)** the material functions and **(b)** the stretching of the dumbbells as a function of the shear rate in steady shear flow; also find **(c)** the components of the complex viscosity.

SOLUTION **(a)** For the steady-state shear flow $v_x = \dot{\gamma}y$, $v_y = 0$, $v_z = 0$, Eq. 13.4-4 can be shown to give (see Appendix C):

$$\begin{pmatrix} \tau_{p,xx} & \tau_{p,xy} & \tau_{p,xz} \\ \tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,xz} & \tau_{p,yz} & \tau_{p,zz} \end{pmatrix} + \lambda_H \begin{pmatrix} -2\tau_{p,xy} & -\tau_{p,yy} & -\tau_{p,yz} \\ -\tau_{p,yy} & 0 & 0 \\ -\tau_{p,yz} & 0 & 0 \end{pmatrix} \dot{\gamma} = -nkT\lambda_H \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \dot{\gamma} \tag{13.4-14}$$

This matrix equation is equivalent to a set of six linear algebraic equations. The solution to these equations is

$$\tau_{p,xx} = -2nkT\lambda_H^2\dot{\gamma}^2 \tag{13.4-15}$$

$$\tau_{p,xy} = \tau_{p,yx} = -nkT\lambda_H\dot{\gamma} \tag{13.4-16}$$

all the other $\tau_{p,ij}$ being zero.[4] Then using $\tau = -\eta_s\dot{\gamma} + \tau_p$ and the definitions of the material functions given in Eqs. D.5-1 to 3, we find

$$\eta = \eta_s + nkT\lambda_H \tag{13.4-17}$$

$$\Psi_1 = 2nkT\lambda_H^2 \tag{13.4-18}$$

$$\Psi_2 = 0 \tag{13.4-19}$$

It is found thus that all the material functions are constant. But we know (see Fig. 3.3-4) that even for extremely dilute polymer solutions, the viscosity decreases with increasing shear rate. Therefore we have to conclude that the model is inadequate for describing the behavior of dilute polymer solutions as the shear rate is increased.

(b) From the stress-tensor components in part **(a)** we find that $\text{tr}\,\boldsymbol{\tau}_p = \tau_{p,xx} + \tau_{p,yy} + \tau_{p,zz} = -2nkT\lambda_H^2\dot{\gamma}^2$. Substitution into the first line of Eq. 13.4-11 then gives:

$$\frac{\langle Q^2 \rangle}{\langle Q^2 \rangle_{\text{eq}}} = 1 + \tfrac{2}{3}(\lambda_H\dot{\gamma})^2 \tag{13.4-20}$$

This shows that the Hookean dumbbells continue to stretch as the shear rate is increased. The failure of the model to give a non-Newtonian (shear-rate dependent) viscosity may be linked to this infinite extensibility.

[4] The stresses $\tau_{p,xz}$, $\tau_{p,yz}$, $\tau_{p,zx}$, and $\tau_{p,zy}$ turn out to be zero according to the kinetic theory; this is consistent with the continuum mechanics arguments given in §3.2.

(c) For small-amplitude oscillatory motion, Eq. 13.4-4 simplifies to the Maxwell model for linear viscoelasticity, Eq. 5.2-2, so that

$$\eta' = \eta_s + \frac{nkT\lambda_H}{1 + (\lambda_H\omega)^2} \tag{13.4-21}$$

$$\eta'' = \frac{nkT\lambda_H^2\omega}{1 + (\lambda_H\omega)^2} \tag{13.4-22}$$

It is clear that the suspension of Hookean dumbbells does not predict the observed similarities in the shapes of $\eta(\dot{\gamma})$ and $\eta'(\omega)$ (cf. §3.6) and in the shapes of $\Psi_1/2$ and η''/ω. The curves predicted from Eqs. 13.4-21 and 22 are, however, qualitatively reasonable.

EXAMPLE 13.4-2 Elongational Flow Material Functions and Molecular Stretching

For an arbitrary simple elongational flow, specified by $v_z = \dot{\varepsilon}(t)z$, $v_x = -\frac{1}{2}\dot{\varepsilon}(t)x$, and $v_y = -\frac{1}{2}\dot{\varepsilon}(t)y$, find the expressions for the components of the polymer contribution to the stress tensor. Then find the expression for $\langle Q^2\rangle/\langle Q^2\rangle_{eq}$ for **(a)** a sudden elongational displacement, **(b)** the sudden inception of steady elongational flow, and **(c)** steady-state elongational flow.

SOLUTION For time-dependent simple elongational flow the rate-of-strain tensor is

$$\dot{\gamma} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}\dot{\varepsilon}(t) \tag{13.4-23}$$

Substitution of this into Eq. 13.4-4 gives for the polymer contribution to the stress tensor

$$\left(1 + \lambda_H\frac{\partial}{\partial t}\right)\begin{pmatrix} \tau_{p,xx} & \tau_{p,xy} & \tau_{p,xz} \\ \tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,xz} & \tau_{p,yz} & \tau_{p,zz} \end{pmatrix} - \lambda_H\dot{\varepsilon}\begin{pmatrix} -\tau_{p,xx} & -\tau_{p,xy} & \frac{1}{2}\tau_{p,xz} \\ -\tau_{p,xy} & -\tau_{p,yy} & \frac{1}{2}\tau_{p,yz} \\ \frac{1}{2}\tau_{p,xz} & \frac{1}{2}\tau_{p,yz} & 2\tau_{p,zz} \end{pmatrix}$$
$$= -nkT\lambda_H\dot{\varepsilon}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{13.4-24}$$

From this matrix equation, three differential equations for $\tau_{p,xx}$, $\tau_{p,yy}$, and $\tau_{p,zz}$ are obtained.[5] The solutions of these equations are

$$\tau_{p,xx} = \tau_{p,yy} = nkT\int_{-\infty}^{t}\dot{\varepsilon}(t')\exp\left\{-\frac{1}{\lambda_H}\int_{t'}^{t}[1 + \lambda_H\dot{\varepsilon}(t'')]dt''\right\}dt' \tag{13.4-25}$$

$$\tau_{p,zz} = -2nkT\int_{-\infty}^{t}\dot{\varepsilon}(t')\exp\left\{-\frac{1}{\lambda_H}\int_{t'}^{t}[1 - 2\lambda_H\dot{\varepsilon}(t'')]dt''\right\}dt' \tag{13.4-26}$$

We now use these results to get information about the stretching of the dumbbells in various flows.

(a) Sudden Elongational Displacement

Let the fluid sample be subjected to a sudden elongational displacement at $t = 0$; that is, we take

$$\dot{\varepsilon}(t) = \varepsilon_0\delta(t) \tag{13.4-27}$$

[5] We obtain all $\tau_{p,ij}$ equal to zero for $i \neq j$; this is consistent with the continuum mechanics arguments given in §3.2.

where $\delta(t)$ is the Dirac delta function (see §E.4). Then for $t > 0$

$$\tau_{p,xx} = \tau_{p,yy} = nkT\varepsilon_0 \exp\left[-\frac{t}{\lambda_H} - \varepsilon_0\right] \tag{13.4-28}$$

$$\tau_{p,zz} = -2nkT\varepsilon_0 \exp\left[-\frac{t}{\lambda_H} + 2\varepsilon_0\right] \tag{13.4-29}$$

Hence

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{\text{eq}}} = 1 + \tfrac{2}{3}\varepsilon_0(e^{2\varepsilon_0} - e^{-\varepsilon_0})e^{-t/\lambda_H} \tag{13.4-30}$$

Thus, the molecules reach maximum extension at the instant of sudden strain and then gradually go back to their equilibrium lengths. There is no limit to the extent to which the dumbbells can be stretched.

(b) Sudden Inception of Steady Elongational Flow

Next consider the inception of a steady simple elongational flow at $t = 0$.

$$\dot{\varepsilon}(t) = \dot{\varepsilon}_0 H(t) \tag{13.4-31}$$

where $H(t)$ is the Heaviside unit step function.[6] This gives for $-1/\lambda_H < \dot{\varepsilon}_0 < 1/2\lambda_H$

$$\tau_{p,xx} = \tau_{p,yy} = \frac{nkT\lambda_H\dot{\varepsilon}_0}{1 + \lambda_H\dot{\varepsilon}_0}[1 - e^{-(1+\lambda_H\dot{\varepsilon}_0)t/\lambda_H}] \tag{13.4-32}$$

$$\tau_{p,zz} = -\frac{2nkT\lambda_H\dot{\varepsilon}_0}{1 - 2\lambda_H\dot{\varepsilon}_0}[1 - e^{-(1-2\lambda_H\dot{\varepsilon}_0)t/\lambda_H}] \tag{13.4-33}$$

The elastic Hookean dumbbell models then stretch by an amount

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{\text{eq}}} = 1 + \frac{2}{3}\left\{\frac{\lambda_H\dot{\varepsilon}_0}{1 - 2\lambda_H\dot{\varepsilon}_0}[1 - e^{-(1-2\lambda_H\dot{\varepsilon}_0)t/\lambda_H}] - \frac{\lambda_H\dot{\varepsilon}_0}{1 + \lambda_H\dot{\varepsilon}_0}[1 - e^{-(1+\lambda_H\dot{\varepsilon}_0)t/\lambda_H}]\right\} \tag{13.4-34}$$

Note that if $\dot{\varepsilon}_0 > 1/2\lambda_H$ or $\dot{\varepsilon}_0 < -1/\lambda_H$ steady state will not be attained and the molecules will continue stretching without limit.

(c) Steady Simple Elongational Flow

From Eq. 13.4-34 the stretch ratio for steady state is easily found to be

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{\text{eq}}} = \frac{1 - \lambda_H\dot{\varepsilon}_0}{(1 + \lambda_H\dot{\varepsilon}_0)(1 - 2\lambda_H\dot{\varepsilon}_0)} \tag{13.4-35}$$

In addition from Eqs. 13.4-32 and 33 and the definition of the elongational viscosity in Eq. D.5-14 we find

$$\bar{\eta} = 3\eta_s + \frac{3nkT\lambda_H}{(1 + \lambda_H\dot{\varepsilon}_0)(1 - 2\lambda_H\dot{\varepsilon}_0)} \tag{13.4-36}$$

Equation 13.4-36 predicts that the elongational viscosity goes to infinity for a steady-state elongational rate of $1/2\lambda_H$ or $-1/\lambda_H$. However, we see from Eq. 13.4-35 that the molecules are also being stretched to infinite length at the same elongational rate. Inasmuch as real macromolecules have finite extensibility, neither one of these results can be taken seriously for high elongational rates. Once again we are confronted with the serious defect of the Hookean dumbbell model: it puts no limit on the

[6] $H(t) = 0$ for $t < 0$, and $H(t) = 1$ for $t > 0$.

extent to which the molecules can be elongated. In the next section, therefore, we turn our attention to the finitely extensible nonlinear elastic dumbbells (FENE dumbbells) in order to get some improvement in the prediction of material functions.

§13.5 NON-HOOKEAN DUMBBELLS[1,2,3,4]

In the previous section we saw that the Hookean dumbbell suspension gives steady-state shear flow material functions that are independent of the shear rate, and also a steady-state elongational viscosity that goes to infinity at a finite elongation rate; evidence was presented that this unlikely behavior results because the Hookean dumbbell model permits infinite extension. However we know from the elementary statistical mechanical considerations in Chapter 11 that for small extensions the Hookean spring seems appropriate. It therefore seems reasonable, as a second attempt to model a flexible macromolecule, to try a force law of the following form:

$$\boldsymbol{F}^{(c)} = \frac{H\boldsymbol{Q}}{1 - (Q/Q_0)^2} \qquad Q \leq Q_0 \tag{13.5-1}$$

A spring with this force law will be linear (Hookean) for small extensions, but will get stiffer as the spring is extended; furthermore the spring cannot be extended beyond a separation Q_0. This *f*initely *e*xtensible *n*onlinear *e*lastic (FENE) connector force law was first used for kinetic theory calculations by Warner,[2] and later by Armstrong.[3] Equation 13.5-1 is simpler than the inverse Langevin function (Eq. 11.3-23) that had been used earlier by Stevenson[4] and by Peterlin.[1]

For the FENE dumbbells we can define two time constants, one (λ_H) that is the same as that which we used in §13.4 for Hookean dumbbells, and another (λ_Q) that is constructed like the time constant used for rigid dumbbells (in Chapter 14):

$$\lambda_H = \frac{\zeta}{4H} \tag{13.5-2}$$

$$\lambda_Q = \frac{\zeta Q_0^2}{12kT} \tag{13.5-3}$$

where ζ is the friction coefficient defined in §13.2. In addition it will be useful to have a symbol for the dimensionless ratio:

$$b = \frac{3\lambda_Q}{\lambda_H} = \frac{HQ_0^2}{kT} \tag{13.5-4}$$[5]

[1] A. Peterlin, *Makr. Chem.*, **44–46**, 338–346 (1961); *Kolloid-Zeitschrift*, **182**, 110–115 (1962).

[2] H. R. Warner, Jr., Ph.D. Thesis, University of Wisconsin, Madison (1971); *Ind. Eng. Chem. Fundamentals*, **11**, 379–387 (1972). In the latter the factors of $(b + 7)$ in the denominators in the second and third lines of Eq. 40 on p. 385 should be removed; also, in Figure 7, the curves should approach zero at high ω. We thank Dr. Warner for communicating these errors to us.

[3] R. C. Armstrong, *J. Chem. Phys.*, **60**, 724–728, 729–733 (1974).

[4] J. F. Stevenson, *Trans. Soc. Rheol.*, **15**, 135–145 (1971).

[5] From Eq. 11.3-20 it may be seen that for a chain of $N - 1$ freely jointed rods of length a, $H = 3kT/(N - 1)a^2$. If we take $Q_0 \doteq (N - 1)a$, then $b \doteq 3(N - 1)$. Since one link is approximately 10 to 20 monomer units, we can expect that b will be roughly in the range 50 to 1000. Comparison of the material functions with experimental data gives b values that are roughly in this range [R. L. Christiansen and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **3**, 161–177 (1977/1978)].

Here all the kinetic theory results will be expressed in terms of one time constant (we usually use λ_H) and the dimensionless constant b. We also note that if b is allowed to approach infinity, then the formulas for the Hookean dumbbell are recovered.

For a nonlinear force law, such as that in Eq. 13.5-1, we cannot go directly to a constitutive equation as we did for the Hookean dumbbell in §13.4. Instead we must first solve the partial differential equation for the distribution function. We do this here only for steady-state flows so that the left side of Eq. 13.2-13 is zero. We already know that at equilibrium, the normalized distribution function, ψ_{eq}, is given by Eq. L of Table 11.5-1. In order to get the distribution function for slow flow conditions we then expand about the known equilibrium function thus:

$$\psi = \psi_{eq}\phi_{f1} = \psi_{eq}(1 + \phi_1 + \phi_2 + \cdots) \tag{13.5-5}$$

Here ϕ_k is of kth order in the velocity gradients.

The configurational distribution function for steady-state, homogeneous, potential flow, given in Eq. 13.2-14, can be put in the form of Eq. 13.5-5 by expanding in powers of the velocity gradients, thus:

$$\psi = \psi_{eq}\left\{1 + \left(\frac{\zeta}{8kT}\right)(\dot{\gamma} : \boldsymbol{QQ}) + \left(\frac{\zeta}{8kT}\right)^2\left[\frac{1}{2}(\dot{\gamma} : \boldsymbol{QQ})^2 - \frac{1}{15}\langle Q^4\rangle_{eq}(\dot{\gamma} : \dot{\gamma})\right] + \cdots\right\} \tag{13.5-6}$$

in which $\langle Q^4\rangle_{eq} = \int Q^4\psi_{eq}\, d\boldsymbol{Q}$ and, for potential flow, $\dot{\gamma}$ equals $2\boldsymbol{\kappa}$. (See Problem 13B.4 for further details.) Therefore in solving Eq. 13.2-13 in the form of Eq. 13.5-5, the ϕ_k must include the corresponding terms in Eq. 13.5-6 as well as some additional terms containing $\boldsymbol{\omega}$.

When the assumed form of ψ in Eq. 13.5-5 is substituted into Eq. 13.2-13, we then get a series of differential equations for the ϕ_k (see Problem 13B.5):

$$\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \frac{\partial}{\partial \boldsymbol{Q}}\phi_1\right) - \left(\frac{\boldsymbol{F}^{(c)}}{kT} \cdot \frac{\partial}{\partial \boldsymbol{Q}}\phi_1\right) = -\frac{\zeta}{2kT}\left([\boldsymbol{\kappa} \cdot \boldsymbol{Q}] \cdot \frac{\boldsymbol{F}^{(c)}}{kT}\right) \tag{13.5-7}$$

$$\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \frac{\partial}{\partial \boldsymbol{Q}}\phi_2\right) - \left(\frac{\boldsymbol{F}^{(c)}}{kT} \cdot \frac{\partial}{\partial \boldsymbol{Q}}\phi_2\right) = -\frac{\zeta}{2kT}\left([\boldsymbol{\kappa} \cdot \boldsymbol{Q}] \cdot \left[\frac{\boldsymbol{F}^{(c)}\phi_1}{kT} - \frac{\partial}{\partial \boldsymbol{Q}}\phi_1\right]\right) \tag{13.5-8}$$

$$\vdots$$

These equations must be solved for $\phi_1, \phi_2, \ldots$ subject to the condition that ψ be normalized to unity. Since ψ_{eq} in Eq. L of Table 11.5-1 has been normalized to unity, we then must require that

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{eq}\phi_k Q^2\, dQ \sin\theta\, d\theta\, d\phi = 0 \qquad k = 1, 2, \ldots \tag{13.5-9}$$

In addition the ϕ_k must be such that $\psi_{eq}\phi_k$ remains bounded at all points in the configuration space. Let us now work through the details for ϕ_1 and ϕ_2.

There are several ways of attacking this problem. One is to write out Eqs. 13.5-7, 13.5-8, and so on, in spherical coordinates and then solve the equations for specific flows.[2] Another is to guess the general form of the solution and then get the coefficients by substituting the postulated solution into the differential equation.[3] We shall take the latter

approach here since it is somewhat speedier, although it does require more maturity and insight. We know that ϕ_k must:

i. Be of kth order in the velocity gradients (i.e., $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa}^\dagger$ or, alternatively, $\dot{\boldsymbol{\gamma}}$ and $\boldsymbol{\omega}$, as defined in Eqs. D.1-2 and D.1-3).
ii. Be a scalar.
iii. Be formed from $\dot{\boldsymbol{\gamma}}$, $\boldsymbol{\omega}$, and $\boldsymbol{Q}$.
iv. Vanish for any flow that is a rigid rotation. (This excludes any tensor products containing $\boldsymbol{\omega}$ but no $\dot{\boldsymbol{\gamma}}$.)
v. Simplify to the kth order term in Eq. 13.5-6 for steady-state, homogeneous, potential flows.

Note that these requirements are satisfied by the expansion in Eq. 13.5-6.

In order to guess the form of ϕ_1, we have to construct scalars, of first order in the velocity gradients, from $\dot{\boldsymbol{\gamma}}$, $\boldsymbol{\omega}$, and $\boldsymbol{Q}$. The only possible combination satisfying requirements i to v above is $(\dot{\boldsymbol{\gamma}} : \boldsymbol{QQ})$. By comparing Eqs. 13.5-5 and 13.5-6 we are led to the conclusion that for any spring force law, we must have

$$\phi_1 = \frac{\zeta}{8kT}(\dot{\boldsymbol{\gamma}} : \boldsymbol{QQ}) \tag{13.5-10}$$

It is not too difficult to verify that this satisfies Eq. 13.5-7 (see Problem 13B.6).

Guessing the form of ϕ_2 is somewhat more difficult. From $\dot{\boldsymbol{\gamma}}$, $\boldsymbol{\omega}$, and $\boldsymbol{Q}$ three scalars can be constructed, satisfying restrictions i to iv, which contain products of velocity gradients: $(\dot{\boldsymbol{\gamma}} : \mathbf{QQ})^2$, $(\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})$, and $(\{\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\omega}\} : \boldsymbol{QQ})$. By looking at Eq. 13.5-6 we then know that ϕ_2 must have the form

$$\phi_2 = \left(\frac{\zeta}{8kT}\right)^2 \left(\frac{1}{2}(\dot{\boldsymbol{\gamma}} : \boldsymbol{QQ})^2 - \frac{1}{15}\langle Q^4 \rangle_{\text{eq}} (\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}}) + A(Q)(\{\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\omega}\} : \boldsymbol{QQ}) \right) \tag{13.5-11}$$

in which $A(Q)$ is a function of Q, which has to be be determined by requiring that ϕ_2 satisfy the differential equation in Eq. 13.5-8. If into the latter we substitute ϕ_2 from Eq. 13.5-11 we obtain

$$\frac{d^2A}{dQ^2} + \left(\frac{6}{Q} - \frac{F^{(c)}}{kT}\right)\frac{dA}{dQ} - \frac{2}{Q}\frac{F^{(c)}A}{kT} = -4 \tag{13.5-12}$$

Equations 13.5-11 and 12 and the boundary conditions constitute a formal solution for ϕ_2 for *any* kind of elastic dumbbell.

If we now specialize to the FENE dumbbell with force law given by Eq. 13.5-1, then Eq. 13.5-12 can be solved for $A(Q)$ to get

$$A(Q) = \frac{4Q_0^2}{2b+7}\left[1 - \frac{1}{2}\left(\frac{Q}{Q_0}\right)^2\right] \tag{13.5-13}$$

Since Eq. 13.5-12 is a second-order differential equation the general solution consists of the particular integral (given in Eq. 13.5-13) plus a complementary function containing two constants. It may be shown, however, that this complementary function does not satisfy the

boundary conditions. In addition $\langle Q^4\rangle_{eq}$ is given explicitly as

$$\langle Q^4\rangle_{eq} = \frac{15}{(b+5)(b+7)} Q_0^4 \tag{13.5-14}$$

Therefore we obtain finally for the configurational distribution function for the suspension of FENE dumbbells:

$$\psi = \frac{1}{J_{eq}}\left[1-\left(\frac{Q}{Q_0}\right)^2\right]^{b/2}\left(1+\left(\frac{H\lambda_H}{2kT}\right)(\dot\gamma : \boldsymbol{QQ}) + \left(\frac{H\lambda_H}{2kT}\right)^2\left[-\frac{Q_0^4}{(b+5)(b+7)}(\dot\gamma:\dot\gamma)\right.\right.$$
$$\left.\left. + \frac{4Q_0^2}{(2b+7)}\left(1-\frac{1}{2}\left(\frac{Q}{Q_0}\right)^2\right)(\{\dot\gamma\cdot\boldsymbol{\omega}\}:\boldsymbol{QQ}) + \frac{1}{2}(\dot\gamma:\boldsymbol{QQ})^2\right] + \cdots\right) \tag{13.5-15}$$

where J_{eq} is the normalization constant given in fn. *a* of Table 11.5-1.

Next we turn to the development of an expression for the stress tensor, taking as our starting point the Giesekus expression, Eq. D in Table 13.3-1. If into the latter we insert Eqs. 13.5-5, 13.5-10, and 13.5-11, we get for *any* kind of elastic dumbbell to second order

$$\boldsymbol{\tau}_p = -\frac{n\zeta}{12}\langle Q^2\rangle_{eq}\dot\gamma + \frac{n\zeta^2}{480kT}\langle Q^4\rangle_{eq}(\{\boldsymbol{\omega}\cdot\dot\gamma - \dot\gamma\cdot\boldsymbol{\omega}\} - 2\{\dot\gamma\cdot\dot\gamma\}) + \cdots \tag{13.5-16}$$

[6]

When we specialize to the FENE dumbbells and include in addition the results from Eq. 13.5-15, we get

$$\boldsymbol{\tau}_p = -\frac{bnkT\lambda_H}{b+5}\dot\gamma + \frac{1}{2}\frac{b^2nkT\lambda_H^2}{(b+5)(b+7)}(\{\boldsymbol{\omega}\cdot\dot\gamma - \dot\gamma\cdot\boldsymbol{\omega}\} - 2\dot\gamma^2)$$
$$-\frac{1}{4}\frac{b^3(2b+11)nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)}\{\boldsymbol{\omega}\cdot\{\boldsymbol{\omega}\cdot\dot\gamma - \dot\gamma\cdot\boldsymbol{\omega}\} - \{\boldsymbol{\omega}\cdot\dot\gamma - \dot\gamma\cdot\boldsymbol{\omega}\}\cdot\boldsymbol{\omega}\}$$
$$+\frac{1}{4}\frac{b^3(6b+25)nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)}\{\boldsymbol{\omega}\cdot\dot\gamma^2 - \dot\gamma^2\cdot\boldsymbol{\omega}\}$$
$$-\frac{1}{2}\frac{b^3(b+3)nkT\lambda_H^3}{(b+5)^2(b+7)(b+9)}(\dot\gamma:\dot\gamma)\dot\gamma + \cdots \tag{13.5-17}$$

[7]

where λ_H and b are defined by Eqs. 13.5-2 and 13.5-4. Equation 13.5-17 is the principal result of this section; in sharp contrast with the Hookean dumbbells for which we obtained a complete constitutive equation, we have succeeded here in getting an analytical expression only for steady state, and then only up to the terms cubic in the velocity gradients.

[6] See Eqs. E.7-4, E.7-5, and E.7-6 for the evaluation of the integrals of polyads of the unit normal over the surface of a sphere.

[7] To get this result we need the following formula for FENE dumbbells

$$\frac{\langle Q^n\rangle_{eq}}{\langle Q^{n-2}\rangle_{eq}} = \frac{(n+1)Q_0^2}{n+b+3} \tag{13.5-17a}$$

The result in Eq. 13.5-17 can be used to relate the constants in a constitutive equation from continuum mechanics to the structural parameters in the model. For example, if we simplify Eq. D.4-3 for steady, homogeneous flow, we can then make a term-by-term comparison with Eq. 13.5-17 and obtain the following expressions for the b's in Eq. D.4-3 (the retarded-motion expansion):

$$b_1 = \eta_s + \frac{bnkT\lambda_H}{b+5} \tag{13.5-18}$$

$$b_2 = -\frac{b^2 nkT\lambda_H^2}{(b+5)(b+7)} \tag{13.5-19}$$

$$b_{11} = 0 \tag{13.5-20}$$

$$b_3 = \frac{b^3(2b+11)nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)} \tag{13.5-21}$$

$$b_{12} = \frac{4b^3 nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)} \tag{13.5-22}$$

$$b_{1:1\,1} = \frac{6b^3 nkT\lambda_H^3}{2(2b+7)(b+5)^2(b+7)(b+9)} \tag{13.5-23}$$

Thus the b's are given explicitly in terms of the spring constant H, the maximum extension Q_0, the number density n, the solvent viscosity η_s, and the temperature. It should be noted that whereas Eq. 13.5-17 applies only to steady-state flow, Eq. D.4-3 with the above expressions for the b's is valid for slowly varying flows. By making use of continuum mechanics results we have thus succeeded in generalizing slightly the molecular theory results.

From the retarded-motion expansion we can get the viscometric functions for small shear rates and the components of the complex viscosity for small frequencies; to get the $\dot{\gamma}^2$-term in Ψ_1 and the ω^2 term in η''/ω, it is necessary to solve Eq. 13.2-13 for the specific flows of interest. The results are

$$\frac{\eta - \eta_s}{nkT\lambda_H} = \frac{b}{b+5}\left[1 - \frac{2b^2(4b+17)}{(b+5)(b+7)(b+9)(2b+7)}(\lambda_H\dot{\gamma})^2 + \cdots\right] \tag{13.5-24}$$

$$\frac{\Psi_1}{nkT\lambda_H^2} = \frac{2b^2}{(b+5)(b+7)}\left[1 - \frac{2b^2(20b^3+315b^2+1578b+2569)}{(b+5)(b+7)(b+9)(b+11)(2b+7)^2}(\lambda_H\dot{\gamma})^2 + \cdots\right] \tag{13.5-25}$$

and

$$\frac{\eta' - \eta_s}{nkT\lambda_H} = \frac{b}{b+5}\left[1 - \frac{b^2(2b+11)}{(b+7)(b+9)(2b+7)}(\lambda_H\omega)^2 + \cdots\right] \tag{13.5-26}$$

$$\frac{\eta''/\omega}{nkT\lambda_H^2} = \frac{b^2}{(b+5)(b+7)}\left[1 - \frac{b^2(4b^2+52b+151)}{(b+9)(b+11)(2b+7)^2}(\lambda_H\omega)^2 + \cdots\right] \tag{13.5-27}^2$$

From Eq. 13.2-13 one can also get an expansion in powers of $1/\omega$ for the small-amplitude oscillatory properties:

$$\frac{\eta' - \eta_s}{nkT\lambda_H} = \frac{(b+3)(b^2-6b+14)}{(b-2)(b-4)(b-6)} \frac{1}{(\lambda_H\omega)^2} + \cdots \tag{13.5-28}$$

$$\frac{\eta''/\omega}{nkT\lambda_H^2} = \frac{b}{b-2} \frac{1}{(\lambda_H\omega)^2} + \cdots \tag{13.5-29}$$

The functions $\eta'(\omega)$ and $\eta''(\omega)$ are shown in Fig. 13.5-1.

The perturbation series of Eq. 13.5-5 probably converges only for $\lambda_H\dot{\gamma}$ somewhat less than unity (see comments following Eq. 14.4-20). To describe nonlinear behavior for larger $\lambda_H\dot{\gamma}$, it is necessary to solve the diffusion equation numerically.[8]

Figure 13.5-2 shows some intrinsic viscosity data for a series of monodisperse poly-α-methylstyrene samples in toluene plotted along with some curves calculated for FENE dumbbells, Hookean dumbbells, and rigid dumbbells. In plotting the FENE dumbbell curves, the time constant has been determined from the zero-shear-rate intrinsic viscosity by using only the zero-shear-rate term in Eq. 13.5-24, so that

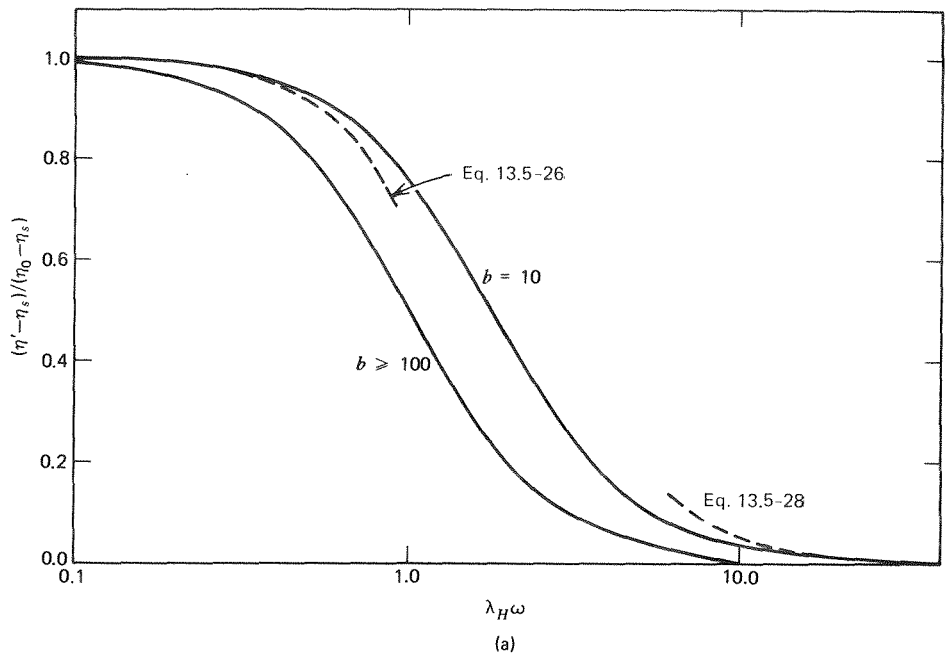
$$\lambda_H = \left(\frac{b+5}{b}\right) \frac{[\eta]_0\eta_s M}{\tilde{N}kT} \tag{13.5-30}$$

It can be seen that the calculated curves for the FENE dumbbells have approximately the correct shape and that they allow for a series of curves; this is a considerable improvement over the Hookean dumbbells. Values of b between 10 and 100 seem to be appropriate for describing the data in Fig. 13.5-2.

In Fig. 13.5-3 we see a comparison of the FENE dumbbell results with experimental data for the material functions for small-amplitude oscillatory motion. It can be seen that no value of b can be chosen to match the η' and η'' data, and that the FENE dumbbell model offers virtually no improvement over the Hookean dumbbell. This is to be expected, since the small-amplitude experiment does not probe the nonlinear aspect of the spring representing the polymer. To describe this experiment we need to incorporate more beads and springs into the model to simulate the large number of degrees of freedom and the spectrum of time constants (see Chapter 15). The apparent ability of the model to describe $\eta(\dot{\gamma})$ but not $\eta'(\omega)$ is investigated further in Problem 13A.1.

We would like to conclude from the above that taking into account the nonlinear stretching of the polymer molecules is the most important correction that should be made to the Hookean model in order to describe real systems. However, there are many other effects—such as hydrodynamic interaction,[9] excluded volume,[10] internal viscosity,[11] perturbation of the velocity gradient,[12] wall effects,[13] friction coefficient varying with dumbbell

[8] X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 125-144 (1985).
[9] See §13.6 and Problem 13B.2.
[10] In connection with the many effects that can be included in bead-spring theories see the survey articles of A. Peterlin, *Adv. in Macr. Chem.*, **1**, 225-281 (1968) and M. Fixman and W. H. Stockmayer, *Ann. Rev. Phys. Chem.*, **21**, 407-428, (1970).
[11] See Problem 13C.2.
[12] K. Higashitani, Ph.D. Thesis, University of Wisconsin, Madison (1973), Appendix G, pp. 238 253. P. Schümmer and B. Otten, *Proc. IXth Internat. Congress on Rheology*, Mexico (1984), pp. 399-403.
[13] P. Brunn, *Rheol. Acta*, **15**, 23 29 (1976).



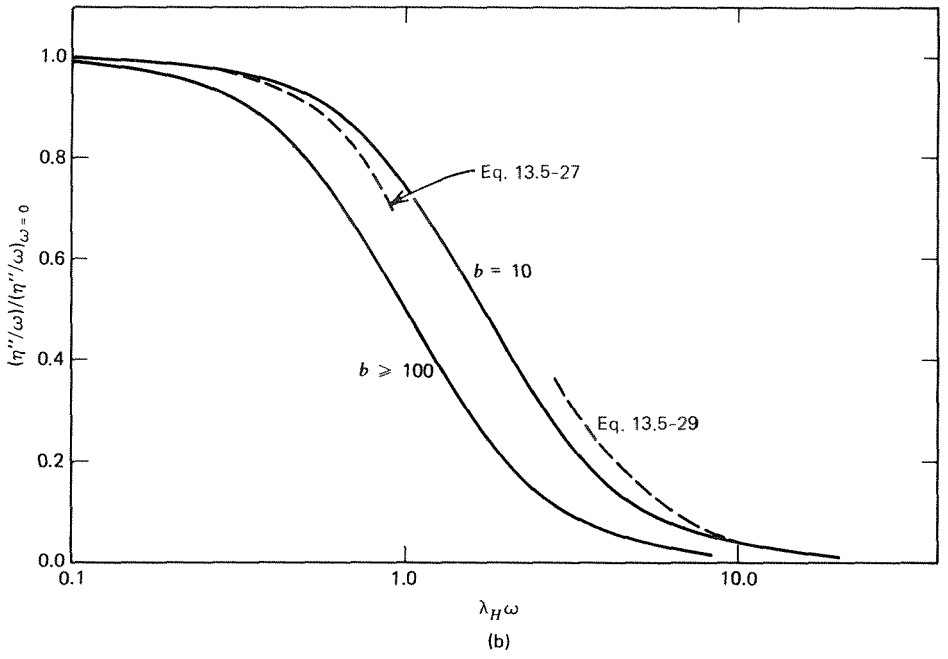


FIGURE 13.5-1. The small-amplitude oscillatory material functions for FENE dumbbells. The solid curves for $b = 10$ and $b \geq 100$ were calculated by Warner.[2] The dashed lines are obtained from the first few terms of asymptotic expansions given in Eqs. 13.5-26 to 13.5-29. The time constant is defined as $\lambda_H = \zeta/4H$, and the dimensionless parameter b is HQ_0^2/kT. Reprinted from R. L. Christiansen and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **3**, 161–177 (1977/1978).

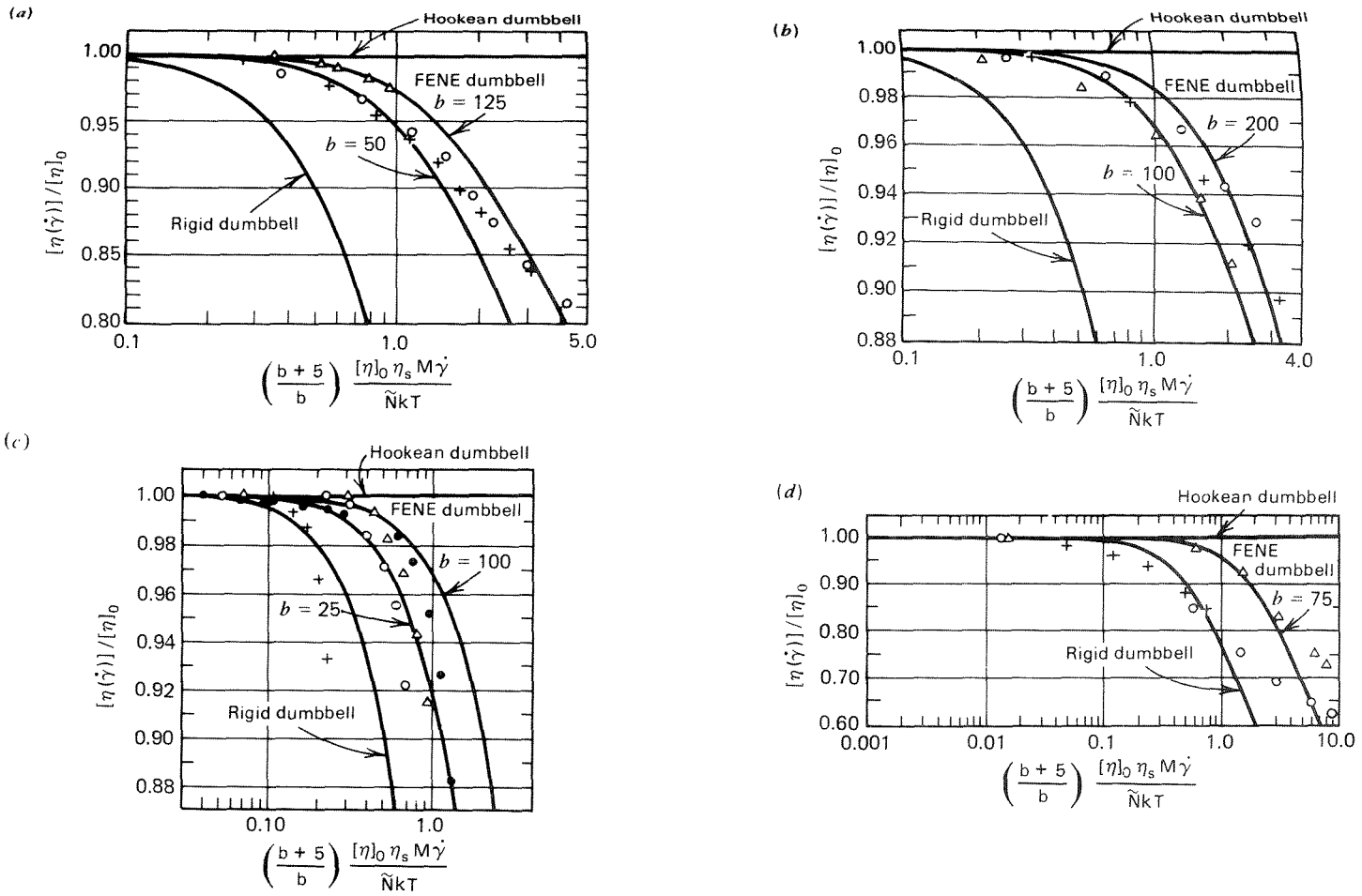


FIGURE 13.5-2. Comparison of experimental intrinsic viscosities and calculated curves from the FENE dumbbell model. (*a*) Polystyrene in benzene at 30° C for several molecular weights: 6×10^6 (+), 7.14×10^6 (○), 3.16×10^6 (△). Data of H. Suzuki, T. Kotaka, and H. Inagaki, *J. Chem. Phys.*, **51**, 1279–1285 (1969). (*b*) Polystyrene (molecular weight 10^7) in toluene for several temperatures: 20 C (+), 40 C (○), 60 C (△). Data of H. van Oene and L. H. Cragg, *J. Polym. Sci.*, **57**, 209–225 (1962). (*c*) Poly-α-methylstyrene in toluene at 25 C for several molecular weights: 0.696×10^6 (+), 1.24×10^6 (○), 1.46×10^6 (△), 1.82×10^6 (●). Data of I. Noda, Y. Yamada, and M. Nagasawa, *J. Phys. Chem.*, **72**, 2890–2898 (1968). (*d*) Cellulose in cadoxene at 25° C for several molecular weights: 0.330×10^6 (△), 0.109×10^6 (+), 0.429×10^6 (○). Data of E. Riande and J. M. Pereña, *Makromol. Chemie*, **175**, 2923–2938 (1974). Reprinted with permission from X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 125–144 (1985).

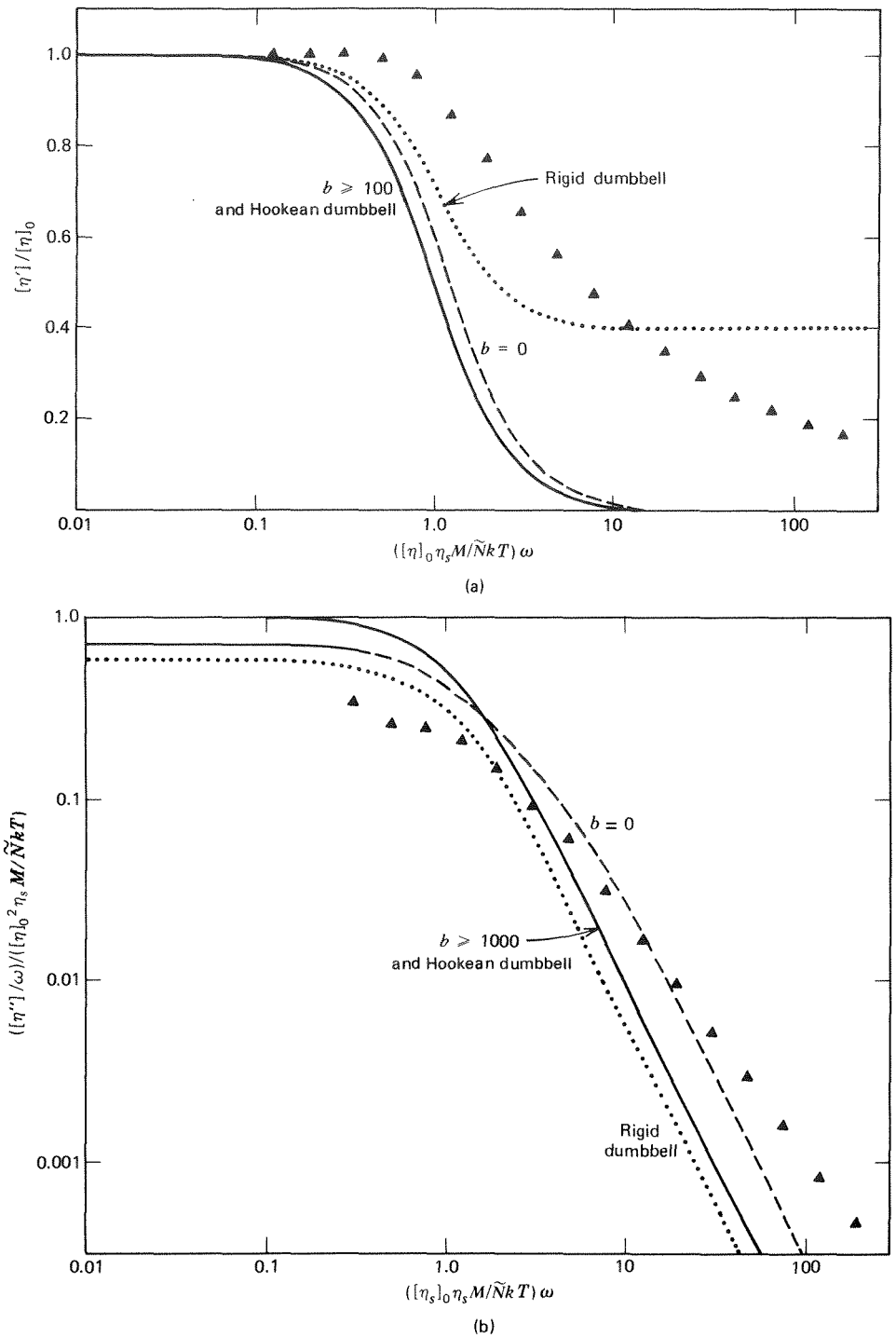


FIGURE 13.5-3. Comparison of theoretical calculations of FENE dumbbell solutions with experimental data. The solid triangles are the data points of D. J. Massa, Ph.D. Thesis, University of Wisconsin, Madison (1970); the experimental fluid is polystyrene ($\bar{M}_w = 860{,}000$; $\bar{M}_w/\bar{M}_n = 1.15$) in Aroclor 1248. The FENE dumbbell curves for $b \geq 1000$ are indistinguishable from that for Hookean dumbbells; the $b = 0$ curves (dashed) are only approximate, included in order to give some estimate as to the limited spread of the curves for various b values. The rigid dumbbell curves (dotted lines) are shown for comparison. Based on R. L. Christiansen and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **3**, 161–177 (1977/1978).

extension,[14] and nonisotropic frictional drag[15]—that can also be invoked, and that might be able to describe the shear-rate dependence of the viscosity. Keep in mind also that the dumbbell models allow only for interaction with the solvent at two points in the molecule (that is, at the two beads), whereas in any real molecule there will be many points along the molecule where the "hydrodynamic drag" will be felt. Nonetheless this section has shown how we can compare model results with experimental data to evolve better macromolecular models.

EXAMPLE 13.5-1 Steady Elongational Flow (FENE Dumbbells)

Obtain a formal expression for the elongational viscosity of a dilute solution of FENE dumbbells. Then obtain an approximate expression asymptotically valid for large rates of elongation. Finally obtain the perturbation expansion for small rates of elongation. Combine these two asymptotic calculations to sketch the elongational viscosity over the entire elongation-rate range.

SOLUTION **(a)** Formal Solution for $\bar{\eta}$.

This is a steady, homogeneous, potential flow for which $\psi(\boldsymbol{Q})$ is given by Eq. 13.2-14; when this expression is used in the Giesekus form for the stress tensor we get

$$\boldsymbol{\tau} = -\eta_s\dot{\gamma} - \frac{n\zeta}{4}\int\{\boldsymbol{\kappa}\cdot\boldsymbol{QQ} + \boldsymbol{QQ}\cdot\boldsymbol{\kappa}\}\psi_{eq}\phi_{fl}\,d\boldsymbol{Q} \tag{13.5-31}$$

For this flow $\boldsymbol{\kappa}$ is given in Eq. (B) of Table 13.1-1 with $b = 0$ and $\dot{\varepsilon}$ = a constant, and

$$\{\boldsymbol{\kappa}\cdot\boldsymbol{QQ} + \boldsymbol{QQ}\cdot\boldsymbol{\kappa}\} = \begin{pmatrix} -S^2c^2 & -S^2sc & \frac{1}{2}SCc \\ -S^2sc & -S^2s^2 & \frac{1}{2}SCs \\ \frac{1}{2}SCc & \frac{1}{2}SCs & 2C^2 \end{pmatrix} Q^2\dot{\varepsilon} \tag{13.5-32}$$

$$(\boldsymbol{\kappa}:\boldsymbol{QQ}) = -\tfrac{1}{2}Q^2(1 - 3C^2)\dot{\varepsilon} \tag{13.5-33}$$

in which Q, θ, and ϕ give the length and polar angles of the $\boldsymbol{Q}$ vector and $S = \sin\theta$, $C = \cos\theta$, $s = \sin\phi$, and $c = \cos\phi$. Then from the definition of $\bar{\eta}$ given in Eq. D.5-14 (or Eq. 3.5-3) we get from Eq. 13.5-31

$$\begin{aligned}\bar{\eta} &= \frac{\tau_{yy} - \tau_{zz}}{\dot{\varepsilon}} \\ &= 3\eta_s + \frac{n\zeta}{4}\frac{\int_0^{2\pi}\int_0^{\pi}\int_0^{Q_0} Q^2(S^2s^2 + 2C^2)\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta\,d\phi}{\int_0^{2\pi}\int_0^{\pi}\int_0^{Q_0}\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta\,d\phi} \\ &= 3\eta_s + \frac{n\zeta}{4}\frac{\int_0^{\pi/2}\int_0^{Q_0} Q^2(\frac{1}{2}S^2 + 2C^2)\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta}{\int_0^{\pi/2}\int_0^{Q_0}\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta}\end{aligned} \tag{13.5-34}$$

[14] P. G. deGennes, *J. Chem. Phys.*, **60**, 5030–5042 (1974); R. I. Tanner, *Trans. Soc. Rheol.*, **19**, 557–582 (1975); E. J. Hinch, *Phys. Fluids*, **20**, S22–S30 (1977); G. G. Fuller and L. G. Leal, *J. Non-Newtonian Fluid Mech.*, **8**, 271–310 (1981); N. Phan-Thien, O. Manero, and L. G. Leal, *Rheol. Acta*, **23**, 151–162 (1984); X. J. Fan, R. B. Bird, and M. Renardy, *J. Non-Newtonian Fluid Mech.*, **18**, 255–272 (1985).

[15] H. Giesekus, *J. Non-Newtonian Fluid Mech.*, **11**, 69–109 (1982); R. B. Bird and J. M. Wiest, *J. Rheol.*, **29**, 519–532 (1985); see also §13.7.

in which

$$\psi'_{eq} = \left[1 - \left(\frac{Q}{Q_0}\right)^2\right]^{b/2} \tag{13.5-35}$$

$$\phi'_{fl} = \exp\left[-\frac{b}{2}\left(\frac{Q}{Q_0}\right)^2 (1 - 3C^2)\lambda_H \dot{\varepsilon}\right] \tag{13.5-36}$$

Here we have replaced $\psi = \psi_{eq}\phi_{fl}$ of Eq. 13.2-14 by $(1/J)\psi'_{eq}\phi'_{fl}$; note that the triple integral in the denominator of the second line of Eq. 13.5-34 is just J.

(b) Asymptotic Expansion for High Elongation Rates

Now consider the integrands in the limit as $\lambda_H\dot{\varepsilon}$ approaches infinity. We see that both integrands in the last line of Eq. 13.5-34 have a maximum close to the point $(Q, \theta) = (Q_0, 0)$. Moreover, because of the exponential function we expect this maximum to become very sharp in the limit as $\lambda_H\dot{\varepsilon}$ tends to infinity. Let us therefore consider the integrands close to the point $(Q, \theta) = (Q_0, 0)$. First we introduce a change of variable such that

$$x = 1 - \frac{Q}{Q_0} \tag{13.5-37}$$

With this change the peak is now close to $(x, \theta) = (0, 0)$. We now expand the various functions in the integrands as follows:

$$\phi'_{fl} = e^{(b/2)\lambda_H\dot{\varepsilon}(2 - 4x - 3\theta^2 + \cdots)} \tag{13.5-38a}$$

$$Q^2\psi'_{eq} = Q_0^2(2x)^{b/2}\left(1 - \frac{b+8}{4}x + \cdots\right) \tag{13.5-38b}$$

$$Q^4\psi'_{eq} = Q_0^4(2x)^{b/2}\left(1 - \frac{b+16}{4}x + \cdots\right) \tag{13.5-38c}$$

$$S = \theta\left(1 - \frac{\theta^2}{6} + \cdots\right) \tag{13.5-38d}$$

$$(\tfrac{1}{2}S^2 + 2C^2)S = 2\theta(1 - \tfrac{11}{12}\theta^2 + \cdots) \tag{13.5-38e}$$

Roughly speaking we have expanded the "smooth" part of the functions around $(x, \theta) = (0, 0)$. Notice that ψ'_{eq} does not have a Taylor expansion around (0, 0) but that it has been written as a fractional power multiplied by a polynomial expansion. Now both integrands in Eq. 13.5-34 may be factored into parts containing the x-dependence and the θ-dependence separately. These factors have the general forms

$$f(\theta) = \theta(1 - \alpha\theta^2 + \cdots)e^{-(3b/2)\theta^2\lambda_H\dot{\varepsilon}} \tag{13.5-39}$$

$$g(x) = x^{b/2}(1 - \beta x + \cdots)e^{-2bx\lambda_H\dot{\varepsilon}} \tag{13.5-40}$$

By taking derivatives of these functions we see that in the limit $\lambda_H\dot{\varepsilon} \to \infty$ the maximum in the integrands in Eq. 13.5-34 is to a first approximation located at $(x, \theta)_{max} = ((4\lambda_H\dot{\varepsilon})^{-1}, (3b\lambda_H\dot{\varepsilon})^{-1/2})$. Indeed since b is positive, the peak approaches (0, 0) in the limit $\lambda_H\dot{\varepsilon} \to \infty$. Loosely we may say that the peak is located inside the radius of convergence of the polynomial expansions in Eq. 13.5-39 and 13.5-40, and that we have obtained good approximations to the integrands in the neighborhood of the peak. With this information we may now approximate Eqs. 13.5-34 to 13.5-36 by

$$\bar{\eta} \doteq 3\eta_s + \frac{n\zeta Q_0^2 I_{Nx} I_{N\theta}}{4 I_{Dx} I_{D\theta}} \tag{13.5-41}$$

where the I-integrals are dimensionless quantities given by

$$I_{Nx} = \int_0^\infty x^{b/2}\left(1 - \frac{b+16}{4}x\right)e^{-2b\lambda_H\dot{\varepsilon}x}\,dx$$
$$= \frac{\Gamma[(b+2)/2]}{(2b\lambda_H\dot{\varepsilon})^{(b+2)/2}}\left[1 - \frac{(b+16)(b+2)}{16b}\frac{1}{\lambda_H\dot{\varepsilon}}\right] \tag{13.5-42}$$

$$I_{N\theta} = 2\int_0^\infty \theta\left(1 - \frac{11}{12}\theta^2\right)e^{-(3b/2)\lambda_H\dot{\varepsilon}\theta^2}\,d\theta$$
$$= \frac{2}{3b\lambda_H\dot{\varepsilon}}\left[1 - \frac{11}{12}\left(\frac{2}{3b}\right)\frac{1}{\lambda_H\dot{\varepsilon}}\right] \tag{13.5-43}$$

I_{Dx} is the same as I_{Nx} with the factor $(b + 16)$ replaced by $(b + 8)$, and $I_{D\theta}$ is one-half $I_{N\theta}$ with the factor $\frac{11}{12}$ replaced by $\frac{1}{6}$. In obtaining these integrals we have made use of an important property of the approximations written symbolically in Eqs. 13.5-39 and 13.5-40; the approximating functions approach zero exponentially away from the peak. Hence in the limit $\lambda_H\dot{\varepsilon} \to \infty$ the ranges of integration may be extended to infinity with negligible error. When the expressions for I_{Nx}, $I_{N\theta}$, I_{Dx}, and $I_{D\theta}$ are introduced in Eq. 13.5-41, we obtain finally in the limit of large elongation rates:

$$\bar{\eta} = 3\eta_s + 2bnkT\lambda_H\left[1 - \frac{b+3}{2b}\frac{1}{\lambda_H\dot{\varepsilon}} + \cdots\right] \tag{13.5-44}$$

We see that for finite b the elongational viscosity approaches a limiting value as $\lambda_H\dot{\varepsilon} \to \infty$. This is in contrast with the behavior of Hookean dumbbells.

(c) Expansion for Low Elongation Rates

An expansion for $\bar{\eta}$ for small elongation rates may be obtained directly from the general slow flow expansion in Eq. 13.5-17. With the velocity field represented by Eq. (B) of Table 13.1-1, with $b = 0$, we find

$$\bar{\eta} = 3\eta_s + \frac{3bnkT\lambda_H}{b+5}\left[1 + \frac{b}{b+7}(\lambda_H\dot{\varepsilon}) + \frac{3b^2(b+3)}{(b+5)(b+7)(b+9)}(\lambda_H\dot{\varepsilon})^2 + \cdots\right] \tag{13.5-45}$$

Equations 13.5-44 and 13.5-45 may be combined to give a good approximation to $\bar{\eta}$ over the entire range of elongation rates, as illustrated in Fig. 13.5-4. For small elongation rates the elongational viscosity is assumed to follow the perturbation expansion in Eq. 13.5-45. In a small intermediate region the perturbation expansion and the asymptotic expansion overlap. For larger elongation rates the elongational viscosity is assumed to follow the asymptotic expansion. The validity of this simple graphical splicing procedure in the region around $\lambda_H\dot{\varepsilon} = \frac{1}{2}$ is supported by numerical calculations.[2] Unfortunately no experimental $\bar{\eta}(\dot{\varepsilon})$ data are available to compare with the theory.[16]

[16] The main results of this illustrative example have been used with some success in studies on turbulent drag reduction and on flows in porous media [F. Durst and R. Haas, *Rheol. Acta*, **20**, 179–192 (1981); R. Haas and F. Durst, *ibid.*, **21**, 150–166 (1982); F. Durst, R. Haas, and W. Interthal, *Rheol. Acta*, **21**, 572–577 (1982); F. Durst, R. Haas, W. Interthal, and T. Keck, *Chemie-Ingenieur Technik*, **54**, 213–221 (1982). The analogous results for the Kramers bead-rod chain (see §16.5) have been used by S. T. J. Peng and R. F. Landel [in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Plenum, New York (1980), pp. 385–391] in their study of the tubeless siphon experiment.

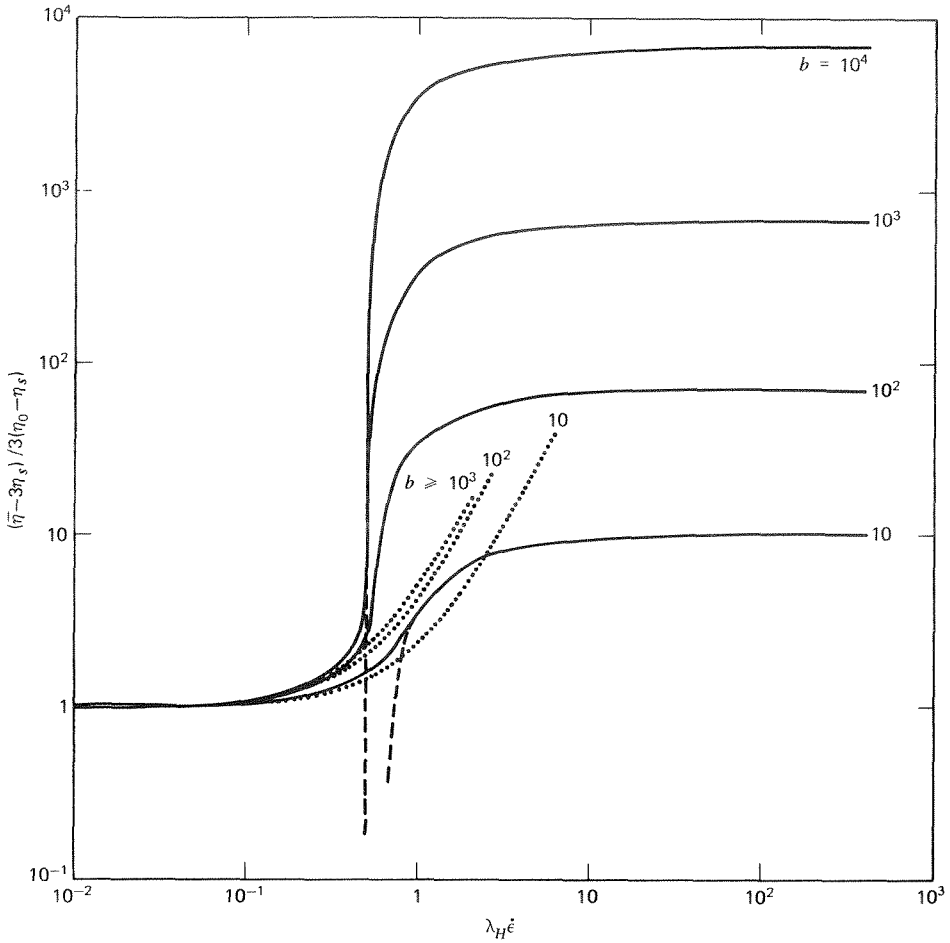


FIGURE 13.5-4. Elongational viscosity curves for FENE dumbbells. An approximation for arbitrary rates of elongation is obtained by graphical splicing of a perturbation expansion valid for small elongation rates and an asymptotic expansion valid for large elongation rates. ....., Perturbation expansion Eq. 13.5-45; ------, Asymptotic expansion Eq. 13.5-44; _____, Graphically matched approximation.

EXAMPLE 13.5-2 An Approximate Constitutive Equation (FENE Dumbbells)

For the FENE dumbbell model the Kramers and Giesekus forms of the polymer contribution to the stress tensor are

$$\text{Kramers:} \quad \boldsymbol{\tau}_p = -nH\left\langle \frac{\boldsymbol{QQ}}{1-(Q^2/Q_0^2)} \right\rangle + nkT\boldsymbol{\delta} \tag{13.5-46}$$

$$\text{Giesekus:} \quad \boldsymbol{\tau}_p = \frac{n\zeta}{4}\langle \boldsymbol{QQ} \rangle_{(1)} \tag{13.5-47}$$

It is not possible to apply the procedure used in Eqs. 13.4-2 to 13.4-5 to get a constitutive equation by eliminating the average values. Show that this procedure can, however, be applied if in Eq. 13.5-46 we

approximate the average value in the following way:

$$\left\langle \frac{\boldsymbol{QQ}}{1-(Q^2/Q_0^2)} \right\rangle \doteq \frac{\langle \boldsymbol{QQ} \rangle}{1-\langle Q^2/Q_0^2 \rangle} + \varepsilon Q_0^2 \boldsymbol{\delta} \tag{13.5-48}$$

where ε is a constant. That is, replace the average of the ratio by the ratio of averages, and then add an extra isotropic term containing a constant in order to improve the approximation.[8,17] Determine the constant ε by requiring that the trace of the above relation be true at equilibrium.

SOLUTION **(a)** Let $x = Q/Q_0$, and then require that

$$\left\langle \frac{x^2}{1-x^2} \right\rangle_{eq} = \frac{\langle x^2 \rangle_{eq}}{1-\langle x^2 \rangle_{eq}} + 3\varepsilon \tag{13.5-49}$$

Since $\psi_{eq} \propto (1-x^2)^{b/2}$ (according to Eq. L of Table 11.5-1) these integrals can be evaluated and we find that

$$\frac{3}{b} = \frac{3/(b+5)}{1-[3/(b+5)]} + 3\varepsilon \tag{13.5-50}$$

and hence

$$\varepsilon = \frac{2}{b(b+2)} \tag{13.5-51}$$

Then we can replace Eq. 13.5-46 by

$$\text{Kramers (approximate):} \qquad \boldsymbol{\tau}_p = -\frac{nH\langle \boldsymbol{QQ} \rangle}{1-\langle Q^2/Q_0^2 \rangle} + (1-\varepsilon b)nkT\boldsymbol{\delta} \tag{13.5-52}$$

(b) Now to get an approximate constitutive equation, we have to eliminate all $\langle\ \rangle$ quantities appearing in Eqs. 13.5-47 and 13.5-52. To do this we take the trace of Eq. 13.5-52 and solve for $\langle Q^2/Q_0^2 \rangle$:

$$\left\langle \frac{Q^2}{Q_0^2} \right\rangle = 1 - Z^{-1} \tag{13.5-53}$$

where

$$Z = 1 + \frac{3}{b}\left((1-\varepsilon b) - \frac{\operatorname{tr}\boldsymbol{\tau}_p}{3nkT}\right) \tag{13.5-54}$$

Then Eq. 13.5-52 can be rewritten

$$\text{Kramers (approximate):} \qquad \boldsymbol{\tau}_p = -nHZ\langle \boldsymbol{QQ} \rangle + (1-\varepsilon b)nkT\boldsymbol{\delta} \tag{13.5-55}$$

[17] R. B. Bird, P. J. Dotson, and N. L. Johnson [*J. Non-Newtonian Fluid Mech.*, **7**, 213-235 (1980)] did a similar analysis for $\varepsilon = 0$. In this paper Eq. 58 and all subsequent equations are in error.

Now we can form the convected derivative $(\boldsymbol{\tau}_p/Z)_{(1)}$ from Eq. 13.5-55 and then use Eq. 13.5-47 to eliminate $\langle \boldsymbol{QQ} \rangle_{(1)}$. This leads after some rearrangement to[18]

$$\boxed{Z\boldsymbol{\tau}_p + \lambda_H \boldsymbol{\tau}_{p(1)} - \lambda_H[\boldsymbol{\tau}_p - (1 - \varepsilon b)nkT\boldsymbol{\delta}]\frac{D \ln Z}{Dt} = -(1 - \varepsilon b)nkT\lambda_H \boldsymbol{\gamma}_{(1)}} \tag{13.5-56}$$

which is an approximate constitutive equation.[19] Note that this equation is not linear in $\boldsymbol{\tau}_p$; it contains the parameters $\lambda_H = \zeta/4H$ (time constant), $b = HQ_0^2/kT$ (dimensionless), and nkT.

(c) For steady-state shear flow ($v_x = \dot{\gamma}y$) Eq. 13.5-56 becomes

$$Z\begin{pmatrix} \tau_{p,xx} & \tau_{p,xy} & \tau_{p,xz} \\ \tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,xz} & \tau_{p,yz} & \tau_{p,zz} \end{pmatrix} - \lambda_H\dot{\gamma}\begin{pmatrix} 2\tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,yy} & 0 & 0 \\ \tau_{p,yz} & 0 & 0 \end{pmatrix} = -(1 - \varepsilon b)nkT\lambda_H\dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{13.5-57}$$

From this we find that $\tau_{p,yy} = \tau_{p,zz} = 0$, and we get a pair of algebraic equations for $\tau_{p,xy}$ and $\tau_{p,xx}$, from which we can extract the following equation for $\mathscr{S} = \tau_{p,xy}/[3nkT(1 - \varepsilon b)]$:

$$\mathscr{S}^3 + 3p\mathscr{S} + 2q = 0 \tag{13.5-58}$$

where

$$p = \frac{b}{54(1 - \varepsilon b)} + \frac{1}{18}; \qquad q = \frac{b\lambda_H\dot{\gamma}}{108(1 - \varepsilon b)} \tag{13.5-59}$$

The only real root of this equation is[20]

$$\mathscr{S} = -2p^{1/2}\sinh(\tfrac{1}{3}\operatorname{arcsinh} qp^{-3/2}) \tag{13.5-60}$$

From this $\eta(\dot{\gamma})$ can be obtained, and with $\varepsilon = 2/[b(b + 2)]$:

$$\text{For } \dot{\gamma} = 0: \quad \eta - \eta_s = nkT\lambda_H\left(\frac{b}{b + 5}\right) \tag{13.5-61}$$

$$\text{For } \dot{\gamma} \to \infty: \quad \eta - \eta_s \sim nkT\lambda_H\left(\frac{\sqrt{b/2}}{\lambda_H\dot{\gamma}}\frac{b}{b + 2}\right)^{2/3} \tag{13.5-62}$$

[18] An alternative formulation of the constitutive equation is

$$\boldsymbol{\tau}_p = nkT\lambda_H\boldsymbol{\alpha}_{(1)} \tag{13.5-56a}$$

where the "structure tensor" $\boldsymbol{\alpha} \equiv H\langle \boldsymbol{QQ} \rangle/kT$ is given by

$$(1 - b^{-1}\operatorname{tr}\boldsymbol{\alpha})^{-1}\boldsymbol{\alpha} + \lambda_H\boldsymbol{\alpha}_{(1)} = [b/(b + 2)]\boldsymbol{\delta} \tag{13.5-56b}$$

In the limit of very large b ("nearly Hookean dumbbells"), R. C. Armstrong and S. Ishikawa [*J. Rheol.*, **24**, 143-165 (1980)] found the following equation for $\boldsymbol{\alpha}$, *exact* to order $1/b$:

$$\boldsymbol{\alpha} + \lambda_H\boldsymbol{\alpha}_{(1)} + b^{-1}\{(\operatorname{tr}\boldsymbol{\alpha})\boldsymbol{\alpha} + 2\boldsymbol{\alpha}\cdot\boldsymbol{\alpha}\} = \boldsymbol{\delta} \tag{13.5-56c}$$

[see also R. C. Armstrong, S. K. Gupta, and O. Basaran, *Polym. Eng. Sci.*, **20**, 466-472 (1980), Eq. (9), for another equation for $\boldsymbol{\alpha}$, which provides a matching between Eq. 13.5-56c and Eq. 13.5-56 with $\varepsilon = 0$].

[19] The same equation (for $\varepsilon = 0$) was obtained by R. I. Tanner [*Trans. Soc. Rheol.*, **19**, 37-65 (1975)] by a different method (see Problem 13B.9).

[20] K. Rektorys, *Survey of Applicable Mathematics*, MIT Press, Cambridge, Mass. (1969), pp. 78-79 (in Table 1.1, the b in the third column should be q).

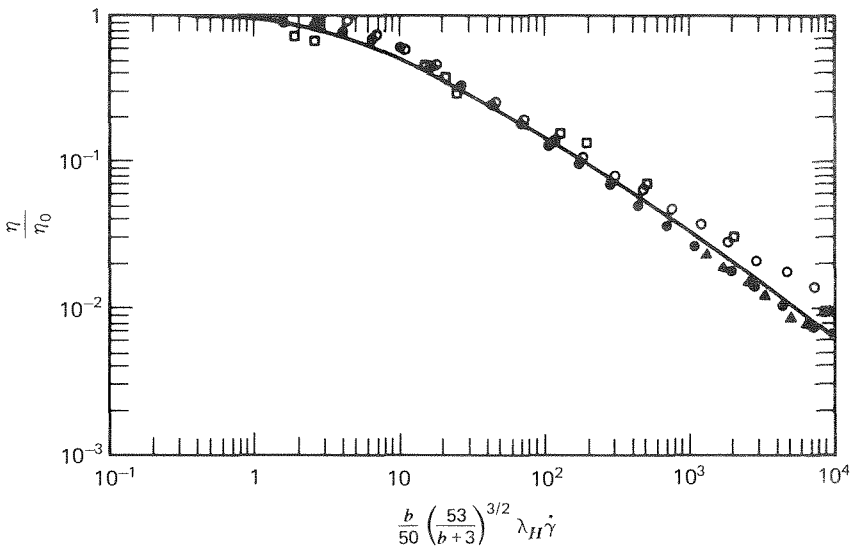


FIGURE 13.5-5. Comparison of Eq. 13.5-60 with experimental viscosity data for several nondilute polymer solutions. ○ polyacrylamide in glycerin; $\lambda_H = 510$ s. [P. J. Leider, *Ind. Eng. Chem. Fund.*, **13**, 342–346 (1974)], ● polyisobutylene in Oppanol-B-1; $\lambda_H = 1915$ s [P. J. Leider, *op. cit.*], □ hydroxyethylcellulose in glycerin/water; $\lambda_H = 2.91$ s [R. J. Grimm, *AIChE J.*, **24**, 427–439 (1978)], and ▲ polyethylene oxide in water; $\lambda_H = 9.23$ s [R. J. Grimm, *op. cit.*]. In making the data comparison b was taken to be 50 for all solutions, and ε is set equal to zero. Reprinted with permission from Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **9**, 157–178 (1981)].

The result for $\dot{\gamma} = 0$ agrees precisely with the exact expression in Eq. 13.5-24, and the simple power-law result for large $\dot{\gamma}$ has been shown to be in good agreement, between $b = 10$ and $b = 300$, with exact numerical calculations.[8] For a comparison of the $\eta(\dot{\gamma})$ curve from Eq. 13.5-60 with some experimental solution data, see Fig. 13.5-5. From Eq. 13.5-57 we can also get the result $\Psi_1 = 2(\eta - \eta_s)^2/[(1 - \varepsilon b)nkT]$.

(d) For steady elongational flow ($v_z = \dot{\varepsilon}z$, $v_x = -\frac{1}{2}\dot{\varepsilon}x$, $v_y = -\frac{1}{2}\dot{\varepsilon}y$), an analysis similar to that in **(c)** leads to

$$\text{For } \dot{\varepsilon} = 0: \qquad \bar{\eta} - 3\eta_s = 3nkT\lambda_H\left(\frac{b}{b+5}\right) \tag{13.5-63}$$

$$\text{For } \dot{\varepsilon} \to \infty: \qquad \bar{\eta} - 3\eta_s \sim 2nkT\lambda_H b$$

$$\text{For } \dot{\varepsilon} \to -\infty: \quad \bar{\eta} - 3\eta_s \sim \tfrac{1}{2}nkT\lambda_H b \tag{13.5-64}$$

These results agree precisely with the exact results given in Eqs. 13.5-45 and 13.5-44 respectively.

It has been further demonstrated that (for $\varepsilon = 0$) the constitutive equation in Eq. 13.5-56 gives qualitatively reasonable results for shear and normal stresses at sudden inception of shear flow, and for steady shear flow with superposed oscillatory motion.[21] The constitutive equation has, in addition, been used to solve several flow problems: the fast squeezing flow between two parallel disks[22] and the transient development of velocity profiles at the inception of Couette flow.[23] Once the flow field has been determined the information about molecular stretching can be obtained from Eq. 13.5-53; this has been done for a sudden-contraction flow, and the results have been compared with limited data on light scattering.[24]

[21] Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **9**, 179–184 (1981).
[22] Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **9**, 157–178 (1981).
[23] Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **12**, 135–152 (1983).
[24] R. C. Armstrong, S. K. Gupta, and O. Basaran, *op. cit.*

Hence for the FENE-dumbbell model, it has been possible to go through almost the complete sequence of activities:[25]

Molecular model		
↓		
Constitutive equation	←	Use experimental data on material functions to determine constants in the constitutive equation.
↓		
Solution of fluid dynamics problem	⇆	Compare with experimental data on the flow system (velocity profiles, forces, torques, etc.).
↓		
Calculation of molecular stretching in the flow field	⇆	Compare with molecular stretching determined by light scattering.

The execution of such a sequence is one of the goals of polymer fluid dynamics.

§13.6 HYDRODYNAMIC INTERACTION

Thus far in our study of dumbbell kinetic theory we have assumed that the two beads of the dumbbell move through the solvent without disturbing the velocity field. In this section we wish to discuss a method for removing this "free-draining" assumption, at least approximately. We follow here the approach of Kirkwood and Riseman,[1] who seem to have been the first to introduce the idea of *hydrodynamic interaction* into polymer kinetic theory; they drew heavily on the earlier hydrodynamic studies of Burgers[2] and Oseen.[3]

We begin with Eqs. 13.2-1 through 13.2-4, let the friction tensor ζ be isotropic ($\zeta = \zeta\boldsymbol{\delta}$), and use the Maxwellian velocity distribution in the expression for the Brownian force. Then the bead equations of motion become

$$\mathbf{0} = -\zeta[[\dot{\boldsymbol{r}}_1]] - (\boldsymbol{v}_1 + \boldsymbol{v}'_1)] - kT\frac{\partial}{\partial \boldsymbol{r}_1}\ln\Psi + \boldsymbol{F}_1^{(\phi)} + \boldsymbol{F}_1^{(e)} \tag{13.6-1}$$

$$\mathbf{0} = -\zeta[[\dot{\boldsymbol{r}}_2]] - (\boldsymbol{v}_2 + \boldsymbol{v}'_2)] - kT\frac{\partial}{\partial \boldsymbol{r}_2}\ln\Psi + \boldsymbol{F}_2^{(\phi)} + \boldsymbol{F}_2^{(e)} \tag{13.6-2}$$

Next we need to specify $\boldsymbol{v}'_1$ and $\boldsymbol{v}'_2$.

[25] L. E. Wedgewood and R. B. Bird, in *Integration of Fundamental Polymer Science and Technology*, L. A. Kleintjens and P. J. Lemstra (Eds.), Elsevier, London (1986), pp. 337–345.

[1] J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565–573 (1948); **22**, 1626–1627 (1954); see also A. Peterlin, *J. Polym. Sci.*, **5**, 473–482 (1950).

[2] J. M. Burgers, *Verhandelingen Koninkl. Ned. Akad. Wetenschap.*, **16**, (Section 1, Chapter 3), 113–184 (1938).

[3] C. W. Oseen, *Ark. f. Mat. Astr. og Fys.*, **6**, No. 29, 1–20 (1910).

Recall that in Example 1.4-1 (part c) we obtained an expression for the velocity disturbance produced at a position $\boldsymbol{r}$ by a sphere moving through the origin as it exerts a hydrodynamic force $\boldsymbol{F}_s$ on the fluid; this expression is $\boldsymbol{v}'(\boldsymbol{r}) = [\boldsymbol{\Omega} \cdot \boldsymbol{F}_s] + O(a^3/r^3)$, where $\boldsymbol{\Omega}$ is the *Oseen-Burgers tensor* in Eq. 1.4-33 and a is the bead radius. If we apply this result (omitting the a^3/r^3 and smaller contributions), we find that the velocity disturbance at bead "1" owing to the movement of bead "2" is

$$\boldsymbol{v}'_1 = [\boldsymbol{\Omega} \cdot \{\zeta([\![\dot{\boldsymbol{r}}_2]\!] - (\boldsymbol{v}_2 + \boldsymbol{v}'_2))\}] \tag{13.6-3}$$

in which the quantity inside braces is the hydrodynamic force exerted by "2" on the solvent. Then, using Eq. 13.6-2, we get

$$\boldsymbol{v}'_1 = \left[\boldsymbol{\Omega} \cdot \left\{-kT \frac{\partial}{\partial \boldsymbol{r}_2} \ln \Psi + \boldsymbol{F}_2^{(\phi)} + \boldsymbol{F}_2^{(e)}\right\}\right] \tag{13.6-4}$$

The Oseen-Burgers tensor in the notation of the present discussion is

$$\boldsymbol{\Omega} = \frac{1}{8\pi\eta_s Q}\left[\boldsymbol{\delta} + \frac{\boldsymbol{QQ}}{Q^2}\right] \tag{13.6-5}$$

Then Eqs. 13.6-1 and 13.6-2 can be rewritten for the unperturbed homogeneous flow field $\boldsymbol{v} = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}]$:

$$\begin{aligned}[\![\dot{\boldsymbol{r}}_1]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_1] &+ \left[\boldsymbol{\delta} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_1} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_1^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_1^{(e)}\right)\right] \\ &+ \left[\zeta\boldsymbol{\Omega} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_2} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_2^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_2^{(e)}\right)\right]\end{aligned} \tag{13.6-6}$$

$$\begin{aligned}[\![\dot{\boldsymbol{r}}_2]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_2] &+ \left[\boldsymbol{\delta} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_2} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_2^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_2^{(e)}\right)\right] \\ &+ \left[\zeta\boldsymbol{\Omega} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_1} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_1^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_1^{(e)}\right)\right]\end{aligned} \tag{13.6-7}$$

Next we take two linear combinations of these equations to get the time rate of change of the connector vector $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, and the time rate of change of the center of mass location $\boldsymbol{r}_c = \frac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$. We assume that $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = n\psi(\boldsymbol{Q}, t)$ as was done earlier in Eq. 13.2-7; we also write $\boldsymbol{F}^{(c)} = +\boldsymbol{F}_1^{(\phi)} = -\boldsymbol{F}_2^{(\phi)}$ as before. Then we get

$$[\![\dot{\boldsymbol{Q}}]\!] = [\boldsymbol{\kappa} \cdot \boldsymbol{Q}] + \left[(\boldsymbol{\delta} - \zeta\boldsymbol{\Omega}) \cdot \left(-\frac{2kT}{\zeta}\frac{\partial}{\partial \boldsymbol{Q}} \ln \psi - \frac{2}{\zeta}\boldsymbol{F}^{(c)} + \frac{1}{\zeta}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\right)\right] \tag{13.6-8}$$

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c] + \tfrac{1}{2}\left[\left(\frac{1}{\zeta}\boldsymbol{\delta} + \boldsymbol{\Omega}\right) \cdot (\boldsymbol{F}_1^{(e)} + \boldsymbol{F}_2^{(e)})\right] \tag{13.6-9}$$

From the last equation we see that, in the absence of external forces, the center of mass moves with the fluid. Equation 13.6-8 is the equation for the internal motion.

The inclusion of $\boldsymbol{\Omega}$ in Eq. 13.6-8 complicates the theory considerably. In most of the polymer literature it has been customary to replace $\boldsymbol{\Omega}$ by an "equilibrium-averaged" or "preaveraged" Oseen tensor, defined by[4]

$$\langle \boldsymbol{\Omega} \rangle_{eq} = \int \boldsymbol{\Omega} \psi_{eq} \, d\boldsymbol{Q} = \Omega \boldsymbol{\delta} \tag{13.6-10}$$

where ψ_{eq} is the normalized configurational distribution function at equilibrium. That the average will yield a scalar times the unit tensor is evident from the fact that the integral is isotropic. Then Eq. 13.6-8 becomes identical with Eq. 13.2-7, but with $1/\zeta$ being replaced by $(1/\zeta) - \Omega$, and the differential equation of ψ, in the absence of external forces, is the same as Eq. 13.2-13 with the same replacement.

The Kramers expression for the stress tensor in Eq. A of Table 13.3-1 is unaltered by the inclusion of hydrodynamic interaction. The Giesekus form, however, is obtained from the Kramers form by using an integral over the diffusion equation and, therefore, the final expression for the stress tensor for preaveraged hydrodynamic interaction is the same as that in Eq. D of Table 13.3-1 but with $1/\zeta$ replaced by $(1/\zeta) - \Omega$ (see Problem 13B.8 for Hookean dumbbells with no preaveraging). Also Eq. 13.4-4 is valid if λ_H is replaced by $\tilde{\lambda}_H$ where $\tilde{\lambda}_H = 1/[4H(\zeta^{-1} - \Omega)]$. Thus the inclusion of preaveraged hydrodynamic interaction presents no particular problems; the final results have the same form as those without hydrodynamic interaction. In other words, for Hookean dumbbells we once again get a shear-rate independent viscosity, and an elongational viscosity that increases to infinity at a finite elongation rate.

Inclusion of the non-preaveraged hydrodynamic interaction does lead to a shear-rate-dependent viscosity.[5,6] In recent years attention has shifted away from the use of the Oseen-Burgers hydrodynamic interaction tensor in favor of the Rotne-Prager-Yamakawa tensor,[7,8] since it was found that the Oseen-Burgers tensor can lead to negative values of the translational diffusivity in multibead models.[9,10] The Rotne-Prager-Yamakawa tensor is discussed in §14.6.

EXAMPLE 13.6-1 The Effect of Hydrodynamic Interaction on the Intrinsic Viscosity of a Suspension of Hookean Dumbbells

By using the equilibrium-averaged hydrodynamic interaction, obtain an expression for the intrinsic viscosity of a dilute suspension of Hookean dumbbells.

SOLUTION For this problem Eq. 13.6-10 can be written as follows:

$$\langle \boldsymbol{\Omega} \rangle_{eq} = \frac{\int (1/8\pi\eta_s Q)(\boldsymbol{\delta} + \boldsymbol{QQ}/Q^2) e^{-HQ^2/2kT} d\boldsymbol{Q}}{\int e^{-HQ^2/2kT} d\boldsymbol{Q}} = \Omega \boldsymbol{\delta} \tag{13.6-11}$$

[4] B. H. Zimm, *J. Chem. Phys.*, **24**, 269 278 (1956); J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).

[5] H. C. Öttinger [*J. Chem. Phys.*, **83**, 6535-6536 (1985); **84**, 4068-4073 (1986)] has developed a method of self-consistent averaging, which leads to $\Psi_2 \neq 0$ and viscometric functions that depend on shear rate.

[6] B. H. Zimm, *Ann. N. Y. Acad. Sci.*, **89**, 670-671 (1961).

[7] J. Rotne and S. Prager, *J. Chem. Phys.*, **50**, 4831-4837 (1969).

[8] H. Yamakawa, *J. Chem. Phys.*, **53**, 436-443 (1970).

[9] R. E. DeWames, W. F. Hall, and M. C. Shen, *J. Chem. Phys.*, **46**, 2782-2794 (1967).

[10] R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Nat. Acad. Sci.*, **60**, 381-386 (1968).

These integrals can be evaluated with the help of §E.3 to give

$$\langle \boldsymbol{\Omega} \rangle_{eq} = \sqrt{\frac{H}{2\pi kT}} \frac{1}{3\pi\eta_s} \boldsymbol{\delta} = \Omega\boldsymbol{\delta} \tag{13.6-12}$$

For Hookean dumbbells without hydrodynamic interaction, the intrinsic viscosity can be obtained from Eqs. 13.4-17 and D.5-4:

$$[\eta] = \frac{\tilde{N}kT\zeta}{4MH\eta_s} \tag{13.6-13}$$

where $\tilde{N}$ is Avogadro's number. Therefore for Hookean dumbbell solutions with preaveraged hydrodynamic interaction we have immediately

$$[\eta] = \frac{\tilde{N}kT\zeta}{4MH\eta_s(1 - \sqrt{H/2\pi kT(\zeta/3\pi\eta_s)})} \tag{13.6-14}$$

This shows that the effect of the hydrodynamic interaction is to increase the viscosity. However, with preaveraged hydrodynamic interaction, the viscosity does not decrease as the shear rate increases.

EXAMPLE 13.6-2 Translational Diffusivity of Hookean Dumbbells

The translational diffusivity D_{tr} is related to the friction coefficient Z for the entire molecule (in this case, the dumbbell) by the *Nernst–Einstein equation*[11]

$$D_{tr} = \frac{kT}{Z} \tag{13.6-15}$$

Obtain an expression for the translational diffusivity by considering the motion of the center of mass of the dumbbell as it moves through a quiescent fluid with a force $\boldsymbol{F}^{(e)} = \boldsymbol{F}_1^{(e)} = \boldsymbol{F}_2^{(e)}$ acting on each bead.

SOLUTION From Eq. 13.6-9, with $\boldsymbol{v}_0 = \boldsymbol{0}$ and $\boldsymbol{\kappa} = \boldsymbol{0}$, we get

$$[\![\dot{\boldsymbol{r}}_c]\!] = \frac{1}{\zeta}(\boldsymbol{\delta} + \zeta\boldsymbol{\Omega}) \cdot \boldsymbol{F}^{(e)} \tag{13.6-16}$$

When this equation is multiplied by ψ and integrated over all configurations, then we get

$$\langle \dot{\boldsymbol{r}}_c \rangle = \left[\frac{1}{\zeta}\int (\boldsymbol{\delta} + \zeta\boldsymbol{\Omega})\psi d\boldsymbol{Q}\right] \cdot \boldsymbol{F}^{(e)} \tag{13.6-17}$$

Since the fluid is at rest, we can replace ψ by ψ_{eq} to get

$$\langle \dot{\boldsymbol{r}}_c \rangle = \frac{1}{\zeta}(1 + \zeta\Omega)\boldsymbol{F}^{(e)} \tag{13.6-18}$$

[11] For a derivation of this equation from the general expression for the mass flux, see R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960), Eq. 18.4-14a on p. 568.

The dumbbell friction coefficient Z is defined by

$$2\boldsymbol{F}^{(e)} = Z\langle \dot{\boldsymbol{r}}_c \rangle \tag{13.6-19}$$

By combining Eqs. 13.6-15, 13.6-18, and 13.6-19 we get

$$D_{tr} = \frac{kT}{2\zeta}(1 + \zeta\Omega) \tag{13.6-20}$$

When hydrodynamic interaction is neglected, the term $\zeta\Omega$ does not appear; for the analogous result for the rotatory diffusivity, see Eq. 13.2-13b.

§13.7 ANISOTROPIC EFFECTS

We now wish to go back to Eqs. 13.2-2 and 13.2-3 and explore the consequences of allowing the hydrodynamic drag and the Brownian motion to be anisotropic. That is, we use Eq. 13.2-2 with the symmetric friction tensor $\boldsymbol{\zeta}$ (but without the hydrodynamic interaction perturbation $\boldsymbol{v}'_v$) and Eq. 13.2-3 in which the velocity-space average is taken with respect to a velocity distribution that is not isotropic. Specifically we replace Eq. 13.1-3 by

$$\Xi = \frac{\exp(-(m/2kT)\boldsymbol{\xi} : \sum_v (\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}))}{\iint \exp(-(m/2kT)\boldsymbol{\xi} : \sum_v (\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}))d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2} \tag{13.7-1}$$

in which the tensor $\boldsymbol{\xi}$ may depend on the configuration coordinates and time; if $\boldsymbol{\xi}$ is the unit tensor this velocity distribution reduces to the Maxwellian distribution.

The velocity distribution in Eq. 13.7-1 should satisfy two conditions. First, we note that the temperature is defined by requiring that the kinetic energy of the beads of a dumbbell with respect to the mass-average velocity $\boldsymbol{v}$ be $3kT$. This requirement is satisfied if $\text{tr}\,\boldsymbol{\xi}^{-1} = 3$. Second, it should be noted that unless $\boldsymbol{\xi}$ reduces to the unit tensor in the limit of no velocity gradient, Eq. 13.7-1 is inconsistent with equilibrium statistical mechanics. The empiricism for $\boldsymbol{\xi}^{-1}$ in Eq. 13.7-7 below is inconsistent with the first requirement, but consistent with the second. The empiricism in Eq. 13.7-13 below satisfies the first requirement, but satisfies the second only if α and β are taken to be functions such that α and β both become unity as the velocity gradient goes to zero.

When Eq. 13.7-1 is used to evaluate the average value in Eq. 13.2-3 we get for the Brownian force on bead v

$$\boldsymbol{F}_v^{(b)} = -\frac{kT}{\Psi}\left[\frac{\partial}{\partial \boldsymbol{r}_v} \cdot \boldsymbol{\xi}^{-1}\Psi\right] \tag{13.7-2}$$

When these anisotropic effects are taken into account, the *diffusion equation* for $\psi(\boldsymbol{Q}, t)$ becomes[1]

$$\boxed{\frac{\partial \psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \left[\boldsymbol{\kappa} \cdot \boldsymbol{Q}\psi - 2kT\,\boldsymbol{\zeta}^{-1} \cdot \left[\frac{\partial}{\partial \boldsymbol{Q}} \cdot \boldsymbol{\xi}^{-1}\psi\right] - 2\boldsymbol{\zeta}^{-1} \cdot \boldsymbol{F}^{(c)}\psi\right]\right)} \tag{13.7-3}$$

[1] R. B. Bird and J. M. Wiest, *J. Rheol.*, **29**, 519–532 (1985); in this paper alternatives to the empiricism in Eq. 13.7-6 are suggested.

When this equation is multiplied by $\boldsymbol{QQ}$ and integrated over all orientations we get the *equation of change for* $\langle \boldsymbol{QQ} \rangle$:

$$\tfrac{1}{2}\langle \boldsymbol{QQ} \rangle_{(1)} = kT\left\langle \xi^{-1} : \left\{ \left(\frac{\partial}{\partial \boldsymbol{Q}} \zeta^{-1} \right) \boldsymbol{Q} + \left[\left(\frac{\partial}{\partial \boldsymbol{Q}} \zeta^{-1} \right) \boldsymbol{Q} \right]^{\dagger} \right\} \right\rangle + kT\langle \{ \zeta^{-1} \cdot \xi^{-1} \} + \{ \xi^{-1} \cdot \zeta^{-1} \} \rangle - \langle \{ \zeta^{-1} \cdot \boldsymbol{F}^{(c)} \boldsymbol{Q} \} + \{ \boldsymbol{Q} \boldsymbol{F}^{(c)} \cdot \zeta^{-1} \} \rangle \tag{13.7-4}$$

When $\xi = \delta$ and $\zeta = \zeta\delta$, these last two equations simplify to Eqs. 13.2-13 and 13.2-17 respectively.

When the anisotropic velocity distribution in Eq. 13.7-1 is used to evaluate the last term in Eq. 13.3-14 we are led to[1]

$$\boxed{\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\langle \boldsymbol{Q}\boldsymbol{F}^{(c)} \rangle + 2nkT \langle \xi^{-1} \rangle} \tag{13.7-5}$$

We now consider two special cases of the above results.

a. Empiricisms for the Anisotropy Tensors

We now explore the consequences of the following empirical expressions which give the anisotropy tensors ξ and ζ in terms of the macroscopic quantity $\boldsymbol{\tau}_p = \boldsymbol{\tau} - \boldsymbol{\tau}_s$:[2]

$$\zeta^{-1} = \frac{1}{\zeta}\left(\boldsymbol{\delta} - \frac{a}{nkT} \boldsymbol{\tau}_p \right) \tag{13.7-6}$$

$$\xi^{-1} = \boldsymbol{\delta} - \frac{b}{nkT} \boldsymbol{\tau}_p \tag{13.7-7}$$

where a and b are arbitrary parameters, that have to be determined a posteriori by fitting experimental data. When these expressions for the anisotropy tensors are substituted into Eq. 13.7-5, written for Hookean dumbbells [$\boldsymbol{F}^{(c)} = H\boldsymbol{Q}$], we then get

$$(1 + 2b)\boldsymbol{\tau}_p = -nH\langle \boldsymbol{QQ} \rangle + nkT\boldsymbol{\delta} \tag{13.7-8}$$

Convected differentiation gives

$$(1 + 2b)\boldsymbol{\tau}_{p(1)} = -nH\langle \boldsymbol{QQ} \rangle_{(1)} - nkT\dot{\boldsymbol{\gamma}} \tag{13.7-9}$$

These equations can be solved for $\langle \boldsymbol{QQ} \rangle$ and $\langle \boldsymbol{QQ} \rangle_{(1)}$ respectively, and these are then substituted into Eq. 13.7-4 after it has been written for Hookean dumbbells with the expressions for ξ^{-1} and ζ^{-1} given above. This leads to the constitutive equation for $\boldsymbol{\tau}_p$:

$$\boldsymbol{\tau}_p + \lambda'_H \boldsymbol{\tau}_{p(1)} - \frac{a}{nkT}\{\boldsymbol{\tau}_p \cdot \boldsymbol{\tau}_p\} = -nkT\lambda''_H \dot{\boldsymbol{\gamma}} \tag{13.7-10}$$

[2] H. Giesekus, *J. Non-Newtonian Fluid Mech.*, **11**, 69–109 (1982); **12**, 367–374 (1983); the idea of a non-isotropic Stokes' law was introduced earlier in H. Giesekus, *Rheol. Acta*, **5**, 29–36 (1966), fn. 11. Giesekus introduced a nonisotropic Brownian motion as we have done in Eq. 13.7-7, but with $b = a$.

where $\lambda_H' = [(1 + 2b)/(1 + b)](\zeta/4H) = (1 + 2b)\lambda_H''$. The constitutive equation can also be written in terms of τ:

$$\tau + \lambda_H'\tau_{(1)} - \frac{a}{nkT}\{\tau\cdot\tau\} - \frac{a\eta_s}{nkT}\{\tau\cdot\gamma_{(1)} + \gamma_{(1)}\cdot\tau\}$$
$$= -(\eta_s + nkT\lambda_H'')\gamma_{(1)} + \frac{a\eta_s^2}{nkT}\{\gamma_{(1)}\cdot\gamma_{(1)}\} - \lambda_H'\eta_s\gamma_{(2)} \qquad (13.7\text{-}11)$$

It should be noted that the constitutive equation with $b = 0$ (for which $\operatorname{tr}\xi^{-1} = 3$) is the same as Eqs. 13.7-10 and 13.7-11 but with λ_H' and λ_H'' both equal to $\lambda_H = \zeta/4H$; for that case reasonably shaped curves were obtained for the material functions when a is in the range $0 \le a \le \frac{1}{2}$.

b. The Encapsulated Dumbbell Model

Bird and DeAguiar[3] developed a simple theory for concentrated solutions and melts by using the elastic dumbbell model. In a melt the molecules are crowded together, so that motion in the direction of the backbone may be easier than motion perpendicular to it. Hence it seems reasonable to introduce a modified Stokes' law that has different friction coefficients in the directions of dumbbell vibration and rotation. This is accomplished by letting

$$\zeta^{-1} = \frac{1}{\zeta}[\sigma\boldsymbol{\delta} + (1 - \sigma)\boldsymbol{uu}] \qquad (13.7\text{-}12)$$

in which ζ and σ are constants, and $\boldsymbol{u} = \boldsymbol{Q}/Q$ is the unit vector pointing from bead "1" to bead "2." In addition, we wish to explore the consequences of introducing anisotropy into the velocity distribution (and hence also into the Brownian force in the bead equation of motion and into the bead contribution to the stress tensor) by writing

$$\xi^{-1} = \beta\boldsymbol{\delta} + (\alpha - \beta)\boldsymbol{uu} \qquad (13.7\text{-}13)$$

Here α and β are constants; the requirement that $\operatorname{tr}\xi^{-1} = 3$ implies that $\alpha + 2\beta = 3$. If β is in the range $1 \le \beta \le \frac{3}{2}$, ξ is positive definite.

For these choices for ζ and ξ, Eqs. 13.7-4 and 13.7-5 give

$$\langle\boldsymbol{QQ}\rangle_{(1)} = \frac{4kT}{\zeta}\sigma\beta\boldsymbol{\delta} - \frac{4}{\zeta}\langle\boldsymbol{QF}^{(c)}\rangle + \frac{4kT}{\zeta}(\alpha + 2\beta - 3\sigma\beta)\left\langle\frac{\boldsymbol{QQ}}{Q^2}\right\rangle \qquad (13.7\text{-}14)$$

$$\tau_p = -n\langle\boldsymbol{QF}^{(c)}\rangle + 2nkT(\alpha - \beta)\left\langle\frac{\boldsymbol{QQ}}{Q^2}\right\rangle + \tfrac{1}{3}nkT(-\alpha + 4\beta)\boldsymbol{\delta} \qquad (13.7\text{-}15)$$

Bird and DeAguiar considered FENE dumbbells (cf. §13.5) and introduced these approximations:[4]

$$\left\langle\frac{H\boldsymbol{QQ}}{1 - (Q^2/Q_0^2)}\right\rangle \doteq \frac{H\langle\boldsymbol{QQ}\rangle}{1 - \langle Q^2/Q_0^2\rangle}; \qquad \left\langle\frac{\boldsymbol{QQ}}{Q^2}\right\rangle \doteq \frac{\langle\boldsymbol{QQ}\rangle}{\langle Q^2\rangle} \qquad (13.7\text{-}16a,b)$$

[3] R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983); J. R. DeAguiar, *ibid.*, 161–179 (1983).

[4] X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 251–265 (1985), has solved the diffusion equation numerically for steady shear flow, thereby avoiding the approximations in Eq. 13.7-16.

Then, following the procedures used in §13.4 and Example 13.5-2, they eliminated the average values to get a constitutive equation for $\boldsymbol{\tau}_p$:

$$B_\tau \boldsymbol{\tau}_p + \lambda_H \boldsymbol{\tau}_{p(1)} = -(2\beta - 1)nkT\lambda_H \dot{\boldsymbol{\gamma}} + B_\delta \boldsymbol{\delta} \tag{13.7-17}$$

in which

$$B_\tau = \frac{(\sigma\beta - \mathscr{T})Z}{(2\beta - 1 - \mathscr{T})} - \lambda_H \frac{D \ln Z}{Dt} \tag{13.7-18}$$

$$B_\delta = \frac{(\sigma\beta - 2\beta + 1)\mathscr{T}Z}{3(2\beta - 1 - \mathscr{T})} - \frac{1}{3}\lambda_H(2\beta - 1)\frac{D \ln Z}{Dt} \tag{13.7-19}$$

$$Z = \frac{[1 + (3/b)(1 - \mathscr{T})](2\beta - 1 - \mathscr{T})}{1 - \mathscr{T}} \tag{13.7-20}$$

$$\mathscr{T} = \frac{\operatorname{tr} \boldsymbol{\tau}_p}{3nkT} \tag{13.7-21}$$

and, as before, $\lambda_H = \zeta/4H$, and the relation $\alpha + 2\beta = 3$ has been used to eliminate α. DeAguiar[3] found that values of λ_H, b, σ, and β could be obtained to fit experimental data on concentrated polymer solutions. Each of the four parameters is related to some physical aspect of the model: the time constant $\lambda_H = \zeta/4H$ describes the relaxation processes of the model; $b = HQ_0^2/kT$ is a measure of the nonlinearity of the spring; σ indicates the degree of anisotropy in the viscous drag; and β describes the deviation from the Maxwellian velocity distribution. In connection with the parameter β, it may be pointed out that the associated anisotropy in the Brownian motion is closely related to the notion of "reptation"; by the latter one means that the Brownian motion of a chainlike polymer is restricted to the direction along the polymer chain backbone.

PROBLEMS

13A.1 Test of FENE Dumbbell Model

a. From Eqs. 13.5-24 and 13.5-26 obtain the value of shear rate $\dot{\gamma}_0$ for which $\eta - \eta_s$ has dropped to 0.99 of its zero-shear-rate value, and the value of the frequency ω_0 for which $\eta' - \eta_s$ has dropped to 0.99 of its zero-frequency value. Show that

$$\frac{\dot{\gamma}_0}{\omega_0} = \sqrt{\frac{(b + 5)(2b + 11)}{2(4b + 17)}} \xrightarrow[b]{\text{large}} \frac{\sqrt{b}}{2} \tag{13A.1-1}$$

which was obtained by Graessley.[1]

b. Evaluate $\dot{\gamma}_0/\omega_0$ for $b = 10$, 100, and 1000.

c. Compare these results with some sample data shown in Chapter 3. Can any significant conclusions be drawn from the comparison?

13A.2 Molecular Stretching and Non-Newtonian Viscosity

a. Use the FENE dumbbell model to explore the relation between rheological behavior and molecular stretching in the flow field. Specifically use Eqs. 13.5-24 and 13C.4-1 to estimate how much the molecules have to be stretched beyond their equilibrium length in order for the viscosity η to deviate from η_0 by 1%.

[1] W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1–179 (1974), Eq. 8.19.

b. Use Eq. 13.5-53 to find out whether or not the molecules are stretched out to nearly their maximum length at a shear rate for which $\eta/\eta_0 = 0.01$.

13A.3 Estimation of Kinetic Theory Time Constant

In Fig. 13.5-3 a comparison is given between experimental and theoretical curves for $[\eta']$ and $[\eta'']$. The time constant λ_Q was determined by fitting the data to be $\lambda_Q = 4.215$s. The definition of λ_Q in terms of the model parameters ζ and Q_0^2 is given in Eq. 13.5-3. Use this formula to estimate λ_Q from the molecular weight of the polystyrene ($\bar{M}_w = 860{,}000$, $\bar{M}_w/\bar{M}_n = 1.15$), the structural formula for polystyrene (from which Q_0 can be inferred), and the solvent viscosity $\eta_s = 0.3$ Pa·s.

13B.1 Constitutive Equation for Hookean Dumbbells in Non-Isothermal Flow

The development leading to Eq. 11.3-20 makes it clear that the Hookean spring constant H in general depends on the temperature T. Show that when the development in Eqs. 13.4-1 to 13.4-4 is followed for $H = H(T)$ the following constitutive equation[2] is obtained for τ_p:

$$\boldsymbol{\tau}_p + \frac{\zeta}{4H}\left[\boldsymbol{\tau}_{p(1)} - (\boldsymbol{\tau}_p - nkT\boldsymbol{\delta})\frac{d\ln H}{d\ln T}\frac{D\ln T}{Dt} - nkT\boldsymbol{\delta}\,\frac{D\ln T}{Dt}\right] = -nkT\left(\frac{\zeta}{4H}\right)\dot{\boldsymbol{\gamma}} \tag{13B.1-1}$$

This emphasizes the fact that in nonisothermal systems one cannot simply replace the time constant λ_H in Eq. 13.4-4 by a temperature-dependent function.

13B.2 The Effective-Velocity-Gradient Assumption

In §13.6 the hydrodynamic interaction effect is accounted for by using the Oseen-Burgers tensor and then, because of mathematical complications, one replaces this tensor by its equilibrium-averaged value. An alternative procedure is to replace the fluid velocity at bead v (that is $\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_v]$ in Eq. 13.2-5) by

$$\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_v] - \tfrac{1}{2}\xi[\dot{\boldsymbol{\gamma}}\cdot(\boldsymbol{r}_v - \boldsymbol{r}_c)] \tag{13B.2-1}$$

where ξ is a small quantity[3] that accounts for the difference between the velocity gradient "seen" by the macromolecule and the velocity gradient imposed on the fluid by external forces.

a. Show how the introduction of ξ via Eq. 13B.2-1 changes the dumbbell kinetic theory in §§13.2 and 13.3.

b. Show that the constitutive equation for Hookean dumbbells becomes

$$\boldsymbol{\tau}_p + \lambda_H[\boldsymbol{\tau}_{p(1)} + \tfrac{1}{2}\xi\{\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\tau}_p + \boldsymbol{\tau}_p\cdot\dot{\boldsymbol{\gamma}}\}] = -nkT\lambda_H(1-\xi)\dot{\boldsymbol{\gamma}} \tag{13B.2-2}$$

This is a special case of the Oldroyd 6-constant model of Chapter 7 (see also Eq. D.4-5).

[2] G. Marrucci, *Trans. Soc. Rheol*, **16**, 321-330 (1972). Marrucci's equation was used by R. J. Fisher and M. M. Denn, *AIChE J.*, **23**, 23-28 (1977), to describe nonisothermal polymer-melt spinning.

[3] The parameter ξ was first introduced by R. J. Gordon and W. R. Schowalter, *Trans. Soc. Rheol.*, **16**, 79-97, (1972); see also N. Phan-Thien, O. Manero, and L. G. Leal, *Rheol. Acta*, **23**, 151-162 (1984), and M. W. Johnson, Jr., and D. Segalman, *J. Non-Newtonian Fluid Mech.*, **2**, 255-270 (1977). A relation between ξ and hydrodynamic interaction has been suggested by R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **5**, 1-12 (1979) and R. B. Bird and C. F. Curtiss, *ibid.*, **14**, 85-101 (1984).

c. Show that

$$\eta - \eta_s = \frac{nkT\lambda_H(1-\xi)}{1+2\xi(1-\frac{1}{2}\xi)(\lambda_H\dot{\gamma})^2} \tag{13B.2-3}$$

$$\Psi_1 = \frac{2nkT\lambda_H^2(1-\xi)}{1+2\xi(1-\frac{1}{2}\xi)(\lambda_H\dot{\gamma})^2} \tag{13B.2-4}$$

$$\Psi_2 = -\tfrac{1}{2}\xi\Psi_1 \tag{13B.2-5}$$

Are these results realistic as $\dot{\gamma} \to \infty$?

d. Show further that in steady shear flow

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{eq}} = 1 + \frac{2(1-\xi)^2}{3}\frac{(\lambda_H\dot{\gamma})^2}{1+2\xi(1-\frac{1}{2}\xi)(\lambda_H\dot{\gamma})^2} \tag{13B.2-6}$$

What is the value of this ratio in the limit of very large shear rates for some reasonable value of ξ?

13B.3 Configurational Distribution Function for Steady Shear Flow of a Dilute Solution of Hookean Dumbbells

a. Show that, for steady shear flow $v_x = \dot{\gamma}y$, the tensor $\boldsymbol{\alpha}$ in Eq. 13.4-13 is

$$\boldsymbol{\alpha} = \begin{pmatrix} 1+2\lambda_H^2\dot{\gamma}^2 & \lambda_H\dot{\gamma} & 0 \\ \lambda_H\dot{\gamma} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{13B.3-1}$$

b. Next show that Eq. 13.4-12 becomes[4]

$$\psi = \left(\frac{H}{2\pi kT}\right)^{3/2}\frac{1}{\sqrt{1+\lambda_H^2\dot{\gamma}^2}} \times \exp\left[-\frac{H}{2kT}\left\{\frac{X^2 - 2\lambda_H\dot{\gamma}XY + (1+2\lambda_H^2\dot{\gamma}^2)Y^2 + (1+\lambda_H^2\dot{\gamma}^2)Z^2}{1+\lambda_H^2\dot{\gamma}^2}\right\}\right] \tag{13B.3-2}$$

where $\lambda_H = \zeta/4H$ and X, Y, and Z are the components of $\boldsymbol{Q}$, which range from $-\infty$ to $+\infty$.

c. Verify that this $\psi(X, Y, Z)$ satisfies Eq. 13.2-13, when the latter is written for steady simple shear flow and for Hookean dumbbells.

d. Obtain the viscosity for the solution by using the Kramers expression for the stress tensor. First show that

$$\eta - \eta_s = \frac{nH}{\dot{\gamma}}\langle XY\rangle = \frac{nH}{\dot{\gamma}}\iiint \psi(X, Y, Z)XY\,dX\,dY\,dZ \tag{13B.3-3}$$

where $\psi(X, Y, Z)$ is the function given in Eq. 13B.3-2. The integrations are made easier by making the changes of variables:

$$\bar{X} = X - \lambda_H\dot{\gamma}Y; \qquad \bar{Y} = \sqrt{1+\lambda_H^2\dot{\gamma}^2}\,Y; \qquad \bar{Z} = \sqrt{1+\lambda_H^2\dot{\gamma}^2}\,Z \tag{13B.3-4}$$

[4] H. A. Kramers, as cited in footnote 8 of J. J. Hermans, *Physica*, **10**, 777–789 (1943); it seems to us that $\exp\mu^2[\ ]$ in that reference should be replaced by $\exp\frac{1}{2}\mu^2[\ ]$.

This leads to

$$\eta - \eta_s = \frac{nH}{\dot{\gamma}} \frac{\lambda_H \dot{\gamma}}{1 + \lambda_H^2 \dot{\gamma}^2} \frac{\int_{-\infty}^{+\infty} \bar{Y}^2 e^{-a\bar{Y}^2} d\bar{Y}}{\int_{-\infty}^{+\infty} e^{-a\bar{Y}^2} d\bar{Y}} \tag{13B.3-5}$$

where $a = (H/2kT)/(1 + \lambda_H^2 \dot{\gamma}^2)$. Show that this leads to Eq. 13.4-17.

e. Repeat part (**b**) using the Giesekus expression for the stress tensor (Eq. D of Table 13.3-1).

f. Next use Eq. 13B.3-2 to obtain the expression in Eq. 13.4-20 for the stretching of elastic dumbbells in a shear flow.

13B.4 Expansion of the Potential Flow Distribution Function

In Eq. 13.2-14 the exact distribution function for a dilute solution of elastic dumbbells in steady, homogeneous, potential flow is given. Here we consider how to expand this result to obtain Eq. 13.5-6.

a. Expand $\exp[(\zeta/4kT)(\boldsymbol{\kappa} : \boldsymbol{QQ})]$ as a power series in the argument $(\zeta/kT)(\boldsymbol{\kappa} : \boldsymbol{QQ})$.

b. Determine J/J_{eq} as a power series in $\dot{\gamma}$ by using the fact that ψ is normalized together with the power series expression developed in (**a**). Show that the result through second order is

$$\frac{J}{J_{eq}} = 1 + \frac{1}{15}\left(\frac{\zeta}{8kT}\right)^2 \langle Q^4 \rangle_{eq} (\dot{\gamma} : \dot{\gamma}) + \cdots \tag{13B.4-1}$$

The averages given in Eqs. E.7-4 and E.7-5 are useful in performing the averages over θ and ϕ, which must be done in order to obtain this equation.

c. Insert the expansions in (**a**) and (**b**) into $\psi = \psi_{eq}\phi_{fl}$ and obtain Eq. 13.5-6.

13B.5 Verification of Intermediate Step in Nonlinear Elastic Dumbbell Kinetic Theory

a. First simplify Eq. 13.2-13 for equilibrium and obtain

$$kT \frac{1}{Q^2} \frac{d}{dQ}\left(Q^2 \frac{d\psi_{eq}}{dQ}\right) + \frac{1}{Q^2} \frac{d}{dQ}[Q^2 F^{(c)} \psi_{eq}] = 0 \tag{13B.5-1}$$

To get this it has been recognized that ψ_{eq} is a function of Q alone and that $\boldsymbol{F}^{(c)}$ can also be written as its scalar magnitude $F^{(c)}$ multiplied by $\boldsymbol{Q}/Q$.

b. Substitute Eq. 13.5-5 into Eq. 13.2-13 and obtain

$$\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \left\{[\boldsymbol{\kappa} \cdot \boldsymbol{Q}]\psi_{eq} \sum \phi_k - \frac{kT}{2H\lambda_H} \frac{\partial}{\partial \boldsymbol{Q}}(\psi_{eq} \sum \phi_k) - \frac{1}{2H\lambda_H} \boldsymbol{F}^{(c)} \psi_{eq} \sum \phi_k\right\}\right) = 0 \tag{13B.5-2}$$

Differentiate the first term as a product of a scalar and a vector and show that one term vanishes; use Eq. 12.3-7 to combine the second two terms. This gives

$$\left([\boldsymbol{\kappa} \cdot \boldsymbol{Q}] \cdot \frac{\partial}{\partial \boldsymbol{Q}} \psi_{eq} \sum \phi_k\right) - \left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \left(\frac{kT}{2H\lambda_H} \psi_{eq} \frac{\partial}{\partial \boldsymbol{Q}} \sum \phi_k\right)\right) = 0 \tag{13B.5-3}$$

Performing the differentiations and using Eq. 12.3-7 again then yields

$$\left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\left[-\frac{\boldsymbol{F}^{(c)}}{kT}\psi_{eq}\sum\phi_k+\psi_{eq}\frac{\partial}{\partial\boldsymbol{Q}}\sum\phi_k\right]\right)$$
$$-\frac{kT}{2H\lambda_H}\left(-\frac{\boldsymbol{F}^{(c)}}{kT}\psi_{eq}\cdot\frac{\partial}{\partial\boldsymbol{Q}}\sum\phi_k\right)-\frac{kT}{2H\lambda_H}\left(\psi_{eq}\frac{\partial}{\partial\boldsymbol{Q}}\cdot\frac{\partial}{\partial\boldsymbol{Q}}\sum\phi_k\right)=0 \qquad (13B.5\text{-}4)$$

The factor ψ_{eq} can now be removed. When this is done Eqs. 13.5-7, 13.5-8, and so on can be obtained by equating terms of the same order in the velocity gradients.

13B.6 Verification of First-Order Perturbation Solution in the Nonlinear Elastic Dumbbell Kinetic Theory

Verify that Eq. 13.5-10 does satisfy Eq. 13.5-7. Proceed as follows:

a. First show that Eq. 13.5-10 can also be written as

$$\phi_1=\frac{\zeta}{4kT}(\boldsymbol{\kappa}:\boldsymbol{QQ}) \qquad (13B.6\text{-}1)$$

b. Then show that

$$\frac{\partial}{\partial\boldsymbol{Q}}(\boldsymbol{\kappa}:\boldsymbol{QQ})=[\boldsymbol{\kappa}\cdot\boldsymbol{Q}]+[\boldsymbol{\kappa}^{\dagger}\cdot\boldsymbol{Q}] \qquad (13B.6\text{-}2)$$

c. Next show that

$$\left(\frac{\partial}{\partial\boldsymbol{Q}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\right)=0 \qquad (13B.6\text{-}3)$$

d. Use all the above results to complete the proof.

13B.7 The Second Normal Stress Coefficient

In Eq. 13.4-19 it was found that the second normal stress coefficient Ψ_2 is zero. Show that $\Psi_2=0$ is an immediate consequence of the molecular expression for the stress tensor by writing Eq. D of Table 13.3-1 for steady shear flow.

13B.8 Giesekus Form of the Stress Tensor for Hookean Dumbbells with Oseen-Burgers Hydrodynamic Interaction (No Preaveraging)

Show that for Hookean dumbbells Eq. D of Table 13.3-1 has to be replaced by

$$\boldsymbol{\tau}_p=\frac{n\zeta}{4}\langle\boldsymbol{QQ}\rangle_{(1)}+\frac{nkT\zeta}{8\pi\eta_s}\left\langle\frac{1}{Q}\boldsymbol{\delta}+\frac{1}{Q^3}\boldsymbol{QQ}\right\rangle-\frac{n\zeta H}{4\pi\eta_s}\left\langle\frac{1}{Q}\boldsymbol{QQ}\right\rangle \qquad (13B.8\text{-}1)$$

when complete Oseen-Burgers hydrodynamic interaction is taken into account.

13B.9 Approximate Constitutive Equation for FENE-Dumbbells

An interesting derivation of an approximate constitutive equation for nonlinear elastic dumbbells was suggested by Tanner.[5] The main idea is that we have to make a guess for the distribution function. A very simple proposition is that *all* dumbbells have exactly the same orientation and stretching, so that

$$\psi(\boldsymbol{Q}, t) = \delta(\boldsymbol{Q} - \boldsymbol{S}(t)) \tag{13B.9-1}$$

Substitute this rough guess for $\psi(\boldsymbol{Q}, t)$ into Eqs. 13.5-46 and 13.5-47. Follow the general procedure of Example 13.5-2 to eliminate $\boldsymbol{SS}$ and S^2 from the two resulting equations. Show that Eq. 13.5-56, with $\varepsilon = 0$, is obtained as a constitutive equation. Can you suggest any other functions that might be better than that in Eq. 13B.9-1?

13B.10 Zero-Shear-Rate Viscosity of Fraenkel Dumbbells

Show that for Fraenkel dumbbells (see Table 11.5-1)

$$\eta_0 - \eta_s = \frac{n\zeta \int_0^\infty Q^4 \exp[-H(Q - Q_0)^2/2kT]dQ}{12 \int_0^\infty Q^2 \exp[-H(Q - Q_0)^2/2kT]dQ} \tag{13B.10-1}$$

Show that in the limit of $H \to \infty$, Eq. 13B.10-1 gives the *rigid dumbbell* result:

$$\eta_0 - \eta_s = nkT\lambda \tag{13B.10-2}$$

where $\lambda = \zeta Q_0^2/12kT$, and that for small HQ_0^2/kT one can obtain systematic deviations from the *Hookean dumbbell* result:

$$\eta_0 - \eta_s = nkT\lambda_H\left(1 + \frac{4}{3}\sqrt{\frac{HQ_0^2}{2\pi kT}} + \cdots\right) \tag{13B.10-3}$$

where $\lambda_H = \zeta/4H$.

13B.11 An Approximate Constitutive Equation for Modified Fraenkel Dumbbells

a. Apply the method of Problem 13B.9 to the modified Fraenkel dumbbell model in which Q_0/Q is replaced by $(Q_0/Q)^2$ in Eq. C of Table 11.5-1. Show that this leads to

$$Z\boldsymbol{\tau}_p + \lambda_H\boldsymbol{\tau}_{p(1)} - \lambda_H(\boldsymbol{\tau}_p - nkT\boldsymbol{\delta})\frac{D \ln Z}{Dt} = -nkT\lambda_H\dot{\boldsymbol{\gamma}} \tag{13B.11-1}$$

in which $\lambda_H = \zeta/4H$, and $Z(\text{tr } \boldsymbol{\tau}_p)$ is given by

$$Z = \frac{1 - \mathscr{T}}{1 - \mathscr{T} + (b/3)} \tag{13B.11-2}$$

where $\mathscr{T} = (\text{tr } \boldsymbol{\tau}_p)/3nkT$ and $b = HQ_0^2/kT$.

b. Let H approach ∞ so that a rigid dumbbell of length Q_0 is produced. Show that a constitutive equation of the form of Eq. 13B.11-1 is obtained, but with λ_H replaced by $\lambda = \zeta Q_0^2/12kT$ and Z replaced by $Y = 1 - \mathscr{T}$. How well do the results of this approximate constitutive equation agree with the exact results in Chapter 14?

[5] R. I. Tanner, *Trans. Soc. Rheol.*, **19**, 37–65 (1975).

13C.1 Retarded-Motion-Expansion Constants for Hookean Dumbbell Solutions

Start with Eq. 13.4-9 and expand the finite strain tensor $\gamma_{[0]}(t, t')$ about $t' = t$; then perform the integration term by term. Compare the result with the retarded-motion expansion in Eq. 6.2-1 and obtain expressions for the coefficients in the expansion. Show that

$$b_1 = \eta_s + nkT\lambda_H \tag{13C.1-1}$$

$$b_k = (-1)^k nkT\lambda_H^k \tag{13C.1-2}$$

and that all other b's are zero. Compare these results with those in Eqs. 13.5-18 to 13.5-23.

13C.2 Dumbbells with "Internal Viscosity"

In this chapter we have discussed dumbbells in which the beads are joined together by some kind of linear or nonlinear spring. One could also invent other kinds of connectors that would account intuitively for other sorts of effects when the molecules are stretched. In one such connector, which has received considerable attention in the literature, the connector tension is represented as a Hookean spring and a linear dashpot in parallel.[6] That is, it is imagined that the molecule has some kind of "internal viscosity." We thus write

$$\boldsymbol{F}^{(c)} = H\boldsymbol{Q} + K\left(\frac{\boldsymbol{Q}}{Q}\right)\dot{Q} \tag{13C.2-1}$$

in which H and K are constants. This kind of force law presents a problem: since it involves non-conservative forces, we cannot use the methods of Chapter 12 to obtain the equilibrium configurational distribution function, and hence we do not have a proper starting point for doing the nonequilibrium kinetic theory.

The various publications on this subject[6] have essentially replaced $\dot{Q}$ in Eq. 13C.2-1 by $[\![\dot{Q}]\!]$. Show that this allows Eq. 13C.2-1 to be written as

$$\boldsymbol{F}^{(c)} = H\boldsymbol{Q} + K\left(\frac{\boldsymbol{QQ}}{Q^2}\right)\cdot[\![\dot{\boldsymbol{Q}}]\!] \tag{13C.2-2}$$

According to this equation the internal-viscosity contribution to $\boldsymbol{F}^{(c)}$ depends on the *average* rate of stretching of the dumbbells.

Next show that for the force law of Eq. 13C.2-2, the internal equation of motion corresponding to Eq. 13.2-7 is, in the absence of external forces,

$$[\![\dot{\boldsymbol{Q}}]\!] = \left[\left(\boldsymbol{\delta} - \frac{1}{(\zeta/2K)+1}\frac{\boldsymbol{QQ}}{Q^2}\right)\cdot\left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}] - \frac{2kT}{\zeta}\frac{\partial}{\partial\boldsymbol{Q}}\ln\psi - \frac{2}{\zeta}H\boldsymbol{Q}\right)\right] \tag{13C.2-3}$$

This has to be substituted into Eq. 13.2-12 to get the differential equation for ψ; the solution of this equation is not easy. Booij and van Wiechen[7] give a solution in powers of a dimensionless parameter

[6] W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 1533–1579 (1945); **29**, 71–94 (1946); R. Cerf, *Adv. in Polym. Phys.* **1**, 382–450 (1959); A. Peterlin, *J. Polym. Sci.*, **A2**, **5**, 179–193 (1967); A. Peterlin and C. Reinhold, *Trans. Soc. Rheol.*, **11**, 15–37 (1967); E. R. Bazúa and M. C. Williams, *J. Chem. Phys.*, **59**, 2858–2868 (1973); *J. Polym. Sci. (Phys.)*, **A2**, **12**, 825–848 (1974); M. C. Williams, *AIChE J.*, **21**, 1–25 (1975); C. W. Manke and M. C. Williams, *Macromolecules*, **18**, 2045–2051 (1985); *J. Non-Newtonian Fluid Mech.*, **30**, 19–28 (1986); G. G. Fuller and L. G. Leal, *J. Non-Newtonian Fluid Mech.*, **8**, 271–310 (1981); N. Phan-Thien, J. D. Atkinson, and R. I. Tanner [*J. Non-Newtonian Fluid Mech.*, **3**, 309–330 (1978) have used a Langevin approach to do the kinetic theory for a nonlinear dumbbell, with a frictional coefficient that depends on Q, and internal viscosity.

[7] H. C. Booij and P. H. van Wiechen, *J. Chem. Phys.*, **52**, 5056–5068 (1970).

containing K. Their results show that this model (with no "hydrodynamic interaction" included) gives a shear-rate-dependent viscosity, a finite limiting value for $\eta'(\omega)$ as $\omega \to \infty$, and a partial description of the flow experiment in which small amplitude oscillations are superposed on steady shear flow.

13C.3 Energy Dissipation in Hookean Dumbbell Solutions[8]

a. Form the double-dot product of Eq. A of Table 13.3-1 (with the external-force terms omitted) with $\dot{\gamma}$, and then specialize to Hookean dumbbells to get

$$-(\boldsymbol{\tau}:\dot{\boldsymbol{\gamma}}) = \eta_s(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}) + nH(\dot{\boldsymbol{\gamma}}:\langle \boldsymbol{QQ}\rangle) \tag{13C.3-1}$$

b. For steady shear flow we know that $\boldsymbol{\tau}$ can be represented by the CEF equation in Eq. 9.6-18 (or Eq. D.4-4). Show that the introduction of this expression into Eq. 13C.3-1 leads to

$$\eta(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}) = \eta_s(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}) + nH(\dot{\boldsymbol{\gamma}}:\langle \boldsymbol{QQ}\rangle) \tag{13C.3-2}$$

Note that Ψ_1 and Ψ_2 have dropped out. Interpret the result.

c. Specialize to the flow $v_x = \dot{\gamma}y$ with $\dot{\gamma}$ = constant and show that this leads directly to $\eta - \eta_s = (nH/\dot{\gamma})\langle XY\rangle$, in which X and Y are Cartesian components of $\boldsymbol{Q}$.

d. Next show how to derive the result in (**c**) by making dissipation arguments at the molecular level. That is, obtain an expression for the viscosity by considering the viscous dissipation associated with the bead movement through the fluid; this method then avoids going through any of the development in §13.3. The energy dissipated by the motion of a bead through the fluid equals the product of the velocity of the bead relative to that of the fluid multiplied by the hydrodynamic drag force acting on the bead. Therefore in a solution

$$E_v = \text{energy dissipation} = n\zeta \sum_{\nu=1}^{2} \langle (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}_\nu)\cdot(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}_\nu)\rangle \tag{13C.3-3}$$

Now replace the second $(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}_\nu)$ by the sum of the Brownian motion and spring terms using Eq. 13.2-5. Show that the integration over velocities then leads to

$$E_v = n\left\langle \sum_{\nu=1}^{2} [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu]\cdot\left(kT\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi - \boldsymbol{F}_\nu^{(\phi)}\right)\right\rangle \tag{13C.3-4}$$

or

$$E_v = n\left\langle [\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot kT\frac{\partial}{\partial \boldsymbol{Q}}\ln\psi + [\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\boldsymbol{F}^{(c)}\right\rangle \tag{13C.3-5}$$

Show that the Brownian motion term is zero, and that for Hookean dumbbells and for steady simple shear flow $v_x = \dot{\gamma}y$ the remaining term can be simplified to give

$$E_v = nH\dot{\gamma}\langle XY\rangle \tag{13C.3-6}$$

Then obtain the result in (**c**) by equating this to the appropriate macroscopic expression.

[8] This problem is based on a discussion by J. Riseman and J. G. Kirkwood, in *Rheology*, F. R. Eirich (Ed.), Academic Press, New York (1956), Vol. 1, Chapter 13, pp. 495–523; see particularly Section III.

13C.4 Stretching of FENE Dumbbells in Steady-State Shear Flow

Show that the FENE dumbbell analog of Eq. 13.4-20 is

$$\frac{\langle Q^2\rangle}{Q_0^2} = \frac{3}{b+5}\left[1 + \frac{2b^2(b+2)}{3(b+5)(b+7)(b+9)}(\lambda_H\dot{\gamma})^2 + \cdots\right] \tag{13C.4-1}$$

13C.5 Stretching of Hookean Dumbbells in Flow Associated with a Line Sink

In Problem 6B.5 the flow of a third-order fluid near a line sink is discussed; in Example 8.4-1 the same flow is considered for a convected Jeffreys (the "Oldroyd-B") model.

a. Use the results of Problem 6B.5 and the third-order fluid constants for Hookean dumbbells in Problem 13C.1 to find the molecular stretching in the flow $v_r = C/r$, $v_\theta = 0$, $v_z = 0$:

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{eq}} = 1 + \frac{2}{3}\left(\frac{2C\lambda_H}{r^2}\right)^2 + 2\left(\frac{2C\lambda_H}{r^2}\right)^3 \tag{13C.5-1}$$

Interpret the result.

b. Next obtain the components of the $\gamma_{[0]}$ tensor for the line source (or sink) flow, and then use the second line of Eq. 13.4-11 to get the result in Eq. 13C.5-1.

c. Show how to use Eqs. 13.4-12 and 13.4-13 to get the configuration-space distribution function at all points in the flow field.

13C.6 Use of Dumbbell Models in Nondilute Solutions[9]

In §13.6 we show how hydrodynamic interaction can be included in the modeling of dilute polymer solutions. As the polymer concentration is increased the hydrodynamic interaction becomes less important because of the "shielding" of distant parts of a single polymer owing to the fact that other molecules are interposed. Wang and Zimm,[9] using some results from the theory of flow through porous media, obtain an expression for Ω that is different from that in Eq. 13.6-11, namely:

$$\Omega = \frac{1}{6\pi\eta_s}\frac{4\pi\int_0^\infty Q\exp(-2\psi_0\sqrt{HQ^2/2kT})\exp(-HQ^2/2kT)dQ}{(2\pi kT/H)^{3/2}} \tag{13C.6-1}$$

where $\psi_0 = \sqrt{nkT\zeta/H\eta_s}$ is a "shielding coefficient." Show that this can be integrated to give

$$\Omega = \frac{1}{3\pi\eta_s}\sqrt{\frac{H}{2\pi kT}}(1-\Delta) \tag{13C.6-2}$$

where

$$\Delta = \sqrt{\pi}\psi_0(\operatorname{erfc}\psi_0)(\exp\psi_0^2) \tag{13C.6-3}$$

Note that in the limit of infinite dilution ($n \to 0$), both ψ_0 and Δ go to zero. Finally obtain for the viscosity

$$\eta - \eta_s = \frac{nkT\lambda_H}{1 - \sqrt{H/2\pi kT}\,(\zeta/3\pi\eta_s)(1-\Delta)} \tag{13C.6-4}$$

[9] F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polymer Physics Edition* **12**, 1619-1637 (1974); the Wang-Zimm paper deals with bead-spring chains rather than with dumbbells.

In the limit of $n \to 0$, Eq. 13C.6-4 becomes the same as Eq. 13.6-14. The value of ψ_0 for the "free draining result" is obtained setting $\Delta = 1$ in Eq. 13C.6-3. This theory of hydrodynamic shielding describes the transition from "Zimm-like" behavior (infinite dilution) to "Rouse-like" behavior (solution sufficiently concentrated that hydrodynamic effects are unimportant).

13C.7 Thermodynamic Quantities for Flowing Dilute Polymer Solutions (Hookean Dumbbell Model)

To get the *internal energy* of a polymer solution one must add up all the kinetic energies and potential energies of interaction in the system. If we model the polymer as a bead-spring chain, then the polymer contribution to the internal energy is the sum of the kinetic energies of the beads and the potential energies associated with the springs. The polymer contribution to the internal energy (per unit volume) of a flowing polymer solution, with the macromolecules modeled as Hookean dumbbells, is then[10]

$$U_{\text{flow}} = \iiiint \left(\frac{1}{2} HQ^2 + \sum_{v=1}^{2} \frac{1}{2} m\dot{r}_v^2 \right) F(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2) d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2$$

$$= n \int \frac{1}{2} HQ^2\, \psi(\boldsymbol{Q}, t) d\boldsymbol{Q} + \text{const.} \tag{13C.7-1}$$

The constant arises from integrating the kinetic energy over all velocity space, with Eq. 13.1-3 being used for the velocity space distribution; because of the assumption of equilibration in momentum space (Eq. 13.1-3) this constant is independent of the flow field.

a. Use Eqs. 13C.7-1 and 13.4-12 [$\psi(\boldsymbol{Q}, t)$ for any flow field] to get for the *internal energy*:

$$U_{\text{flow}} = \tfrac{1}{2} nkT \operatorname{tr} \boldsymbol{\alpha} + \text{const.} \tag{13C.7-2}$$

Show that the change of internal energy from equilibrium to steady-state shear flow with shear rate $\dot{\gamma}$ is

$$\Delta U = U_{\text{flow}} - U_{\text{eq}} = nkT\, \lambda_H^2 \dot{\gamma}^2 \tag{13C.7-3}$$

Does this agree with your intuition?

b. The *entropy* (per unit volume) of the polymer solution in a flow situation is[11]

$$S_{\text{flow}} = -k \iiiint F \ln F\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2 + \text{const.}$$

$$= -nk \int \psi \ln \psi\, d\boldsymbol{Q} + \text{const.} \tag{13C.7-4}$$

in which F is the distribution function of Eq. 13.1-1, and ψ is that of Eq. 13.1-2. Show that the use of Eq. 13.4-12 leads to

$$\Delta S = S_{\text{flow}} - S_{\text{eq}} = nk \ln \sqrt{\det \boldsymbol{\alpha}} \tag{13C.7-5}$$

or that for steady-state shear flow

$$\Delta S = nk \ln \sqrt{1 + \lambda_H^2 \dot{\gamma}^2} \tag{13C.7-6}$$

[10] See H. C. Booij, *J. Chem. Phys.*, **80**, 4571-4572 (1984); G. Marrucci, *Trans. Soc. Rheol.*, **16**, 321-330 (1972); G. C. Sarti and G. Marrucci, *Chem. Eng. Sci.*, **28**, 1053-1059 (1973).

[11] See, for example, R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, London (1938), or L. Landau and E. M. Lifshitz, *Statistical Physics*, Addison-Wesley, Reading, MA (1958).

That is, as the shear rate increases, the dumbbells tend to become more and more aligned, and the entropy *increases*.

Does this agree with your intuition?

c. The *Helmholtz free energy*, $A = U - TS$, can now be obtained. Show that

$$\Delta A = \tfrac{1}{2}nkT[\mathrm{tr}(\boldsymbol{\alpha} - \boldsymbol{\delta}) - \ln(\det \boldsymbol{\alpha})] \tag{13C.7-7}$$

in agreement with Eq. 10 in the paper by Booij.[10]

For an extension of the ideas in this problem to more general molecular models with constraints see Problem 16C.6.

CHAPTER 14

THE RIGID DUMBBELL AND MULTIBEAD-ROD MODELS

In the preceding chapter we showed how rheological properties of flexible macromolecules, such as polyethylene, polystyrene, and polyisobutylene, can be described approximately by means of elastic dumbbell models. These models account for the orientation and stretching of the individual polymer molecules in the fluid. Admittedly the models are drastic oversimplifications of the true system, but by using these models we can illustrate many problem-solving techniques.

In this chapter we turn to macromolecules that are rodlike, such as isotactic polypropylene, poly-*n*-butylisocyanate, proteins in helical forms, DNA in its helix configuration, and tobacco mosaic virus (see Fig. 11.5-2). Here we use the rigid dumbbell as the simplest mechanical model for these molecules. This model accounts for the orientability of the polymer molecules in flow fields and ignores the less important molecular stretching and bending motions, which are undoubtedly of minor importance in the rheological properties.

Many of the results of this chapter can be generalized rather easily to multibead rod models just by appropriate changes in notation. We indicate in this chapter how these generalizations can be performed, but the justification is postponed until Chapter 16 where the equations for general bead-spring-rod models are given. The notation for the dumbbell and associated multibead-rod models is given in §14.1.

The main kinetic theory equations are presented in §14.2 and 14.3, where the diffusion equation for the orientational distribution function and the expression for the stress tensor are given. In §14.4 we show how to solve the diffusion equation for several simple flows and how to use the results for obtaining the rheological properties. In the next section, §14.5, the analysis is extended to arbitrary, time-dependent, homogeneous flows, and the constitutive equation is expressed in the form of the first several terms of a memory-integral expansion. In the final section, §14.6, we include the hydrodynamic interaction in the modeling of the rodlike macromolecules.

An important reason for including rigid dumbbells immediately after elastic dumbbells is to enable us to compare and contrast the key kinetic theory equations for the two models. Since the rigid dumbbell model has a constraint (i.e., the interbead distance is held constant), we are forced to work in a two-dimensional configuration space and it is convenient to use the two polar angles as the generalized coordinates for the system. As a result the diffusion equation and the stress-tensor expression have forms that are different from the analogous equations for elastic dumbbells. Similar differences occur later in the book between bead-spring chain and bead-rod chain models.

In this chapter we consider only the bead-rod models, but it must be recognized that there is a vast literature on the hydrodynamics of rigid particles, such as ellipsoids, rigid rods, and other bodies of revolution.[1]

§14.1 MODELING OF SOLUTIONS OF RODLIKE POLYMERS

The mechanical model to be used throughout most of this chapter is the rigid dumbbell model shown in Fig. 14.1-1. This model consists of two point masses ("beads") joined by a massless rod, and the interaction with the solvent is presumed to take place only at the beads. We label the beads "-1" and "1" since this enables some equations to be written in a more compact form. Also it is then possible to generalize the rigid dumbbell results rather easily to the multibead rod models of Fig. 14.1-2; such generalizations will be pointed out from time to time during this chapter. Hence, although the chapter is written primarily in terms of the simple rigid dumbbell model, the techniques introduced here apply to a more general class of mechanical models.

As in §13.1 we take the flow field of the polymer solution to be homogeneous, and we use $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^\dagger$ to describe the velocity gradients in the fluid. We replace the phase-space distribution function $f(\boldsymbol{r}_c, \theta, \phi, \boldsymbol{p}_c, P_\theta, P_\phi, t)$ by the corresponding distribution function in the position-generalized-velocity space $F(\boldsymbol{r}_c, \theta, \phi, \dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, t)$. Then we define the distribution function $\Xi(\dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, \boldsymbol{r}_c, \theta, \phi, t)$ by[1]

$$\begin{aligned} F(\boldsymbol{r}_c, \theta, \phi, \dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, t) \\ &= \Psi(\boldsymbol{r}_c, \theta, \phi, t)\Xi(\dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, \boldsymbol{r}_c, \theta, \phi, t) \\ &\doteq n\psi(\theta, \phi, t)\Xi_{eq}(\dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, \theta) \end{aligned} \tag{14.1-1}$$

Because of the constraint in the system (the rigid-rod connector) the configuration is specified by giving just two configuration coordinates, namely the polar angles θ and ϕ, or alternatively the unit vector $\boldsymbol{u}$ pointing from bead "-1" to bead "1." The fraction of dumbbells that at time t are in the orientation range θ, ϕ to $\theta + d\theta, \phi + d\phi$ is then given by $\psi(\theta, \phi, t)d\theta\, d\phi$, where $0 \leq \theta < \pi$ and $0 \leq \phi < 2\pi$. For many purposes it is convenient to use a different configurational distribution function, $f(\boldsymbol{u}, t) = (1/\sin\theta)\psi(\theta, \phi, t)$. At equilibrium the configurational distribution functions ψ and f are given by

$$\psi_{eq}(\theta, \phi) = \frac{\sin\theta}{4\pi}; \qquad f_{eq} = \frac{1}{4\pi} \tag{14.1-2}$$

[1] The pioneering work on rigid ellipsoids includes G. B. Jeffery, *Proc. Roy. Soc.*, **A102**, 161-179 (1922); J. M. Burgers, *Kon. Ned. Akad. Wet. Verhand.* (Eerste Sectie), **16**, 113-184 (1938); A. Peterlin and H. A. Stuart, *Z. Phys.*, **112**, 1-19. 129-147 (1939); N. Saitō, *J. Phys. Soc. Japan*, **6**, 297-301, 302-304 (1951); H. A. Scheraga, *J. Chem. Phys.*, **23**, 1526-1532 (1955); and H. Giesekus, *Rheol. Acta*, **2**, 50-62 (1962). In the Giesekus publication it is reported that $-\Psi_2/\Psi_1$ is $\frac{2}{7}$ for extremely flat (oblate) ellipsoids and $\frac{1}{7}$ for extremely elongated (prolate) ellipsoids. For extensive reviews of suspension rheology see H. Brenner, *Int. J. Multiphase Flow*, **1**, 195-341 (1974); H. Brenner, *Chem. Eng. Sci.*, **27**, 1069-1107 (1972); H. Brenner and D.W. Condiff, *J. Coll. Interface Sci.*, **47**, 199-264 (1974). Exact hydrodynamic analyses of the dumbbell models have been given by S. Wakiya, *J. Phys. Soc. Japan*, **31**, 1581-1587 (1971) and by A. Nir and A. Acrivos, *J. Fluid Mech.*, **59**, 209-223 (1973), the latter for the osculating dumbbell. Analytical results for many limiting cases have been worked out by E. J. Hinch and L. G. Leal, *J. Fluid Mech.*, **52**, 683-712 (1972), **56**, 803-813 (1972), **57**, 753-767 (1973); L. G. Leal and E. J. Hinch, *ibid.*, **46**, 685-703 (1971), **55**, 745-765 (1972).

[1] It is customary to replace the velocity-space distribution function Ξ by its equilibrium expression Ξ_{eq} which is:

$$\Xi_{eq} \propto \exp\left(-\frac{m}{2kT}[2(\dot{\boldsymbol{r}}_c - \boldsymbol{v})^2 + \tfrac{1}{2}L^2\dot{\boldsymbol{u}}^2]\right) \tag{14.1-1a}$$

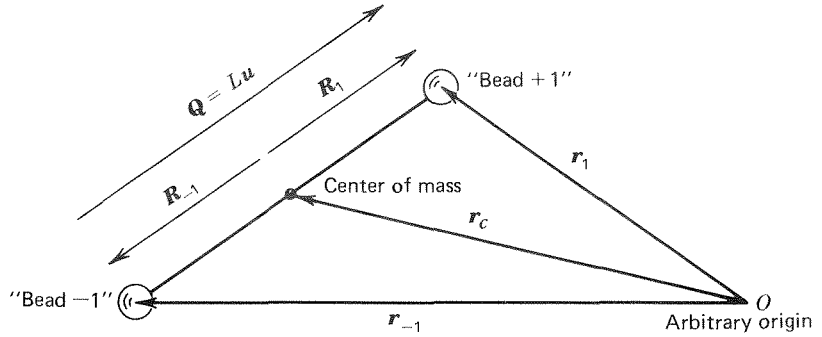


FIGURE 14.1-1. Rigid dumbbell model, with two point masses connected by a massless rigid rod of length L. The unit vector $\boldsymbol{u}$ points in the direction from bead "-1" to bead "$+1$."

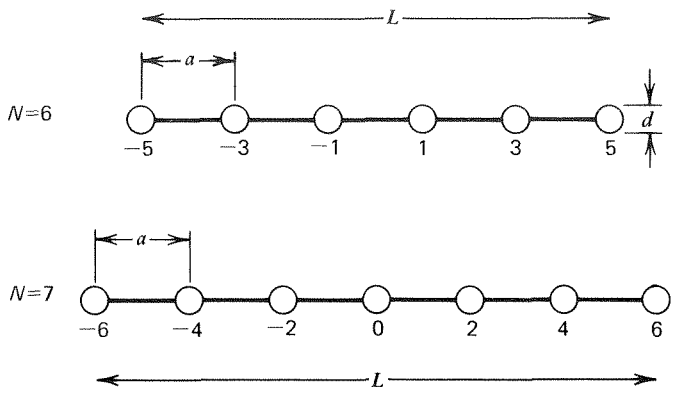


FIGURE 14.1-2. Multibead rods of length L with N evenly spaced beads; note that $L = (N-1)a$. When N is even, beads are numbered $v = \pm 1, \pm 3, \ldots$; when N is odd, beads are numbered $v = 0, \pm 2, \pm 4, \ldots$. The unit vector $\boldsymbol{u}$ gives the direction from $-v$ to $+v$, and $\boldsymbol{R}_v = (Lv/2(N-1))\boldsymbol{u} = (va/2)\boldsymbol{u}$ gives the location of bead v with respect to the center of mass of the rod. The ratio d/a is called ξ, with $0 \le \xi \le 1$. When $\xi = 1$ the beads are just touching, and such a multibead rod is called an "osculating multibead rod."

These equations just state that all orientations are equally likely.

The distribution functions are normalized thus:

$$\iint \psi(\theta, \phi, t)d\theta\, d\phi = 1; \qquad \int f(\boldsymbol{u}, t)d\boldsymbol{u} = 1 \tag{14.1-3}$$

in which $\int \cdots d\boldsymbol{u}$ is exactly the same as $\iint \cdots \sin\theta\, d\theta\, d\phi$. In addition, average values of quantities that depend only on the configuration of the dumbbells are obtained as follows:

$$\langle B \rangle = \iint B(\theta, \phi)\psi(\theta, \phi, t)d\theta\, d\phi \tag{14.1-4a}$$

$$\langle B \rangle = \int B(\boldsymbol{u})f(\boldsymbol{u}, t)d\boldsymbol{u} \tag{14.1-4b}$$

As in the previous chapters the double brackets $[\![\ ]\!]$ are used to indicate averages in momentum (or velocity) space.

In setting up the force balance we proceed as in Chapter 13, except that there is now no intramolecular force. The force balance therefore includes only the hydrodynamic force (the resistance experienced by the bead as it moves through the solution), the Brownian force (a suitably time-smoothed force accounting for the force due to thermal motions), and the external force. The exact form of the Brownian force in a system with constraints is derived in Chapter 18, and in this chapter we take over the results of this later derivation.

It is convenient in this chapter to present most of the formal development by using the orientation vector $\boldsymbol{u}$ rather than the angles θ and ϕ. In so doing we use some shorthand notation, such as $d\boldsymbol{u} = \sin\theta\, d\theta\, d\phi$ already introduced. We also use an operator

$$\frac{\partial}{\partial \boldsymbol{u}} = \boldsymbol{s}\frac{\partial}{\partial\theta} + \boldsymbol{t}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} \tag{14.1-5}$$

in which $\boldsymbol{s}$ and $\boldsymbol{t}$ are the unit vectors described in §11.6 and whose components and derivatives are summarized in §E.5. It should be noted that the $\partial/\partial\boldsymbol{u}$ operator does not obey the usual rules of calculus for the $\partial/\partial\boldsymbol{r}$ (or ∇) operator. Some useful relations involving the $\partial/\partial\boldsymbol{u}$ operator are given in §E.6 in Appendix E.

Finally the time derivative of the orientation vector $\boldsymbol{u}$ is

$$\dot{\boldsymbol{u}} = \boldsymbol{s}\dot{\theta} + \boldsymbol{t}\dot{\phi}\sin\theta \tag{14.1-6}$$

With this and other relations given above we can go back and forth between relations written explicitly in terms of the angles θ and ϕ and those written formally in terms of the orientation vector $\boldsymbol{u}$.

§14.2 THE "DIFFUSION EQUATION" FOR THE CONFIGURATIONAL DISTRIBUTION FUNCTION

We begin by writing the equation of motion for the center of mass of the dumbbell and also that for the internal (i.e., rotatory) motion. The latter may be combined with an equation of continuity in the configuration space to obtain the second-order differential equation for the distribution function $f(\boldsymbol{u}, t)$. The pattern of the development is not quite parallel to that in §13.2 for elastic dumbbells because of the constraint of fixed interbead distance in the rigid dumbbell.

a. The Equations of Motion for the Beads of the Dumbbell

The usual statement of Newton's law of motion as "mass times acceleration equals the sum of the forces" is valid only when there are no constraints in the system. As a consequence we *cannot* write, by analogy with Eq. 13.2-1, a force balance of the form $\boldsymbol{F}_\nu^{(h)} + \boldsymbol{F}_\nu^{(b)} + \boldsymbol{F}_\nu^{(e)} = \boldsymbol{0}$ (here there is no spring force $\boldsymbol{F}_\nu^{(\phi)}$, and, as in §13.2, we assume that inertial forces can be neglected). That is, in a molecular model with constraints, we cannot set the sum of the forces on each bead equal to zero.

To get the equation of motion (i.e., force balance) for the entire molecular model we can, however, set the sum of the forces acting on the center of mass equal to zero; this is equivalent to writing

$$\sum_{v} [\boldsymbol{F}_v^{(h)} + \boldsymbol{F}_v^{(b)} + \boldsymbol{F}_v^{(e)}] = \boldsymbol{0} \tag{14.2-1}$$

where the sum is over the two terms $v = 1$ and $v = -1$. This equation describes the translational motion of the molecular model as a whole; the forces acting on the center of mass sum to zero, since there are no constraints on the location of the center of mass.

To get the equation of motion for the internal degrees of freedom of the rigid dumbbell model (that is, the motion in the θ- and ϕ-directions), we add up the differences of the various types of forces $\boldsymbol{F}_1^{(\ )} - \boldsymbol{F}_{-1}^{(\ )}$ and then "project out" the θ- and ϕ-components by multiplying the sum by $(\boldsymbol{\delta} - \boldsymbol{uu})$:

$$[(\boldsymbol{\delta} - \boldsymbol{uu}) \cdot ((\boldsymbol{F}_1^{(h)} - \boldsymbol{F}_{-1}^{(h)}) + (\boldsymbol{F}_1^{(b)} - \boldsymbol{F}_{-1}^{(b)}) + (\boldsymbol{F}_1^{(e)} - \boldsymbol{F}_{-1}^{(e)}))] = \boldsymbol{0} \tag{14.2-2}$$

Keep in mind that $\boldsymbol{\delta} - \boldsymbol{uu} = \boldsymbol{ss} + \boldsymbol{tt}$, so that $[(\boldsymbol{\delta} - \boldsymbol{uu}) \cdot \boldsymbol{F}] = sF_\theta + tF_\phi$, the latter containing the θ- and ϕ-components of the vector $\boldsymbol{F}$. The rigid dumbbell just has two internal degrees of freedom, described by the configuration coordinates, θ and ϕ, and there is one equation of motion corresponding to each of these two degrees of freedom. The systematic approach for obtaining the equations of motion for arbitrary models with constraints is given in Chapters 16–18.

In order to implement Eqs. 14.2-1 and 14.2-2 above, we need expressions for the various forces acting on the beads:

$$\boldsymbol{F}_v^{(b)} = -v \frac{kT}{L} \frac{\partial}{\partial \boldsymbol{u}} \ln f \qquad (v = \pm 1) \tag{14.2-3}$$

$$\begin{aligned} \boldsymbol{F}_v^{(h)} &= -\zeta([\![\dot{\boldsymbol{r}}_v]\!] - \boldsymbol{v}_v) \\ &= -\zeta([\![\dot{\boldsymbol{r}}_c]\!] + \tfrac{1}{2} vL[\![\dot{\boldsymbol{u}}]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c] - \tfrac{1}{2} vL[\boldsymbol{\kappa} \cdot \boldsymbol{u}]) \qquad (v = \pm 1) \end{aligned} \tag{14.2-4}$$

Here the Brownian motion expression is similar in form to the $-kT(\partial \ln \Psi / \partial \boldsymbol{r}_v)$ term in Eq. 13.2-5 and is consistent with the assumption of a Maxwellian velocity distribution. The Stokes' law expression assumes that the hydrodynamic drag is isotropic, and it is further assumed that the fluid velocity field is homogeneous so that $\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_v]$.

When these expressions for the forces are substituted into Eq. 14.2-1 we get the average velocity for the dumbbell center of mass:

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c] + \frac{1}{2\zeta} (\boldsymbol{F}_1^{(e)} + \boldsymbol{F}_{-1}^{(e)}) \tag{14.2-5}$$

This states that the centers of mass of the dumbbells on the average move with the fluid velocity if no external forces are present.

When the force expressions are substituted into Eq. 14.2-2 we obtain the average time rate of change of the orientation vector $\boldsymbol{u}$:

$$[\![\dot{\boldsymbol{u}}]\!] = [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] - \frac{1}{6\lambda} \frac{\partial}{\partial \boldsymbol{u}} \ln f - \frac{1}{\zeta L} [(\boldsymbol{\delta} - \boldsymbol{uu}) \cdot (\boldsymbol{F}_1^{(e)} - \boldsymbol{F}_{-1}^{(e)})] \tag{14.2-6}$$

in which $\lambda = \zeta L^2/12kT$ is the time constant for the rigid dumbbell. It should be emphasized that this equation contains only a θ- and ϕ-component. Keep in mind that $[\![\dot{\boldsymbol{u}}]\!] = s[\![\dot{\theta}]\!] + t[\![\dot{\phi}]\!] \sin\theta$; that $[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}]$ is the same as $s[\boldsymbol{\kappa}\cdot\boldsymbol{u}]_\theta + t[\boldsymbol{\kappa}\cdot\boldsymbol{u}]_\phi$; and that $\partial/\partial\boldsymbol{u} = \boldsymbol{s}\,\partial/\partial\theta + \boldsymbol{t}\,(\sin\theta)^{-1}\,\partial/\partial\phi$ is a two-dimensional analog of a ∇-operator (see §E.6). In the ensuing discussion we let $[(\boldsymbol{\delta} - \boldsymbol{uu})\cdot(\boldsymbol{F}_1^{(e)} - \boldsymbol{F}_{-1}^{(e)})] = (2/L)\partial\phi^{(e)}/\partial\boldsymbol{u}$, where $\phi^{(e)}$ is the external potential; it is assumed that $\phi^{(e)}$ does not depend on the center of mass location (that is, on $\boldsymbol{r}_c$).

b. The Equation of Continuity for $f(\boldsymbol{u}, t)$

The equation of continuity for $f(\boldsymbol{u}, \mathrm{t})$ is a conservation statement regarding the orientations of an ensemble of rigid dumbbells. The main idea is that dumbbells leaving one orientation must end up in another. Mathematically this is expressed by the following relation:

$$\frac{\partial}{\partial t} f = -\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\![\dot{\boldsymbol{u}}]\!] f\right) \tag{14.2-7}$$

This is a two-dimensional analog of the equation of continuity obtained in Eq. 13.2-12 for elastic dumbbells.

c. The "Diffusion Equation" for $f(\boldsymbol{u}, t)$

Substitution of the expression for $[\![\dot{\boldsymbol{u}}]\!]$ from Eq. 14.2-6 into the equation of continuity above gives the diffusion equation:

$$\boxed{\frac{\partial}{\partial t} f = \frac{1}{6\lambda}\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} f\right) - \frac{\partial}{\partial \boldsymbol{u}} \cdot \left([\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}] f - \frac{1}{6kT\lambda}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)} f\right)} \tag{14.2-8}$$

This is the differential equation that indicates the way in which the distribution of rigid dumbbell orientations changes with time when the imposed time-dependent, homogeneous velocity field is described by $\boldsymbol{\kappa}(t)$. The distribution function must be periodic in ϕ.

No general solution of Eq. 14.2-8 is available. For steady-state homogeneous, potential flow in the absence of external forces the solution is

$$f = \frac{1}{J} e^{3\lambda(\boldsymbol{\kappa}:\boldsymbol{uu})} \tag{14.2-9}$$

as may be shown by substitution into the differential equation; J is the normalization factor.

To conclude this section we obtain the equation of change for any function of dumbbell orientation $B(\boldsymbol{u})$ that is periodic in ϕ. This is done by multiplying Eq. 14.2-8 by B and integrating over all the configuration space, using the integral expressions given in §E.7:

$$\frac{d}{dt}\langle B\rangle = \frac{1}{6\lambda}\left\langle \frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} B\right\rangle + \left\langle \boldsymbol{\kappa}:\boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}} B\right\rangle - \frac{1}{6kT\lambda}\left\langle \left[\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right]\cdot\frac{\partial}{\partial \boldsymbol{u}} B\right\rangle \tag{14.2-10}$$

A similar equation can be obtained for a tensor of any order. In particular for the tensor $\mathbf{B} = \boldsymbol{uu}$ we can specialize Eq. 14.2-10 to

$$\langle \boldsymbol{uu} \rangle_{(1)} = \frac{1}{3\lambda}\boldsymbol{\delta} - \frac{1}{\lambda}\langle \boldsymbol{uu} \rangle - 2\{\boldsymbol{\kappa} : \langle \boldsymbol{uuuu} \rangle\} - \frac{1}{6kT\lambda}\left\langle \left[\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right]\boldsymbol{u} + \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)} \right\rangle \quad (14.2\text{-}11)$$

in which the subscript (1) indicates a convected derivative. This result is used presently.

§14.3 EXPRESSIONS FOR THE STRESS TENSOR

In §13.3 we presented a simple kinetic theory derivation for the stress tensor for a dilute solution of polymer molecules modeled as elastic dumbbells. This led directly to the "Kramers expression" for the stress tensor, given in Eq. A of Table 13.3-1; this expression contains three terms: the solvent contribution, the spring contribution, and the bead momentum-transport contribution. It was then shown that the stress tensor can be transformed into several other forms, in particular the Kramers–Kirkwood and the Giesekus expressions, neither one of which contains the spring force law explicitly.

The derivation for elastic dumbbells in §13.3 is not applicable to rigid dumbbells because the rigid dumbbell contains a constraint. However, it turns out that the stress-tensor expressions in Table 13.3-1 that do not contain the spring force law explicitly can be applied to the rigid dumbbell model. This is certainly not obvious, and proof of this must be postponed to Chapter 18 where the general expression for the stress tensor is derived from first principles using a complete phase-space kinetic theory. Suffice it to say at this point that the Kramers–Kirkwood expression can be used for rigid dumbbells even when hydrodynamic interaction is included, and that the Giesekus expression is valid when hydrodynamic interaction is neglected.

In Table 14.3-1 we summarize the various expressions for the stress tensor for dilute solutions of rodlike polymers modeled as rigid dumbbells. A name has been attached to each expression in order to emphasize the one-to-one correspondence with the formulas of Table 13.3-1. In Example 14.3-1 we show how to go from the Kramers–Kirkwood expression (Eq. C of Table 14.3-1) to the other expressions.

SPECIAL NOTE ON EXTENSION TO MULTIBEAD-ROD MODELS
(without hydrodynamic interaction)

To adapt the equation for $f(\boldsymbol{u}, t)$ in Eq. 14.2-8 and the stress tensor formulas in Eqs. A and D of Table 14.3-1 to multibead rods with N beads distributed uniformly along a rod of length L (see Fig. 14.1-2) replace the rigid dumbbell time constant $\lambda = \zeta L^2/12kT$ by the multibead-rod time constant

$$\lambda_N = \frac{\zeta L^2 N(N+1)}{72(N-1)kT} \quad (14.3\text{-}1)$$

All results in §§14.4 and 14.5 may be generalized to multibead rods in this way.

TABLE 14.3-1

Expressions for the Stress Tensor for Dilute Solutions of Rodlike Polymers Modeled as Rigid Dumbbells[a,b] (Maxwellian velocity distribution assumed)

Kramers:[c]

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - 3nkT\langle\boldsymbol{uu}\rangle - 6nkT\lambda\boldsymbol{\kappa}:\langle\boldsymbol{uuuu}\rangle + nkT\boldsymbol{\delta} - n\left\langle \boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\phi^{(e)}\right\rangle \tag{A}$$

Modified Kramers:

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - 3nkT\left(\frac{2}{L^2}\right)\sum_{\substack{\nu=-1\\ \nu\neq 0}}^{+1}\langle\boldsymbol{R}_\nu\boldsymbol{R}_\nu\rangle - 6nkT\lambda\boldsymbol{\kappa}:\left(\frac{8}{L^4}\right)\sum_{\substack{\nu=-1\\ \nu\neq 0}}^{+1}\langle\boldsymbol{R}_\nu\boldsymbol{R}_\nu\boldsymbol{R}_\nu\boldsymbol{R}_\nu\rangle + nkT\boldsymbol{\delta} - n\left\langle \boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\phi^{(e)}\right\rangle \tag{B}$$

Kramers-Kirkwood:[d]

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\sum_{\substack{\nu=-1\\ \nu\neq 0}}^{+1}\langle\boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)}\rangle \tag{C}$$

Giesekus:[e]

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + 3nkT\lambda\langle\boldsymbol{uu}\rangle_{(1)} + \frac{1}{2}n\left\langle\left(\frac{\partial}{\partial\boldsymbol{u}}\phi^{(e)}\right)\boldsymbol{u} - \boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\phi^{(e)}\right\rangle \tag{D}$$

[a] R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971). H. Giesekus, *Kolloid-Z.*, **147–149**, 29–45 (1956); erratum: *Rheol. Acta*, **1**, 404 (1961), fn. 18.

[b] R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **14**, 85–101 (1984); *J. Polym. Sci.: Polym. Symp.*, **73**, 187–199 (1985).

[c] This form of the stress tensor was given first by S. Prager, *Trans. Soc. Rheol.*, **1**, 53–62 (1957).

[d] H. A. Kramers, *Physica*, **11**, 1–19 (1944); J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281–283 (1951); J. G. Kirkwood and R. J. Plock, *ibid.*, **24**, 665–669 (1956); for a multicomponent generalization, see C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191–204 (1983), Eq. (36). In this table, only Eq. C can be used when hydrodynamic interaction effects are included (see §14.6).

[e] A simplified form of this expression, valid for steady-state flows, was first given by S. Prager, *loc. cit.*

EXAMPLE 14.3-1. Interrelation of Stress Tensor Formulas

Show how to get the Kramers and Giesekus stress tensor expressions from the Kramers-Kirkwood formula; neglect external forces.

SOLUTION **(a)** In Eq. C of Table 14.3-1 we replace $\boldsymbol{R}_\nu$ by $\frac{1}{2}\nu L\boldsymbol{u}$ and $\boldsymbol{F}_\nu^{(h)}$ by $-\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu])$; this gives for $\boldsymbol{\tau}_p = \boldsymbol{\tau} - \boldsymbol{\tau}_s = \boldsymbol{\tau} + \eta_s\dot{\boldsymbol{\gamma}}$:

$$\begin{aligned}\boldsymbol{\tau}_p &= \tfrac{1}{2}n\zeta L\langle\boldsymbol{u}([[\dot{\boldsymbol{r}}_1]] - \boldsymbol{\kappa}\cdot\boldsymbol{r}_1] - [[\dot{\boldsymbol{r}}_{-1}]] - \boldsymbol{\kappa}\cdot\boldsymbol{r}_{-1}])\rangle \\ &= \tfrac{1}{2}n\zeta L^2\langle\boldsymbol{u}[[\dot{\boldsymbol{u}}]] - \boldsymbol{\kappa}\cdot\boldsymbol{u}]\rangle\end{aligned} \tag{14.3-2}$$

Then use Eq. 14.2-6 and neglect the external force terms to get

$$\begin{aligned}\boldsymbol{\tau}_p &= -\tfrac{1}{2}n\zeta L^2\boldsymbol{\kappa}:\langle\boldsymbol{uuuu}\rangle - nkT\left\langle \boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\ln f\right\rangle \\ &= -6nkT\lambda\boldsymbol{\kappa}:\langle\boldsymbol{uuuu}\rangle - 3nkT\langle\boldsymbol{uu}\rangle + nkT\boldsymbol{\delta}\end{aligned} \tag{14.3-3}$$

The details for performing the integral involving $\ln f$ are as follows:

$$\left\langle \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\ln f\right\rangle = \iint \boldsymbol{us}\frac{\partial f}{\partial\theta}\sin\theta\,d\theta\,d\phi + \iint \boldsymbol{ut}\frac{\partial f}{\partial\phi}\,d\theta\,d\phi$$

$$= -\iint f(\boldsymbol{ss} - \boldsymbol{uu} + \boldsymbol{us}\cot\theta)\sin\theta\,d\theta\,d\phi$$

$$-\iint f(\boldsymbol{tt} - \boldsymbol{uu} - \boldsymbol{us}\cot\theta)\sin\theta\,d\theta\,d\phi$$

$$= -\iint f(\boldsymbol{ss} + \boldsymbol{tt} + \boldsymbol{uu} - 3\boldsymbol{uu})\sin\theta\,d\theta\,d\phi \qquad (14.3\text{-}4)$$

In going from the first to the second line, integration by parts has been used as well as the periodicity of f in the variable ϕ. In addition the rules for differentiation of the unit vectors in Table E.5-2 have been used.

(**b**) To get the Giesekus expression multiply Eq. 14.2-11 by $3nkT\lambda$ and subtract from Eq. 14.3-3 to get Eq. D of Table 14.3-1.

§14.4 SOLUTION OF THE KINETIC THEORY EQUATIONS FOR SPECIAL FLOWS[1]

In this section we illustrate the solution to the diffusion equation and the calculation of the stress tensor for simple flows in the absence of external forces. The flows considered here are simple shear and elongation, because of their wide use in rheological characterizations. Detailed derivations for other flows are given elsewhere.[1]

a. Simple Shearing Flows of Rigid Dumbbell Solutions

For simple shear flow, $v_x = \dot\gamma(t)y$ the only nonzero component of the tensor $\boldsymbol{\kappa}$ is $\kappa_{xy} = \dot\gamma$, and the diffusion equation given in Eq. 14.2-8 may be written as

$$6\lambda\frac{\partial f}{\partial t} = \left[\frac{1}{S}\frac{\partial}{\partial\theta}\left(S\frac{\partial f}{\partial\theta}\right) + \frac{1}{S^2}\frac{\partial^2 f}{\partial\phi^2}\right] - (6\lambda\dot\gamma)\left[\frac{sc}{S}\frac{\partial}{\partial\theta}(S^2Cf) - \frac{\partial}{\partial\phi}(s^2f)\right]$$

$$\equiv \Lambda f - (6\lambda\dot\gamma)\Omega_s f \qquad (14.4\text{-}1)$$

where Λ and Ω_s are linear operators; we use the abbreviations $S = \sin\theta$, $C = \cos\theta$, $s = \sin\phi$, and $c = \cos\phi$.

[1] In this section we have drawn heavily from R. B. Bird, H. R. Warner, Jr., and D. C. Evans [*Adv. in Polym. Sci.*, **8**, 1-90 (1971)] where detailed results are given for many material functions. In addition Table 3 gives an extensive summary of rigid and Hookean dumbbell results.

Next we simplify the Giesekus expression for the stress tensor to simple shearing flows. The three combinations of stress components that are of interest for shearing flow are:

$$\tau_{yx} - \dot{\tau}_{yx,s} = \tfrac{1}{2}nkT\lambda\left[\frac{\partial}{\partial t}\langle P_2^2 s_2\rangle - \dot{\gamma}(t)\langle 2(P_0^0 - P_2^0)c_0 - P_2^2 c_2\rangle\right] \tag{14.4-2}$$

$$\tau_{xx} - \tau_{yy} = nkT\lambda\left[\frac{\partial}{\partial t}\langle P_2^2 c_2\rangle - \dot{\gamma}(t)\langle P_2^2 s_2\rangle\right] \tag{14.4-3}$$

$$\tau_{yy} - \tau_{zz} = -nkT\lambda\left[\frac{\partial}{\partial t}\langle 3P_2^0 c_0 + \tfrac{1}{2}P_2^2 c_2\rangle\right] \tag{14.4-4}$$

In these expressions we have rewritten S, C, s, and c in terms of spherical harmonics $P_n^m s_m$ and $P_n^m c_m$. In addition, we have introduced the abbreviations $s_k = \sin k\phi$ and $c_k = \cos k\phi$. Use of the spherical harmonics[2] facilitates the solution of the equation for f and the subsequent evaluation of the stress tensor components.

The Λ-operator of Eq. 14.4-1 acting on a spherical harmonic gives the same spherical harmonic multiplied by the constant $-n(n+1)$:

$$\begin{aligned} \Lambda P_n^m s_m &= -n(n+1)P_n^m s_m \\ \Lambda P_n^m c_m &= -n(n+1)P_n^m c_m \end{aligned} \tag{14.4-5}$$

Furthermore, the result of Ω_s operating on the spherical harmonics can be expressed as a linear combination of spherical harmonics

$$\begin{aligned} \Omega_s P_n^m s_m &= \sum_{j=m-2}^{m+2}\sum_{k=n-2}^{n+2} a_{nk}^{mj} P_k^j c_j \qquad (m > 0) \\ \Omega_s P_n^m c_m &= -\sum_{j=m-2}^{m+2}\sum_{k=n-2}^{n+2} a_{nk}^{mj} P_k^j s_j \qquad (m \geq 0) \end{aligned} \tag{14.4-6}$$

where the a_{nk}^{mj} are given in Table 14.4-1. In particular note that $\Omega_s 1 = \Omega_s P_0^0 c_0 = -\frac{1}{2}P_2^2 s_2$. In applying Eq. 14.4-6 and Table 14.4-1, keep in mind that Table 14.4-1 is valid only for $m \geq 0$, and that $P_n^m = 0$ if $m > n$.

EXAMPLE 14.4-1 Steady Shear Flow[1,3,4,5,6,7]

By means of a perturbation calculation obtain the solution to Eq. 14.4-1 for the flow $v_x = \dot{\gamma}y$, $v_y = 0$, $v_z = 0$ with $\dot{\gamma}$ being a constant (the "shear rate"). Obtain expressions for the viscometric functions as a power series in $\dot{\gamma}$.

[2] See §E.8 for information on spherical harmonics and Legendre polynomials.
[3] H. Giesekus, *Kolloid-Z.*, **147-149**, 29 45 (1956); Erratum: *Rheol. Acta*, **1**, 404 (1961), footnote 18.
[4] J. G. Kirkwood and R. J. Plock, *J. Chem. Phys.*, **24**, 665-669 (1956).
[5] S. Prager, *Trans. Soc. Rheol.*, **1**, 53-62 (1957).
[6] T. Kotaka, *J. Chem. Phys.*, **30**, 1566-1567 (1959).
[7] S. Kim and X. J. Fan, *J. Rheol.*, **28**, 117-122 (1984).

TABLE 14.4-1[a]

Tabulation of the a_{nk}^{mj} of Eq. 14.4-6

$$a_{n,n-2}^{m,m-2} = \frac{(n-2)(n+m)(n+m-1)(n+m-2)(n+m-3)(1-\delta_{m0})}{4(2n+1)(2n-1)}$$

$$a_{n,n}^{m,m-2} = \frac{3(n+m)(n+m-1)(n-m+1)(n-m+2)(1-\delta_{m0})}{4(2n-1)(2n+3)}$$

$$a_{n,n+2}^{m,m-2} = -\frac{(n+3)(n-m+1)(n-m+2)(n-m+3)(n-m+4)(1-\delta_{m0})}{4(2n+1)(2n+3)}$$

$$a_{nn}^{mm} = -\frac{m}{2}$$

$$a_{n,n-2}^{m,m+2} = -\frac{(n-2)(1+\delta_{m0})}{4(2n+1)(2n-1)}$$

$$a_{n,n}^{m,m+2} = -\frac{3(1+\delta_{m0})}{4(2n-1)(2n+3)}$$

$$a_{n,n+2}^{m,m+2} = \frac{(n+3)(1+\delta_{m0})}{4(2n+1)(2n+3)}$$

All other a_{nk}^{mj} are zero.

[a] R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1 90 (1971), Table 1 on p. 23.

SOLUTION **(a)** Solution for the Distribution Function

Since we are considering only flows that are not far from equilibrium we expand $f(\theta, \phi)$ in a power series:

$$f(\theta, \phi) = \frac{1}{4\pi}[1 + (6\lambda\dot{\gamma})\phi_1 + (6\lambda\dot{\gamma})^2\phi_2 + \cdots] \tag{14.4-7}$$

Since f is normalized to unity (Eq. 14.1-3) the $\phi_k(\theta, \phi)$ must satisfy the relations

$$\int_0^{2\pi}\int_0^{\pi} \phi_k(\theta, \phi) S \, d\theta \, d\phi = \int_0^{2\pi}\int_0^{\pi} \phi_k P_0^0 c_0 S \, d\theta \, d\phi = 0 \qquad (k = 1, 2, 3, \ldots) \tag{14.4-8}$$

Substitution of Eq. 14.4-7 into Eq. 14.4-1 with $\partial f/\partial t = 0$ for steady state gives

$$\Lambda[1 + (6\lambda\dot{\gamma})\phi_1 + (6\lambda\dot{\gamma})^2\phi_2 + \cdots] = (6\lambda\dot{\gamma})\Omega_s[1 + (6\lambda\dot{\gamma})\phi_1 + (6\lambda\dot{\gamma})^2\phi_2 + \cdots] \tag{14.4-9}$$

Equating coefficients of equal powers of $(6\lambda\dot{\gamma})$ gives a series of differential equations for the ϕ_k:

$$\begin{aligned} \Lambda\phi_1 &= \Omega_s 1 = -\tfrac{1}{2}P_2^2 s_2 \\ \Lambda\phi_2 &= \Omega_s\phi_1 \\ &\vdots \qquad\quad \vdots \\ \Lambda\phi_k &= \Omega_s\phi_{k-1} \end{aligned} \tag{14.4-10}$$

Using the first member of Eqs. 14.4-10 and 14.4-5 we see that

$$\phi_1 = \tfrac{1}{12} P_2^2 s_2 \tag{14.4-11}$$

Note that we could add a constant to the ϕ_1 given above and still satisfy the differential equation; however, the normalization condition Eq. 14.4-8 requires that this constant be zero. Similarly the integration constants that arise in determining all the other ϕ_k are equal to zero.

Next we use the ϕ_1 just found, together with Eq. 14.4-10 for ϕ_2, to get

$$\begin{aligned} \Lambda\phi_2 = \Omega_s\phi_1 &= \tfrac{1}{12}\Omega_s(P_2^2 s_2) \\ &= \tfrac{1}{12}[\tfrac{6}{7}P_2^0 c_0 - P_2^2 c_2 - \tfrac{6}{7}P_4^0 c_0 + \tfrac{1}{28}P_4^4 c_4] \end{aligned} \tag{14.4-12}$$

Here we have used Eq. 14.4-6 and Table 14.4-1. Once again, the information about the Λ-operator in Eq. 14.4-5 is used with the differential equation for ϕ_2. The result is

$$\phi_2 = -\frac{1}{84} P_2^0 c_0 + \frac{1}{72} P_2^2 c_2 + \frac{1}{280} P_4^0 c_0 - \frac{1}{6720} P_4^4 c_4 \tag{14.4-13}$$

Similarly, we find that

$$\phi_3 = -\frac{19}{7560} P_2^2 s_2 - \frac{1}{18480} P_4^2 s_2 + \frac{1}{221760} P_6^2 s_2 + \frac{1}{25200} P_4^4 s_4 - \frac{1}{15966720} P_6^6 s_6 \tag{14.4-14}$$

This procedure can be continued to get the coefficients in the higher ϕ_k.

(b) Evaluation of the Stress Tensor Components.

To compute the stress components we now substitute the series expansion for the distribution function into Eqs. 14.4-2, 14.4-3, and 14.4-4 written for steady state:

$$\begin{aligned} \tau_{yx} - \tau_{yx,s} = -\frac{nkT\lambda\dot\gamma}{8\pi} \int_0^{2\pi}\int_0^{\pi} \Big[& 2(P_0^0 - P_2^0)c_0 - P_2^2 c_2 \Big] \\ & \times \Big[P_0^0 c_0 + (6\lambda\dot\gamma)\Big(\frac{1}{12} P_2^2 s_2\Big) + (6\lambda\dot\gamma)^2\Big(-\frac{1}{84} P_2^0 c_0 + \frac{1}{72} P_2^2 c_2 \\ & + \frac{1}{280} P_4^0 c_0 - \frac{1}{6720} P_4^4 c_4\Big) + \cdots \Big] S\, d\theta\, d\phi \end{aligned} \tag{14.4-15}$$

$$\begin{aligned} \tau_{xx} - \tau_{yy} = -\frac{nkT\lambda\dot\gamma}{4\pi} \int_0^{2\pi}\int_0^{\pi} P_2^2 s_2 \Big[& P_0^0 c_0 + (6\lambda\dot\gamma)\Big(\frac{1}{12} P_2^2 s_2\Big) \\ & + (6\lambda\dot\gamma)^2\Big(-\frac{1}{84} P_2^0 c_0 + \frac{1}{72} P_2^2 c_2 + \frac{1}{280} P_4^0 c_0 - \frac{1}{6720} P_4^4 c_4\Big) + \cdots \Big] S\, d\theta\, d\phi \end{aligned} \tag{14.4-16}$$

$$\tau_{yy} - \tau_{zz} = 0 \tag{14.4-17}$$

All of the integrals above are easily evaluated using Eq. E.8-7. According to the orthogonality conditions the dashed-underlined terms contribute nothing to the stresses. Evaluation of the

remaining terms, including those arising from ϕ_3, ϕ_4, and ϕ_5 gives the following viscometric functions[1,3,4,5,6] defined in Eqs. D.5-1, 2, and 3:

$$\eta - \eta_s = nkT\lambda\left[1 - \frac{18}{35}(\lambda\dot{\gamma})^2 + \frac{1326}{1925}(\lambda\dot{\gamma})^4 - \cdots\right] \tag{14.4-18}$$

$$\Psi_1 = \frac{6}{5}nkT\lambda^2\left[1 - \frac{38}{35}(\lambda\dot{\gamma})^2 + \frac{38728}{25025}(\lambda\dot{\gamma})^4 - \cdots\right] \tag{14.4-19}$$

$$\Psi_2 = 0 \tag{14.4-20}$$

Kim and Fan[7] have obtained the coefficients in the expansions up to $(\lambda\dot{\gamma})^{40}$ and have determined that the series converge for $\lambda\dot{\gamma} < 0.81$; they also extended their solution to about $\lambda\dot{\gamma} = 1.2$ by analytic continuation and obtained excellent agreement with earlier numerical calculations.[8] The expressions above, including the $(\lambda\dot{\gamma})^4$ term are good to within 1 % only up to about $\lambda\dot{\gamma} = 0.46$. In the limit of very large shear rates Stewart and Sørensen obtained " power law" limiting expressions using numerical methods (see Example 14.6-2):

$$\eta - \eta_s \doteq 0.678\, nkT\lambda(\lambda\dot{\gamma})^{-1/3} \tag{14.4-21}$$

$$\Psi_1 \doteq 1.20\, nkT\lambda^2(\lambda\dot{\gamma})^{-4/3} \tag{14.4-22}$$

these expressions being good approximations for $\lambda\dot{\gamma}$ greater than about 5.

The time constant λ contains ζ and L, which are not experimentally measurable. Hence for making comparisons with experimental data one can determine λ from the zero-shear-rate viscosity in Eq. 14.4-18:

$$\lambda = \frac{\eta_0 - \eta_s}{nkT} = \frac{[\eta]_0\eta_s M}{\tilde{N}kT} \tag{14.4-23}$$

where $[\eta]_0$ is the zero-shear-rate intrinsic viscosity (Eq. D.5-4) and $\tilde{N}$ is Avogadro's number. When this is substituted into Eqs. 14.4-18 and 14.4-19, relations are obtained among measurable quantities (e.g., η, η_s, M, T, and $\dot{\gamma}$).

Figures 14.4-1 and 14.4-2 show comparisons between experimental data for rigid, rodlike macromolecules and the rigid dumbbell results. In Fig. 14.4-1 we show the data of Wada[9] for tobacco mosaic virus in water; the time constant in this case was chosen to give a reasonable fit of the data. The poor agreement may be due to the model itself, to the neglect of hydrodynamic interaction, or to association effects. In Fig. 14.4-2 are given the data of Yang[10] on poly-γ-benzyl-L-glutamate in *m*-cresol, reinterpreted as non-Newtonian intrinsic viscosity; two calculated curves are shown, illustrating two different ways of determining the time constant. Note that the time constant determined from the η versus $\dot{\gamma}$ curve differs from that calculated from $[\eta]_0$, η_s, M, and T using Eq. 14.4-23 only by a factor of 3.5. This is rather good agreement in view of the crudeness of the model and the neglect of hydrodynamic interaction. The $\dot{\gamma}^{-1/3}$ dependence predicted by Eq. 14.4-21 seems to be borne out by the data comparison in Fig. 14.4-2.

b. Elongational Flows of Rigid Dumbbell Solutions

A second class of flows for which we illustrate the use of the kinetic theory equations for rigid dumbbells is simple elongation $v_z = \dot{\varepsilon}(t)z$, $v_x = -\frac{1}{2}\dot{\varepsilon}(t)x$, $v_y = -\frac{1}{2}\dot{\varepsilon}(t)y$. For these

[8] W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1-13 (1972).
[9] E. Wada, *J. Polym. Sci.*, **14**, 305-307 (1954); *J. Sci. Res. Inst.*, **47**, 168-170 (Dec. 1953).
[10] J. T. Yang, *J. Amer. Chem. Soc.*, **80**, 1783-1788 (1958); **81**, 3902-3907 (1959).

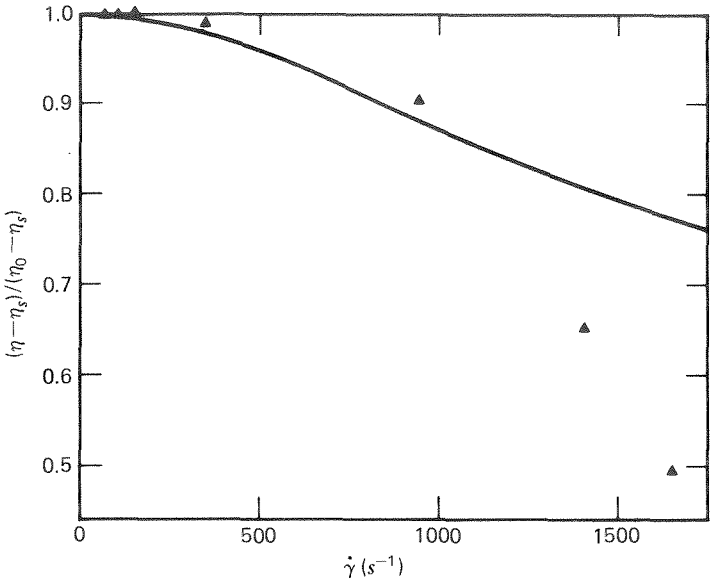


FIGURE 14.4-1. Plot of the ratio $(\eta - \eta_s)/(\eta_0 - \eta_s)$ versus the shear rate $\dot{\gamma}$. The solid triangles are data for tobacco mosaic virus in water at a concentration of 1.14×10^{-3} g/cm^3. The solid curve is a plot of Eq. 14.4-18 or Fig. 14.6-1 (with $h = 0$) for the rigid dumbbell model with the time constant λ chosen to be 6×10^{-4} s, which represents the best fit of the data. Data of E. Wada, *J. Sci. Res. Inst.*, **47**, 168-170 (Dec. 1953). The authors are indebted to Professor J. S. Dahler for correspondence regarding this data comparison; see also A. R. Altenberger and J. S. Dahler, *Macromolecules*, **18**, 1700-1710 (1985).

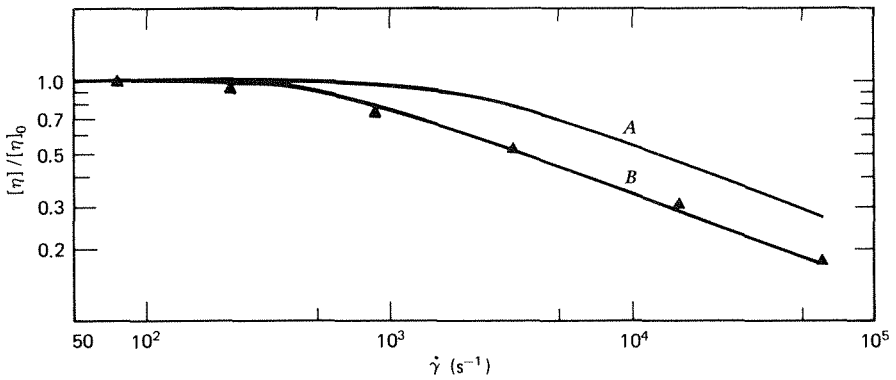


FIGURE 14.4-2. Plot of the ratio $[\eta]/[\eta]_0$ versus the shear rate $\dot{\gamma}$. The solid triangles are data for poly-γ-benzyl-*L*-glutamate ($\bar{M}_w = 2.08 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 1.3$) in *m*-cresol (helix structure) extrapolated to infinite dilution. The solid curves are based on the rigid-dumbbell calculations of Stewart and Sørensen as given in Fig. 14.6-1. Curve A was obtained by getting the time constant ($\lambda = 2.94 \times 10^{-4}$ s) from $\lambda = [\eta]_0 \eta_s M/\tilde{N}kT$ (cf. Eq. 14.4-23) with M taken to be the experimentally determined $\bar{M}_w$ and by assuming that the solution is monodisperse ($\bar{M}_w/\bar{M}_n = 1$). Curve B was obtained by choosing the time constant λ to be 1.04×10^{-3} s, which represents the best fit of the data. Data of J. T. Yang, *J. Am. Chem. Soc.*, **80**, 1783-1788 (1958). [R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1-90 (1971).]

flows $\kappa_{zz} = \dot{\varepsilon}$, $\kappa_{xx} = \kappa_{yy} = -\frac{1}{2}\dot{\varepsilon}$ and all other $\kappa_{ij} = 0$. Substitution of these components of $\boldsymbol{\kappa}$ into Eq. 14.2-8 gives the diffusion equation for elongational flow:

$$6\lambda \frac{\partial}{\partial t} f = \Lambda f + \tfrac{3}{2}(6\lambda\dot{\varepsilon}) \frac{1}{S} \frac{\partial}{\partial \theta} (S^2 C f)$$

$$= \Lambda f + \tfrac{3}{2}(6\lambda\dot{\varepsilon}) \Omega_e f \tag{14.4-24}$$

Here Λ is the same as the operator used for shear flow in Eq. 14.4-1; Ω_e is an operator for elongational flows. The elongation rate $\dot{\varepsilon}$ is in general a function of time.

The stress difference related to the elongational viscosity is found from the Giesekus expression for the stress tensor to be

$$\tau_{xx} - \tau_{zz} = 3\eta_s \dot{\varepsilon}(t) + 6nkT\lambda\dot{\varepsilon}(t)$$

$$+ 3nkT\lambda \left[\frac{\partial}{\partial t} \langle (P_0^0 - P_2^0) + \tfrac{1}{6} P_2^2 c_2 \rangle - \dot{\varepsilon}(t) \langle (P_0^0 - P_2^0) - \tfrac{1}{6} P_2^2 c_2 \rangle \right] \tag{14.4-25}$$

In solving kinetic theory problems for elongational flow we need the information on the Λ-operator and orthogonality conditions given earlier. In addition we need to know how the Ω_e operator affects the P_n^0 (the Legendre polynomials):

$$\Omega_e P_n^0 = -\frac{n(n-1)(n-2)}{(2n+1)(2n-1)} P_{n-2}^0$$

$$+ \left[2 + \frac{n(n+1)^2 - 3(n+1)(n+2)}{(2n+3)(2n+1)} - \frac{n^2(n+1) + 3n(n-1)}{(2n+1)(2n-1)} \right] P_n^0$$

$$+ \frac{(n+1)(n+2)(n+3)}{(2n+1)(2n+3)} P_{n+2}^0 \tag{14.4-26}$$

Note that $\Omega_e 1 = \Omega_e P_0^0 = 2P_2^0$.

EXAMPLE 14.4-2 Steady Elongational Flow[11]

Determine the distribution function for a steady simple elongational flow. Then find the elongational viscosity for a rigid dumbbell suspension.

SOLUTION **(a)** Solution for the Distribution Function

Because of the symmetry of the flow about the z-axis we expect the distribution function to depend on θ alone. Hence we write the diffusion equation as

$$0 = \frac{1}{S} \frac{d}{d\theta} \left(S \frac{d}{d\theta} f \right) + 9\lambda\dot{\varepsilon} \frac{1}{S} \frac{d}{d\theta} (S^2 C f) \tag{14.4-27}$$

Integrating this equation once gives

$$\frac{d}{d\theta} f = -9\lambda\dot{\varepsilon} S C f \tag{14.4-28}$$

[11] R. B. Bird, M. W. Johnson, Jr., and J. F. Stevenson in *Proc. 5th International Congress on Rheology*, S. Onogi (Ed.), University of Tokyo Press, Tokyo (1970), Vol. 4, pp. 159–168.

The integration constant in Eq. 14.4-28 has been set equal to zero because cylindrical symmetry requires that $(df/d\theta) = 0$ at $\theta = 0$ and π. A second integration gives

$$f = \frac{1}{J} e^{(9/2)\lambda\dot{\varepsilon}C^2} \tag{14.4-29}$$

where J is the normalization constant. Note that this result can also be deduced from Eq. 14.2-9, which gives f for any steady-state, homogeneous potential flow.

(b) Evaluation of the Elongational Viscosity

From the definition of the elongational viscosity in Eq. D.5-14 and the normal-stress difference expression in Eq. 14.4-25, we obtain

$$\bar{\eta} - 3\eta_s = 6nkT\lambda - 3nkT\lambda\langle S^2(1 + s^2)\rangle \tag{14.4-30}$$

Then introduction of the distribution function from Eq. 14.4-29 gives

$$\bar{\eta} - 3\eta_s = 6nkT\lambda - 3nkT\lambda \frac{\int_0^{2\pi}\int_0^{\pi} \exp[(9/2)\lambda\dot{\varepsilon}C^2]S^2(1 + s^2)S\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\pi} \exp[(9/2)\lambda\dot{\varepsilon}C^2]S\, d\theta\, d\phi} \tag{14.4-31}$$

The integrals over ϕ can be performed, and then the integrals over θ can be rewritten using the change of variable $\xi = \sqrt{X}\cos\theta$ where $X = (9/2)\lambda|\dot{\varepsilon}|$. This gives

$$\begin{aligned}\frac{\bar{\eta} - 3\eta_s}{3nkT\lambda} &= \frac{1}{2} + \frac{3}{2X}\frac{\int_0^{\sqrt{X}} y^2 \exp(\pm y^2)dy}{\int_0^{\sqrt{X}} \exp(\pm y^2)\, dy} \\ &= \frac{1}{2} \mp \frac{3}{4X} \pm \frac{3}{4\sqrt{X}}\frac{\exp(\pm X)}{\int_0^{\sqrt{X}} \exp(\pm y^2)dy}\end{aligned} \tag{14.4-32}$$

TABLE 14.4-2

Elongational Viscosity for Rigid Dumbbells[a]

	$(\bar{\eta} - 3\eta_s)/3nkT\lambda$	
$\lambda\|\dot{\varepsilon}\|$	Positive $\dot{\varepsilon}$	Negative $\dot{\varepsilon}$
0	1.00	1.00
0.01	1.01	0.98
0.1	1.06	0.94
0.2	1.13	0.83
0.5	1.33	0.77
1.0	1.61	0.66
3.0	1.88	0.56
10.0	1.99	0.52
∞	2.00	0.50

[a] Values for positive $\dot{\varepsilon}$ are taken from R. B. Bird, M. W. Johnson, Jr., and J. F. Stevenson, *Proc. 5th International Congress on Rheology*, S. Onogi, (Ed.), University of Tokyo Press (1970), Vol. 4, pp. 159-168.

in which the upper signs are to be used when $\dot{\varepsilon}$ is positive and the lower for $\dot{\varepsilon}$ negative. To get the second line of Eq. 14.4-32 the integral in the numerator of the first line is integrated by parts. The integral in the denominator is $(\sqrt{\pi}/2)$ erf $\sqrt{X}$ if the minus sign is used; with the plus sign it is closely related[12] to "Dawson's integral." Values of the quantity $(\bar{\eta} - 3\eta_s)/3nkT\lambda$ are shown in Table 14.4-2. It is evident that for rigid dumbbells $\bar{\eta}$ is a far less sensitive function of $\dot{\varepsilon}$ than it is for elastic dumbbells. No experimental data are available for comparison with the theory.

§14.5 SOLUTION OF THE KINETIC THEORY EQUATIONS FOR GENERAL FLOWS

In the foregoing section we showed how to obtain a perturbation expansion for steady-shear flow valid for small shear rates; for steady elongational flow we were able to get a complete solution to the equation for the orientational distribution function. In this section we show how to develop the stress tensor in a "memory-integral expansion" (Eqs. D.4-1 and 9.6-12) valid for a rather wide class of flows.[1] This is done by performing the perturbation expansion of §14.4(a) to get $f(\boldsymbol{u}, t)$ for an arbitrary irrotational, time-dependent, homogeneous flow. With the distribution function thus obtained we can then obtain the stress tensor as a series of integrals, and from the latter it is possible to determine the first few kernel functions in a memory-integral expansion; this expansion can then be used to solve flow problems that are not irrotational. It has been proven that for a wide class of fluids the response to arbitrary irrotational flows is sufficient to determine completely the rheological behavior of the fluid.[2]

We now attempt to solve Eq. 14.2-8, which we write as

$$6\lambda \frac{\partial f}{\partial t} = \Lambda f - 6\lambda \Omega f \tag{14.5-1}$$

where

$$\Lambda f = \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}}\right) f \tag{14.5-2}$$

$$\Omega f = \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] f\right) \tag{14.5-3}$$

with Λ and Ω being operators. Since the fluid is incompressible, $\boldsymbol{\kappa}$ is traceless, and since we are restricting the derivation to irrotational flow, $\boldsymbol{\kappa}$ is symmetric so that $\boldsymbol{\kappa} = \frac{1}{2}\dot{\boldsymbol{\gamma}}$; the tensor $\boldsymbol{\kappa}$ may depend on the time t.

We postulate a solution of the form

$$f = \frac{1}{4\pi} \sum_{k=0}^{\infty} (6\lambda)^k \phi_k \tag{14.5-4}$$

[12] M. Abramowitz and I. A. Stegun (Eds.), *Handbook of Mathematical Functions*, Nat. Bur. of Standards, Washington, D. C. (1964), p. 692, Section 19.14.5.

[1] This method was first given by R. B. Bird and R. C. Armstrong, *J. Chem. Phys.*, **56**, 3680-3682 (1972) and further developed by R. C. Armstrong and R. B. Bird [*J. Chem. Phys.*, **58**, 2715-2723 (1973); erratum: in Eq. 22, replace 27/280 by 27/980]. Later the memory-integral expansion developed through third order by these authors was put into the form of a corotational memory-integral expansion by S. I. Abdel-Khalik, O. Hassager, and R. B. Bird [*J. Chem. Phys.*, **61**, 4312-4316 (1974); erratum: in Eq. 14 change 1/70 to 1/35]. The presentation here in terms of surface spherical harmonics was developed by R. C. Armstrong (unpublished).

[2] B. D. Coleman and C. Truesdell, *ZAMM*, **45**, 547-551 (1965).

in which $\phi_k(\boldsymbol{u}, t)$ is of kth order in $\boldsymbol{\kappa}$; furthermore $\phi_0 \equiv 1$. Since f is normalized to unity the ϕ_k must satisfy the constraints

$$\int \phi_k(\boldsymbol{u}, t) d\boldsymbol{u} = 0 \qquad (k = 1, 2, 3, \ldots) \tag{14.5-5}$$

Substitution of the series solution of Eq. 14.5-4 into the differential equation of Eq. 14.5-1 gives a set of equations for the ϕ_k:

$$6\lambda \frac{\partial}{\partial t} \phi_1 = \Lambda\phi_1 - \Omega 1 \tag{14.5-6}$$

$$6\lambda \frac{\partial}{\partial t} \phi_2 = \Lambda\phi_2 - \Omega\phi_1 \tag{14.5-7}$$

$$\vdots$$

$$6\lambda \frac{\partial}{\partial t} \phi_k = \Lambda\phi_k - \Omega\phi_{k-1} \tag{14.5-8}$$

The main problem in this section is to solve Eqs. 14.5-6 to 14.5-8. This is done by using the surface spherical harmonics defined in Eq. E.10-1.

We start by noting that Eq. 14.5-6 may be written as

$$\begin{aligned} 6\lambda \frac{\partial}{\partial t} \phi_1 &= \Lambda\phi_1 - \boldsymbol{\kappa} : (\boldsymbol{\delta} - 3\boldsymbol{uu}) \\ &= \Lambda\phi_1 + \tfrac{1}{2}(\dot{\boldsymbol{\gamma}} : \mathbf{S}_2) \end{aligned} \tag{14.5-9}$$

To get the last term in this equation we had to evaluate $\Omega 1$, making use of the differential operations in §E.6, as well as Eq. E.10-3. Because of the way in which Λ operates on the surface spherical harmonics, we try a solution of the form

$$\phi_1 = (\boldsymbol{\alpha}(t) : \mathbf{S}_2) \tag{14.5-10}$$

where $\boldsymbol{\alpha}$ is a second-order, symmetric tensor. Note that we could have also included a term $A(t)\mathbf{S}_0$ in the postulated solution. However, it can be shown that the normalization condition, Eq. 14.5-5, requires that the coefficient of $\mathbf{S}_0$ be zero. When the postulated solution is inserted into the differential equation for ϕ_1 we obtain

$$\left(\left\{ 6\lambda \frac{d}{dt} \boldsymbol{\alpha} + 6\boldsymbol{\alpha} - \tfrac{1}{2}\dot{\boldsymbol{\gamma}} \right\} : \mathbf{S}_2 \right) = 0 \tag{14.5-11}$$

In order for this to be satisfied for all θ and ϕ, the coefficient of $\mathbf{S}_2$ must be identically zero. This leads to the following first-order, ordinary differential equation for $\boldsymbol{\alpha}$:

$$\frac{d}{dt} \boldsymbol{\alpha} + \frac{1}{\lambda} \boldsymbol{\alpha} = \frac{1}{12\lambda} \dot{\boldsymbol{\gamma}} \tag{14.5-12}$$

which can be solved to give

$$\boldsymbol{\alpha} = \frac{1}{12\lambda} \int_{-\infty}^{t} e^{-(t-t')/\lambda} \dot{\boldsymbol{\gamma}}' \, dt' \tag{14.5-13}$$

in which $\dot{\gamma}' = \dot{\gamma}(t')$. Substituting these results into the postulated form for ϕ_1 and using Eq. E.10-3 for $\mathbf{S}_2$ gives

$$\phi_1 = \frac{1}{4\lambda}\int_{-\infty}^{t} e^{-(t-t')/\lambda}(\dot{\gamma}' : \boldsymbol{uu})dt' \tag{14.5-14}$$

since tr $\dot{\gamma} = 0$ for an incompressible fluid

Next we proceed to Eq. 14.5-7 for $\phi_2(\boldsymbol{u}, t)$:

$$\begin{aligned} 6\lambda\frac{\partial}{\partial t}\phi_2 &= \Lambda\phi_2 - 3\Omega(\boldsymbol{\alpha} : \boldsymbol{uu}) \\ &= \Lambda\phi_2 - (\dot{\gamma}\boldsymbol{\alpha} : (3\boldsymbol{u\delta u} - \tfrac{15}{2}\,\boldsymbol{uuuu})) \\ &= \Lambda\phi_2 + \tfrac{3}{7}(\{\dot{\gamma}\cdot\boldsymbol{\alpha}\} : \mathbf{S}_2) + \tfrac{1}{14}(\dot{\gamma}\boldsymbol{\alpha} \vdots \mathbf{S}_4) \end{aligned} \tag{14.5-15}$$

In getting the second line we have made use of the tracelessness and symmetry of the $\dot{\gamma}$ tensor; to get the third line we used the expressions for the $\mathbf{S}_k$ given in §E.10. An appropriate postulate for the solution of the ϕ_2 equation is then

$$\phi_2 = (\boldsymbol{\beta}(t) : \mathbf{S}_2) + (\mathbf{B}(t) \vdots \mathbf{S}_4) \tag{14.5-16}$$

When this is put into the differential equation for ϕ_2 in Eq. 14.5-15 and the coefficients multiplying similar surface spherical harmonics equated, we obtain

$$\frac{d}{dt}\boldsymbol{\beta} + \frac{1}{\lambda}\boldsymbol{\beta} = \frac{1}{14\lambda}\{\dot{\gamma}\cdot\boldsymbol{\alpha}\} \tag{14.5-17}$$

$$\frac{d}{dt}\mathbf{B} + \frac{10}{3\lambda}\mathbf{B} = \frac{1}{84\lambda}\dot{\gamma}\boldsymbol{\alpha} \tag{14.5-18}$$

These may be integrated to give

$$\boldsymbol{\beta} = \frac{1}{168\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'} e^{-(t-t'')/\lambda}\{\dot{\gamma}'\cdot\dot{\gamma}''\}dt''dt' \tag{14.5-19}$$

$$\mathbf{B} = \frac{1}{1008\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'} e^{-(7/3)(t-t')/\lambda}e^{-(t-t'')/\lambda}\,\dot{\gamma}'\dot{\gamma}''\,dt''\,dt' \tag{14.5-20}$$

The final expression for ϕ_2 is obtained by putting these expressions into Eq. 14.5-16:

$$\begin{aligned} \phi_2 = \frac{1}{\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'}&\left(-\frac{1}{168}(\dot{\gamma}' : \dot{\gamma}'') + \frac{1}{56}(\{\dot{\gamma}'\cdot\dot{\gamma}''\} : \boldsymbol{uu})\right)e^{-(t-t'')/\lambda}\,dt''\,dt' \\ + \frac{1}{\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'}&\left(+\frac{1}{168}(\dot{\gamma}' : \dot{\gamma}'') - \frac{5}{84}(\{\dot{\gamma}'\cdot\dot{\gamma}''\} : \boldsymbol{uu})\right. \\ &\left. + \frac{5}{48}(\dot{\gamma}' : \boldsymbol{uu})(\dot{\gamma}'' : \boldsymbol{uu})\right)e^{-(7/3)(t-t')/\lambda}e^{-(t-t'')/\lambda}\,dt''\,dt' \end{aligned} \tag{14.5-21}$$

Higher ϕ_k can be found by continuing the process.

Now that the first few terms in the series for $f(\boldsymbol{u}, t)$ have been found, we can substitute f from Eq. 14.5-4 into the Giesekus expression for the stress tensor (Eq. D of Table 14.3-1) and perform the necessary integrations over $\boldsymbol{uu}$, $\boldsymbol{uuuu}$, and so on, to get:

$$\begin{aligned}
\boldsymbol{\tau} &= -\eta_s\dot{\boldsymbol{\gamma}} + 3nkT\lambda\langle\boldsymbol{uu}\rangle_{(1)} \\
&= -\eta_s\dot{\boldsymbol{\gamma}} + 3nkT\lambda\left[\int\frac{1}{4\pi}\sum_{k=0}^{\infty}(6\lambda)^k\phi_k\boldsymbol{uu}\,d\boldsymbol{u}\right]_{(1)} \\
&= -(\eta_s + \tfrac{2}{5}nkT\lambda)\dot{\boldsymbol{\gamma}} - \tfrac{3}{5}nkT\int_{-\infty}^{t}\dot{\boldsymbol{\gamma}}'e^{-(t-t')/\lambda}\,dt' \\
&\quad - \tfrac{6}{35}nkT\lambda\int_{-\infty}^{t}\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}' + \dot{\boldsymbol{\gamma}}'\cdot\dot{\boldsymbol{\gamma}}\}e^{-(t-t')/\lambda}\,dt' \\
&\quad - \tfrac{9}{70}nkT\int_{-\infty}^{t}\int_{-\infty}^{t'}\{\dot{\boldsymbol{\gamma}}'\cdot\dot{\boldsymbol{\gamma}}'' + \dot{\boldsymbol{\gamma}}''\cdot\dot{\boldsymbol{\gamma}}'\}e^{-(t-t'')/\lambda}\,dt''\,dt' - \cdots \qquad (14.5\text{-}22) \\
&\quad + \text{isotropic terms containing integrals of } \dot{\boldsymbol{\gamma}}
\end{aligned}$$

In order to put this expression for $\boldsymbol{\tau}$ in the form of a memory integral expansion, we insert the expansion (from Eq. 9D.1-6 with $\boldsymbol{\omega} = \boldsymbol{0}$):

$$\dot{\boldsymbol{\gamma}}' = \boldsymbol{\gamma}'_{[1]} - \frac{1}{2}\int_{t'}^{t}\{\boldsymbol{\gamma}'_{[1]}\cdot\boldsymbol{\gamma}''_{[1]} + \boldsymbol{\gamma}''_{[1]}\cdot\boldsymbol{\gamma}'_{[1]}\}\,dt'' + \cdots \qquad (14.5\text{-}23)$$

Then if we abbreviate the integrand of this last integral by $\{\ \ \}$, we get[3]:

$$\begin{aligned}
\boldsymbol{\tau} &= -(\eta_s + \tfrac{2}{5}nkT\lambda)\dot{\boldsymbol{\gamma}} - \tfrac{3}{5}nkT\int_{-\infty}^{t}\boldsymbol{\gamma}'_{[1]}e^{-(t-t')/\lambda}\,dt' \\
&\quad + \tfrac{3}{10}nkT\int_{-\infty}^{t}\int_{t'}^{t}\{\ \ \}e^{-(t-t')/\lambda}\,dt''\,dt' \\
&\quad - \tfrac{6}{35}nkT\lambda\int_{-\infty}^{t}\int_{-\infty}^{t}\{\ \ \}2\delta(t-t'')e^{-(t-t')/\lambda}\,dt''\,dt' \\
&\quad - \tfrac{9}{70}nkT\int_{-\infty}^{t}\int_{-\infty}^{t'}\{\ \ \}e^{-(t-t'')/\lambda}\,dt''\,dt' - \cdots \\
&\quad + \text{isotropic terms} \qquad (14.5\text{-}24)
\end{aligned}$$

Next the following operations are performed in order to combine the three double integrals: in the first two integrals interchange t' and t''; then in the first integral change the order of integration so that the inner integral over t'' goes from $-\infty$ to t'; finally change the upper limit of the inner integral in the first and third double integral from t' to t and include in the integrand a factor

$$g(t, t', t'') = \begin{cases} 1 & \text{for } -\infty < t'' \le t' \\ 0 & \text{for } t' < t'' \le t \end{cases} \qquad (14.5\text{-}25)$$

[3] See §E.4 for the definition of the Dirac δ-function.

This then yields a *memory-integral expansion*[4]

$$\boxed{\begin{aligned}\tau = &-\int_{-\infty}^{t} G_1(t-t')\gamma'_{[1]}\,dt' \\ &-\int_{-\infty}^{t}\int_{-\infty}^{t} G_2(t-t', t-t'')\{\gamma'_{[1]}\cdot\gamma''_{[1]} + \gamma''_{[1]}\cdot\gamma'_{[1]}\}dt''\,dt' \\ &-\cdots + \text{isotropic terms}\end{aligned}} \tag{14.5-26}$$

in which

$$\boxed{G_1 = (2\eta_s + \tfrac{4}{5}nkT\lambda)\delta(t-t') + \tfrac{3}{5}nkT\,e^{-(t-t')/\lambda}} \tag{14.5-27}$$

$$\boxed{G_2 = nkT[\tfrac{12}{35}\lambda\delta(t-t') - \tfrac{6}{35}]g(t, t', t'')e^{-(t-t'')/\lambda}} \tag{14.5-28}$$

The third-order contributions to the memory-integral expansion have also been worked out.[1] The function G_1 is the "relaxation modulus" G of linear viscoelasticity (see §5.2), from which all linear viscoelastic material functions can be obtained. Figure 14.5-1 shows how the rigid dumbbell results for $\eta'(\omega) = \int_0^\infty G(s)\cos\omega s\,ds$ and $\eta''(\omega) = \int_0^\infty G(s)\sin\omega s\,ds$ compare with experimental data for tobacco mosaic virus; it can be seen that the predicted shapes of the curves are very nearly correct.

Once the kernel functions $G_1, G_2, \ldots$ are known the retarded-motion expansion (Eq. D.4-3) can be obtained by expanding the kinematic tensor $\gamma_{[1]}$ about $t' = t$ and then designating the resulting integrals over the kernel functions by the constants $b_1, b_2, b_{11}, \ldots$ (see §9.6). When this is done the following constants are obtained:[5]

$$\begin{cases} b_1 = \eta_s + nkT\lambda \\ b_2 = -\tfrac{3}{5}nkT\lambda^2 \\ b_{11} = 0 \end{cases} \qquad \begin{cases} b_3 = \tfrac{3}{5}nkT\lambda^3 \\ b_{12} = \tfrac{12}{35}nkT\lambda^3 \\ b_{1:11} = \tfrac{3}{35}nkT\lambda^3 \end{cases} \tag{14.5-29}$$

Note that $|b_2| > |b_{11}|$ and that $b_3 > b_{12} > b_{1:11}$, the same inequalities having also been found for FENE dumbbells in §13.5. The fourth-order constants have also been obtained for rigid dumbbells.[5] Another way to get the retarded motion expansion constants[6] is to solve Eq. 14.2-8 for a general homogeneous, steady-state flow using the perturbation method of §13.5.

[4] It is also possible to present the rigid-dumbbell results in terms of a "corotational memory-integral expansion" [S. I. Abdel-Khalik, O. Hassager, and R. B. Bird, *J. Chem. Phys.*, **61**, 4312–4316 (1974)]. The first three terms of the corotational expansion represent the rigid dumbbell η, Ψ_1, and $\tilde{\eta}$ curves far better than the first three terms of Eq. 14.5-26.

[5] R. C. Armstrong, Ph.D. Thesis, University of Wisconsin-Madison (1973); see also R. C. Armstrong and R. B. Bird, *op. cit.*

[6] H. Giesekus, *Kolloid-Z.*, **147–149**, 29–45 (1956); *Rheol. Acta*, **3**, 59–71 (1963); S. Prager, *Trans. Soc. Rheol.*, **1**, 53–62 (1957).

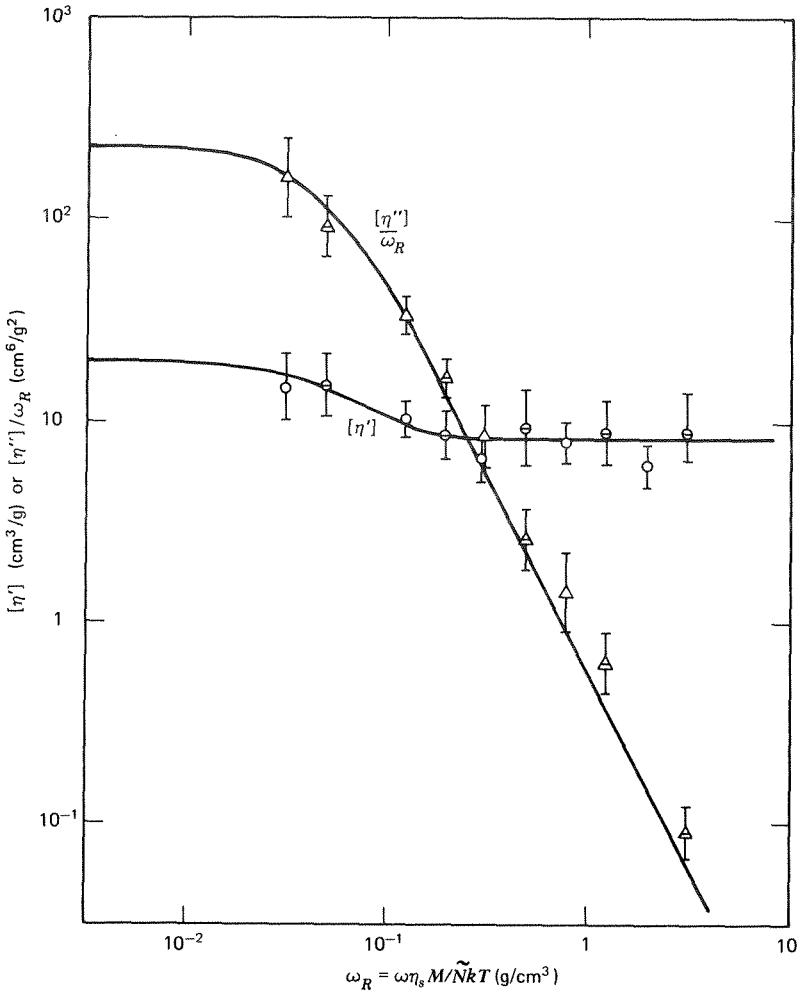


FIGURE 14.5-1. Comparison of the intrinsic complex viscosity predicted by the rigid dumbbell model with experimental data. Both $[\eta']$ (circles) and $[\eta'']/\omega_R$ (triangles) are plotted as functions of reduced frequency $\omega_R = \omega\eta_s M/\tilde{N}kT$. The data are for solutions of tobacco mosaic virus ($M = 3.9 \times 10^7$ g/mol) in a mixture of glycerol and water containing EDTA. Empty symbols represent data taken at 310.0 K; dashed symbols, at 298.2 K. The solvent viscosity at the two temperatures is 3.43×10^{-3} and 5.16×10^{-3} Pa·s, respectively. The rigid dumbbell predictions were computed by using a value $[\eta]_0 = 20$ cm^3/g, which was chosen to provide a best fit with the data. This choice corresponds to choosing λ by Eq. 14.4-23. Furthermore this value for $[\eta]_0$ is of the correct order of magnitude; Nemoto, Schrag, Ferry, and Fulton estimate from literature values that $[\eta]_0 = 27$ cm^3/g. [Data from N. Nemoto, J. L. Schrag, J. D. Ferry, and R. W. Fulton, *Biopolymers*, **14**, 407–417 (1975).]

§14.6 HYDRODYNAMIC INTERACTION[1,2]

Up to this point in the discussion of rigid-dumbbell kinetic theory we have ignored hydrodynamic interaction. We now return to the force balance equations in Eqs. 14.2-1 and 14.2-2 and make a modification in the hydrodynamic force terms to account for the fluid perturbation resulting from the bead motion. After this has been done the diffusion equation and the stress tensor formula are discussed.

a. The Hydrodynamic Interaction Tensor and Stokes' Law

We begin by modifying Eq. 14.2-4 to include the fluid velocity perturbation $\boldsymbol{v}'_\nu$ resulting from bead $-\nu$ (where, as in §14.2, $\nu = +1$ or -1):

$$\boldsymbol{F}^{(h)}_\nu = -\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_\nu - \boldsymbol{v}'_\nu) \tag{14.6-1}$$

where $\boldsymbol{v}'_\nu = -[\boldsymbol{\Omega} \cdot \boldsymbol{F}^{(h)}_{-\nu}]$, in which $\boldsymbol{\Omega}$ is the hydrodynamic interaction tensor (cf. Eq. 13.6-3). We could use the Oseen-Burgers tensor introduced in §13.6, but instead we use the somewhat more general Rotne-Prager-Yamakawa hydrodynamic interaction tensor[3] which for the rigid dumbbell is

$$\boldsymbol{\Omega} = \frac{1}{8\pi\eta_s L}(A\boldsymbol{\delta} + B\boldsymbol{uu}) \tag{14.6-2}$$

where $A = 1 + \frac{1}{6}\xi^2$ and $B = 1 - \frac{1}{2}\xi^2$. The quantity $\xi = d/L$ is the ratio of the bead diameter to the distance between bead centers: when $\xi = 0$ the beads are point masses and Eq. 14.6-2 becomes the Oseen-Burgers tensor, and when $\xi = 1$ the beads are osculating. The Rotne-Prager-Yamakawa tensor accounts approximately for the finite size of the beads and is preferable when many-bead models are used. In fact this improved hydrodynamic interaction tensor was developed because it had been found that for many-bead rods the Oseen-Burgers' tensor led to negative values of the translational diffusivity.[4]

When Eqs. 14.6-1 and 14.6-2 are combined, and when $\boldsymbol{v}_\nu$ is replaced by $\boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_\nu]$, the following expression is obtained for the hydrodynamic force on bead ν:

$$\boldsymbol{F}^{(h)}_\nu = -\boldsymbol{J} - \zeta(\tfrac{1}{2}\nu L[\![\dot{\boldsymbol{u}}]\!] - \tfrac{1}{2}\nu L[\boldsymbol{\kappa} \cdot \boldsymbol{u}]) - h[(A\boldsymbol{\delta} + B\boldsymbol{uu}) \cdot \boldsymbol{F}^{(h)}_{-\nu}] \tag{14.6-3}$$

where $h = \zeta/8\pi\eta_s L$ is the *hydrodynamic interaction parameter* and

$$\boldsymbol{J} = \zeta([\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c]) \tag{14.6-4}$$

[1] R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **14**, 85-101 (1984).

[2] The first work on rigid dumbbells with hydrodynamic interaction was that of H. Giesekus, *Rheol. Acta*, **2**, 50-62 (1962); some of this work was later duplicated by R. B. Bird and H. R. Warner, Jr., *Trans. Soc. Rheol.*, **15**, 741-750 (1971). Much earlier J. G. Kirkwood and P. L. Auer [*J. Chem. Phys.*, **19**, 281-283 (1951)] derived an expression for the complex viscosity for a multibead dumbbell, and T. Kotaka [*J. Chem. Phys.*, **30**, 1566-1567 (1959)] developed the theory for viscosity and normal-stress functions.

[3] J. Rotne and S. Prager, *J. Chem. Phys.*, **50**, 4831-4837 (1969); H. Yamakawa, *J. Chem. Phys.*, **53**, 436-443 (1970).

[4] R. E. DeWames, W. F. Hall, and M. C. Shen, *J. Chem. Phys.*, **46**, 2782-2794 (1967); R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Natl. Acad. Sci.*, **60**, 381-386 (1968).

We now split $\boldsymbol{F}_\nu^{(h)}$ into two vectors, one having only a component in the $\boldsymbol{u}$ direction, and another having components only in the $\boldsymbol{s}$ and $\boldsymbol{t}$ directions:

$$[\boldsymbol{uu}\cdot\boldsymbol{F}_\nu^{(h)}] = -[\boldsymbol{uu}\cdot\boldsymbol{J}] + \tfrac{1}{2}\nu\zeta L[\boldsymbol{\kappa}:\boldsymbol{uuu}] - (A+B)h[\boldsymbol{uu}\cdot\boldsymbol{F}_{-\nu}^{(h)}] \tag{14.6-5}$$

$$[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{F}_\nu^{(h)}] = -[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{J}] - \tfrac{1}{2}\nu\zeta L([\![\dot{\boldsymbol{u}}]\!] - [\boldsymbol{\kappa}\cdot\boldsymbol{u}] + [\boldsymbol{\kappa}:\boldsymbol{uuu}]) - Ah[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{F}_{-\nu}^{(h)}] \tag{14.6-6}$$

If these equations are written for the ith Cartesian component and if each equation is divided by the factor multiplying the "$\frac{1}{2}\nu$" then both equations are found to have the form

$$\phi_\nu + \alpha\phi_{-\nu} + C = \tfrac{1}{2}\nu \qquad (\nu = \pm 1) \tag{14.6-7}$$

where $\alpha = (A+B)h$ in the first equation and $\alpha = Ah$ in the second. Equation 14.6-7 may be solved to give

$$\phi_\nu = \frac{\nu}{2(1-\alpha)} - \frac{C}{1+\alpha} \qquad (\nu = \pm 1) \tag{14.6-8}$$

Consequently Eqs. 14.6-5 and 6 can also be solved:

$$[\boldsymbol{uu}\cdot\boldsymbol{F}_\nu^{(h)}] = \frac{\nu\zeta L[\boldsymbol{\kappa}:\boldsymbol{uuu}]}{2[1-(A+B)h]} - \frac{[\boldsymbol{uu}\cdot\boldsymbol{J}]}{1+(A+B)h} \tag{14.6-9}$$

$$[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{F}_\nu^{(h)}] = \frac{-\nu\zeta L[[\![\dot{\boldsymbol{u}}]\!] - \boldsymbol{\kappa}\cdot\boldsymbol{u} + \boldsymbol{\kappa}:\boldsymbol{uuu}]}{2(1-Ah)} - \frac{[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{J}]}{1+Ah} \tag{14.6-10}$$

These equations are used in lieu of Eq. 14.2-4.

b. The Diffusion Equation for $f(\boldsymbol{u}, t)$

We omit the external force terms in the force balance in Eq. 14.2-1. In this balance the Brownian forces $\boldsymbol{F}_\nu^{(b)}$ are given by Eq. 14.2-3, and the hydrodynamic forces $\boldsymbol{F}_\nu^{(h)}$ can be obtained by adding together Eqs. 14.6-9 and 14.6-10. Then when the sum on ν in Eq. 14.2-1 is performed, we find that $\boldsymbol{J}$ must be zero. Hence from Eq. 14.6-4 we conclude that

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_c] \tag{14.6-11}$$

That is, the center of mass moves, on the average, with the fluid.

Next, from Eqs. 14.2-2, 14.6-9, and 14.6-10 we get, in the absence of external forces

$$[\![\dot{\boldsymbol{u}}]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{u}] - [\boldsymbol{\kappa}:\boldsymbol{uuu}] - \frac{2kT(1-Ah)}{\zeta L^2}\frac{\partial}{\partial\boldsymbol{u}}\ln f \tag{14.6-12}$$

When this is substituted into the equation of continuity for $f(\boldsymbol{u}, t)$ (Eq. 14.2-7) we obtain the *diffusion equation*

$$\boxed{\frac{\partial}{\partial t} f = \frac{1}{6\lambda_2^{(1)}} \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} f \right) - \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] f \right)} \tag{14.6-13}$$

in which $\lambda_2^{(1)}(h, \xi) = (\zeta L^2/12kT)[1 - h(1 + \frac{1}{6}\xi^2)]^{-1}$ is a time constant for the two-bead rod (i.e., rigid dumbbell). This partial differential equation differs from Eq. 14.2-8 only in the definition of the time constant; hence all the solutions to Eq. 14.2-8 given in §14.4 and §14.5 can be taken over at once for rigid dumbbells with hydrodynamic interaction.

c. The Stress Tensor

It is proven later—in Chapter 18—that Eq. C of Table 14.3-1 is the correct expression to use for the stress tensor when hydrodynamic interaction is included. In terms of the $\boldsymbol{u}$ vector this formula becomes

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - \tfrac{1}{2} nL \langle \boldsymbol{u}(\boldsymbol{F}_1^{(h)} - \boldsymbol{F}_{-1}^{(h)}) \rangle \tag{14.6-14}$$

The $\boldsymbol{F}_\nu^{(h)}$ for $\nu = \pm 1$ may be obtained by adding together Eqs. 14.6-9 and 14.6-10, with $\boldsymbol{J} = \boldsymbol{0}$; we also eliminate $[\![\boldsymbol{ii}]\!]$ from the second of these equations by using Eq. 14.6-12. This gives

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - \tfrac{1}{2} nL \left\langle \boldsymbol{u} \left(\frac{\zeta L [\boldsymbol{\kappa} : \boldsymbol{uuu}]}{1 - (A + B)h} + \frac{2kT}{L} \frac{\partial}{\partial \boldsymbol{u}} \ln f \right) \right\rangle \tag{14.6-15}$$

The integral involving $(\partial/\partial \boldsymbol{u}) \ln f$ can be performed (see Eq. 14.3-4) and we get finally

$$\boxed{\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - 6nkT\lambda_2^{(2)} \{\boldsymbol{\kappa} : \langle \boldsymbol{uuuu} \rangle\} - 3nkT \langle \boldsymbol{uu} \rangle + nkT\boldsymbol{\delta}} \tag{14.6-16}$$

where $\lambda_2^{(2)}(h, \xi) = (\zeta L^2/12kT)[1 - 2h(1 - \frac{1}{6}\xi^2)]^{-1}$. This has the same form as Eq. A of Table 14.3-1; only the time constant is different. Note that in the differential equation for $f(\boldsymbol{u}, t)$ the time constant $\lambda_2^{(1)}(h, \xi)$ appears, whereas in the stress tensor it is $\lambda_2^{(2)}(h, \xi)$ that comes in; note further that $\lambda_2^{(2)}(h, \xi)$ may be obtained from $\lambda_2^{(1)}(h, \xi)$ by replacing h by $2h$, and ξ^2 by $-\xi^2$. The stress tensor can also be put in the "Giesekus form":

$$\boxed{\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + 3nkT\lambda_2^{(2)} \langle \boldsymbol{uu} \rangle_{(1)} - \left[1 - \frac{\lambda_2^{(2)}}{\lambda_2^{(1)}} \right] (3nkT \langle \boldsymbol{uu} \rangle - nkT\boldsymbol{\delta})} \tag{14.6-17}$$

which can be compared with Eq. D of Table 14.3-1. When there is no hydrodynamic interaction $\lambda_2^{(1)} = \lambda_2^{(2)} = \lambda = \zeta L^2/12kT$.

SPECIAL NOTE ON EXTENSION TO MULTIBEAD-ROD MODELS
(with hydrodynamic interaction)

To extend Eqs. 14.6-13, 14.6-16, and 14.6-17 to multibead rods with N beads distributed uniformly over a rod of length L with bead centers separated by the distance a (see Fig. 14.1-2), replace $\lambda_2^{(1)}$ by $\lambda_N^{(1)}$, and $\lambda_2^{(2)}$ by $\lambda_N^{(2)}$ where

$$\lambda_N^{(1)}(h, \xi) = \frac{\zeta a^2}{12kT}\left(\sum_{\nu=-(N-1)}^{N-1} \nu\phi_\nu(h, \xi^2, N)\right) \tag{14.6-18a}$$

$$\lambda_N^{(2)}(h, \xi) = \frac{\zeta a^2}{12kT}\left(\sum_{\nu=-(N-1)}^{N-1} \nu\phi_\nu(2h, -\xi^2, N)\right) \tag{14.6-18b}$$

and

$$\phi_\nu(\alpha, \beta, N) + 2\alpha\sum_{\mu}{}' \left(\frac{1}{|\nu-\mu|} + \frac{2}{3}\beta\frac{1}{|\nu-\mu|^3}\right)\phi_\mu(\alpha, \beta, N) = \tfrac{1}{2}\nu \tag{14.6-19}$$

Here $\sum_\mu'$ is a sum from $-(N-1)$ *to* $+(N-1)$, omitting the term $\mu = \nu$, and using even (odd) values of μ if N is odd (even). For multibead dumbbells h is redefined as $h = \zeta/8\pi\eta_s a$. In addition, some sample values of $\lambda_N^{(k)}$ are given in Table 14.6-1. (For detailed discussions of the multibead-rod model, see Examples 16.1-1, 16.2-1, 16.3-1, and 16.4-1.)

EXAMPLE 14.6-1 The Viscometric Functions for Multibead Rods[1]

Obtain the small shear rate expansion of the viscometric functions for a dilute solution of rodlike polymers modeled as multibead rods including hydrodynamic interaction. Find $\Psi_{2,0}/\Psi_{1,0}$ for the model in which the beads are just touching each other.

SOLUTION **(a)** First one has to solve Eq. 14.6-13, with $\lambda_2^{(1)}(h, \xi)$ replaced by $\lambda_N^{(1)}(h, \xi)$, for steady-shear flow. This solution can be immediately taken over from Eqs. 14.4-7, 14.4-11, 14.4-13, and 14.4-14 with λ replaced by $\lambda_N^{(1)}(h, \xi)$. Then we use Eq. 14.6-17 for the stress tensor, appropriately modified for N beads; for steady shear flow this gives for the stress components

$$\tau_{yx} - \tau_{yx,s} = -\tfrac{1}{2}nkT\lambda_N^{(2)}\dot\gamma\langle 2(P_0^0 - P_2^0)c_0 - P_2^2c_2\rangle - \left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right](\tfrac{1}{2}nkT\langle P_2^2 s_2\rangle), \tag{14.6-20}$$

$$\tau_{xx} - \tau_{yy} = -nkT\lambda_N^{(2)}\dot\gamma\langle P_2^2 s_2\rangle - \left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right](nkT\langle P_2^2 c_2\rangle), \tag{14.6-21}$$

$$\tau_{yy} - \tau_{zz} = \left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right](3nkT\langle \tfrac{1}{6}P_2^2 c_2 + P_2^0 c_0\rangle) \tag{14.6-22}$$

When the averaged values are evaluated using the expansion for $f(\boldsymbol{u}, t)$, the following series are obtained for the viscometric functions:

$$\eta - \eta_s = nkT\lambda_N^{(2)}\left\{1 - \frac{18}{35}[\lambda_N^{(2)}\dot\gamma]^2 + \cdots\right\} + \frac{3}{5}nkT\lambda_N^{(1)}\left\{1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right\}\left\{1 - \frac{38}{35}[\lambda_N^{(1)}\dot\gamma]^2\cdots\right\} \tag{14.6-23}$$

$$\Psi_1 = \frac{6}{5} nkT\lambda_N^{(2)}\lambda_N^{(1)}\left\{1 - \frac{38}{35}[\lambda_N^{(1)}\dot{\gamma}]^2 + \cdots\right\}$$
$$+ \frac{6}{5} nkT\lambda_N^{(1)2}\left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right]\left\{1 - \frac{46}{35}[\lambda_N^{(1)}\dot{\gamma}]^2 + \cdots\right\} \quad (14.6\text{-}24)$$

$$\Psi_2 = -\frac{12}{35} nkT\lambda_N^{(1)2}\left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right]\left\{1 - \frac{157}{110}[\lambda_N^{(1)}\dot{\gamma}]^2 + \cdots\right\} \quad (14.6\text{-}25)$$

When hydrodynamic interaction is neglected $h = 0$, and then the time constants become $\lambda_N^{(1)}(h, \xi) = \lambda_N^{(2)}(h, \xi) = \zeta L^2 N(N+1)/72(N-1)kT$, so that Eqs. 14.4-18, 14.4-19, and 14.4-20 are recovered for $N = 2$.

TABLE 14.6-1

Information Required to Obtain $\lambda_N^{(1)}(h, \xi)$ and $\lambda_N^{(2)}(h, \xi)$ for Solutions of Multibead Rods (with Osculating Spheres and Rotne-Prager-Yamakawa Hydrodynamic Interaction)[a]

Number of beads N	$\frac{\lambda_N^{(1)}(\frac{3}{8}, 1)}{(\zeta a^2/6kT)}$	$\frac{\lambda_N^{(2)}(\frac{3}{8}, 1)}{(\zeta a^2/6kT)}$	$1 - \frac{\lambda_N^{(2)}(\frac{3}{8}, 1)}{\lambda_N^{(1)}(\frac{3}{8}, 1)}$
2	0.8889E + 00	0.1333E + 01	−0.50000
3	0.2485E + 01	0.3122E + 01	−0.25810
4	0.5185E + 01	0.5969E + 01	−0.15120
5	0.9121E + 01	0.9842E + 01	−0.07912
6	0.1449E + 02	0.1490E + 02	−0.02842
7	0.2147E + 02	0.2125E + 02	0.01022
8	0.3022E + 02	0.2899E + 02	0.04076
9	0.4091E + 02	0.3822E + 02	0.06570
10	0.5369E + 02	0.4905E + 02	0.08652
11	0.6873E + 02	0.6156E + 02	0.10425
12	0.8617E + 02	0.7587E + 02	0.11956
13	0.1062E + 03	0.9205E + 02	0.13295
14	0.1289E + 03	0.1102E + 03	0.14479
15	0.1544E + 03	0.1304E + 03	0.15535
16	0.1829E + 03	0.1528E + 03	0.16484
17	0.2146E + 03	0.1774E + 03	0.17344
18	0.2495E + 03	0.2043E + 03	0.18136
19	0.2879E + 03	0.2336E + 03	0.18842
20	0.3297E + 03	0.2654E + 03	0.19501
25	0.5970E + 03	0.4648E + 03	0.22148
30	0.9727E + 03	0.7386E + 03	0.24071
35	0.1473E + 04	0.1097E + 04	0.25548
40	0.2113E + 04	0.1548E + 04	0.26737
45	0.2908E + 04	0.2102E + 04	0.27697
50	0.3872E + 04	0.2768E + 04	0.28512
55	0.5021E + 04	0.3554E + 04	0.29210
60	0.6368E + 04	0.4469E + 04	0.29816
65	0.7928E + 04	0.5522E + 04	0.30349
70	0.9714E + 04	0.6720E + 04	0.30823

[a] "E + 04" means "$\times 10^4$."

(b) From Eqs. 14.6-24 and 14.6-25, in the limit as $\dot{\gamma} \to 0$, we get

$$\frac{\Psi_{2,0}}{\Psi_{1,0}} = -\frac{2}{7}\left(1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right) \tag{14.6-26}$$

For the model with osculating dumbbells the bead diameter d is the same as the distance between the bead centers a, so that $\xi = d/a = 1$. The hydrodynamic interaction parameter $h = \zeta/8\pi\eta_s L$ can be estimated by using the Stokes' law expression for ζ, namely $\zeta = 3\pi\eta_s d$; hence $h = \frac{3}{8}$. Values of $\lambda_N^{(1)}(h, \xi)$ and $\lambda_N^{(2)}(h, \xi)$ for $\xi = 1$ and $h = \frac{3}{8}$ are given in Table 14.6-1. It can be seen from the table that

$$\frac{\Psi_{2,0}}{\Psi_{1,0}} > 0 \quad \text{for } N \leq 6; \qquad \frac{\Psi_{2,0}}{\Psi_{1,0}} < 0 \quad \text{for } N \geq 7 \tag{14.6-27}$$

This emphasizes the sensitivity of the second normal stress difference to details of structure. We know of no experimental data on rigid rodlike molecules that corroborate these theoretical results.

EXAMPLE 14.6-2 Steady Shear Flow Properties of Rigid Dumbbell Suspensions at Arbitrary Shear Rates[5] (Numerical Calculation)

Determine the viscometric functions for a dilute suspension of rigid dumbbells, including complete hydrodynamic interaction, for arbitrarily large shear rates. The velocity field is $v_x = \dot{\gamma}y$, $v_y = v_z = 0$. Use Oseen-Burgers hydrodynamic interaction.

SOLUTION The differential equation for $f(\boldsymbol{u})$ is the same as Eq. 14.4-1 except that λ is replaced with $\lambda_2^{(1)}(h, 0) = \lambda/(1 - h) \equiv \lambda_h$

$$\Lambda f = (6\lambda_h\dot{\gamma})\Omega_s f \tag{14.6-28}$$

The distribution function f is normalized to unity. As in Example 14.4-1 we solve Eq. 14.6-28 by expanding f in terms of the spherical harmonics. Here we do not use these functions as coefficients in a power series expansion in shear rate, as before. Instead we use all spherical harmonics of the first $M + 1$ kinds to construct an Mth order approximation to f, denoted by $f^{(M)}$, for any shear rate:

$$f^{(M)} = \sum_{n=0}^{M}\sum_{m=0}^{n}(A_n^m P_n^m c_m + B_n^m P_n^m s_m) \tag{14.6-29}$$

The coefficients A_n^m and B_n^m are functions of the dimensionless shear rate $\lambda_h\dot{\gamma}$ and are to be determined for each approximation $f^{(M)}$ so as to make it close to the actual f in some sense. The quantity multiplying B_n^0 is zero and, hence, these coefficients do not actually enter. However, for convenience we write the sum on m from 0 to n.

To find the coefficients at the Mth level of approximation, we insert Eq. 14.6-29 into Eq. 14.6-28 and use the relations for the Λ and Ω_s operators presented in §14.4:

$$\sum_{n=0}^{M}\sum_{m=0}^{n} n(n+1)(A_n^m P_n^m c_m + B_n^m P_n^m s_m) - (6\lambda_h\dot{\gamma})\sum_{n=0}^{M}\sum_{m=0}^{n}\sum_{j=m-2}^{m+2}\sum_{k=n-2}^{n+2} a_{nk}^{mj}(A_n^m P_k^j s_j - B_n^m P_k^j c_j) \equiv F^{(M)} \tag{14.6-30}$$

The residual function $F^{(M)}$ then tells how nearly the trial function satisfies the differential equation. If we had guessed the correct solution, $F^{(M)}$ would be zero. The coefficients are now determined by

[5] This example is patterned after W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1-13 (1972).

applying Galerkin's method.[6] This method requires that when $F^{(M)}$ is multiplied by a function of θ and ϕ and integrated over all possible orientations, the result is zero; in other words a weighted mean value of $F^{(M)}$ is forced to be zero. Since we have $(M + 1)(M + 2)$ coefficients to evaluate, we use the $(M + 1)(M + 2)$ linearly independent spherical harmonics in $f^{(M)}$ as weighting functions. Because the spherical harmonics form a complete set of functions, these integral requirements will force $f^{(M)}$ to satisfy Eq. 14.6-28 as M approaches infinity. Equivalently, we set $F^{(M)}$ orthogonal to each of the $(M + 1)(M + 2)$ spherical harmonics:

$$\int_0^{2\pi}\int_0^{\pi} F^{(M)} P_q^p \begin{Bmatrix} s_p \\ c_p \end{Bmatrix} S \, d\theta \, d\phi = 0 \qquad \begin{matrix} (p = 0, 1, \ldots, q) \\ (q = 0, 1, \ldots, M) \end{matrix} \tag{14.6-31}$$

where the integral must be zero for both s_p and c_p. It is in the above sense that we require $f^{(M)}$ to be close to f. Insertion of Eq. 14.6-30 for $F^{(M)}$ into Eq. 14.6-31 and application of the orthogonality condition Eq. E.8-7 gives

$$\begin{aligned} q(q+1)A_q^p + (6\lambda_h\dot{\gamma}) \sum_{n=0}^{M} \sum_{m=0}^{n} a_{nq}^{mp} B_n^m = 0, \\ q(q+1)B_q^p - (6\lambda_h\dot{\gamma}) \sum_{n=0}^{M} \sum_{m=0}^{n} a_{nq}^{mp} A_n^m = 0, \end{aligned} \qquad \begin{matrix} (p = 0, 1, \ldots, q) \\ (q = 0, 1, \ldots, M) \end{matrix} \tag{14.6-32}$$

No information is obtained from the above equations for $q = 0$, because they are then identically satisfied. These two equations should give information about A_0^0 and B_0^0. The lost condition on A_0^0 can be replaced by a relation obtained from substituting $f^{(M)}$ into the normalization condition:

$$A_0^0 = 1 \tag{14.6-33}$$

The lost condition on B_0^0 does not need to be replaced, since none of the coefficients B_n^0 are required.

Symmetry requirements can be used to simplify the problem further. The problem description is unchanged by reflections through the xy-plane. Hence the distribution function must be unchanged by replacement of θ with $\pi - \theta$. This means that all A_n^m and B_n^m are zero if n is odd. In addition, a combined rotation through $\phi = 180°$ plus a reflection through the xy-plane is equivalent to a single rotation through $\phi = 360°$. Thus A_n^m and B_n^m must also be zero if m is odd. The problem is thus to determine the remaining $(\frac{1}{2}M + 1)^2$ coefficients from the same number of conditions contained in Eqs. 14.6-32 and 14.6-33.

As an example, we show how to find the coefficients that go with $f^{(2)}$. For $M = 2$, the unknowns are A_0^0, A_2^0, A_2^2, and B_2^2, and from Eqs. 14.6-32 and 14.6-33 they must be solutions to

$$\begin{gathered} A_0^0 = 1; \quad 6A_2^0 + (\tfrac{36}{7})(\lambda_h\dot{\gamma})B_2^2 = 0; \quad -6A_2^2 + (6\lambda_h\dot{\gamma})B_2^2 = 0; \\ 3\lambda_h\dot{\gamma}A_0^0 - \tfrac{3}{7}\lambda_h\dot{\gamma}A_2^0 - 6\lambda_h\dot{\gamma}A_2^2 - 6B_2^2 = 0 \end{gathered} \tag{14.6-34}$$

From this system of equations it is easy to show that

$$f^{(2)} = 1 - \frac{21(\lambda_h\dot{\gamma})P_2^0}{[49 + 46(\lambda_h\dot{\gamma})^2]} + \frac{49(\lambda_h\dot{\gamma})((\lambda_h\dot{\gamma})P_2^2 c_2 + P_2^2 s_2)}{2[49 + 46(\lambda_h\dot{\gamma})^2]} \tag{14.6-35}$$

Once the distribution function has been found, the stresses may be calculated from Eq. 14.6-20, 14.6-21, and 14.6-22. If $f^{(M)}$ is used to compute the ensemble averages in those relations, we

[6] F. B. Hildebrand, *Methods of Applied Mathematics*, Prentice-Hall, Englewood Cliffs, NJ (1965), 2nd ed., p. 286.

can express the viscometric functions in terms of the coefficients of the spherical harmonics. Insertion of Eq. 14.6-29 into Eqs. 14.6-20, 14.6-21, and 14.6-22 gives for $M \geq 2$:

$$\frac{\eta - \eta_s}{nkT\lambda_h} = \left(\frac{1-h}{1-2h}\right)[1 - \tfrac{1}{5}A_2^0 - \tfrac{6}{5}A_2^2] - \frac{6}{5\lambda_h\dot{\gamma}}\frac{h}{(1-2h)}B_2^2 \tag{14.6-36}$$

$$\frac{\Psi_1}{nkT\lambda_h^2} = \frac{12}{5\lambda_h\dot{\gamma}}\left(\frac{1-h}{1-2h}\right)B_2^2 - \frac{12}{5(\lambda_h\dot{\gamma})^2}\frac{h}{(1-2h)}A_2^2 \tag{14.6-37}$$

$$\frac{\Psi_2}{nkT\lambda_h^2} = \frac{3}{5(\lambda_h\dot{\gamma})^2}\frac{h}{(1-2h)}(A_2^0 + 2A_2^2) \tag{14.6-38}$$

Numerical values for these material functions can be obtained over a wide range of dimensionless shear rates. At any given value of $\lambda_h\dot{\gamma}$, the coefficients in $f^{(M)}$ are determined for successively larger values of M until the stress components converge to four digits. Convergence occurs for $M \leq 22$ provided that $\lambda_h\dot{\gamma} \leq 20$. For $\lambda_h\dot{\gamma} \geq 30$, M is always taken to be 22. Figure 14.6-1 shows the viscometric functions found in this way for the maximum and minimum value of the hydrodynamic interaction parameter h. At high shear rates a power-law region is clearly discernable for all three functions. The power-law asymptotes for $\lambda_h\dot{\gamma} \to \infty$ are given by

$$\frac{\eta - \eta_s}{nkT\lambda_h} \doteq 0.678\left(\frac{1-h}{1-2h}\right)(\lambda_h\dot{\gamma})^{-1/3} \tag{14.6-39}$$

$$\frac{\Psi_1}{nkT\lambda_h^2} \doteq 1.20\left(\frac{1-h}{1-2h}\right)(\lambda_h\dot{\gamma})^{-4/3} \tag{14.6-40}$$

$$\frac{\Psi_2}{nkT\lambda_h^2} \doteq 0.93\left(\frac{h}{1-2h}\right)(\lambda_h\dot{\gamma})^{-7/3} \tag{14.6-41}$$

Note that the effect of hydrodynamic interaction on the steady-shear flow properties is dramatic only for Ψ_2. As found in the perturbation calculation, Ψ_2 is positive when hydrodynamic interaction is included.

Now that the distribution function has been determined, it is of interest to see how the orientations of the dumbbells are affected by the shear flow. In Fig. 14.6-2 we show f for several values of the reduced shear rate. Note that as the shear rate is increased the dumbbells spend a greater fraction of their time nearer to the xz-plane. Most of the dumbbells are found to point just above the x-axis; once a dumbbell has been kicked below the x-axis by Brownian fluctuations, it quickly rotates toward the preferred orientation because of the hydrodynamic forces.

EXAMPLE 14.6-3 Translational Diffusivity of Rigid Dumbbells in Dilute Solution[7]

Obtain an expression for D_{tr} for rigid dumbbell solutions using Rotne-Prager-Yamakawa hydrodynamic interaction.

SOLUTION Start with Eq. 14.2-1—the force balance on the center of mass—and use Eq. 14.2-3 for $\boldsymbol{F}_v^{(b)}$ and Eqs. 14.6-9 and 14.6-10 for $\boldsymbol{F}_v^{(h)}$. This leads directly to

$$\frac{[\boldsymbol{uu}\cdot\boldsymbol{J}]}{1 + (A+B)h} + \frac{[(\boldsymbol{\delta} - \boldsymbol{uu})\cdot\boldsymbol{J}]}{1 + Ah} = \tfrac{1}{2}[\boldsymbol{F}_1^{(e)} + \boldsymbol{F}_{-1}^{(e)}] \tag{14.6-42}$$

[7] For multibead rods with hydrodynamic interaction D_{tr} has been obtained by J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 512–516 (1950); see also H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 280.

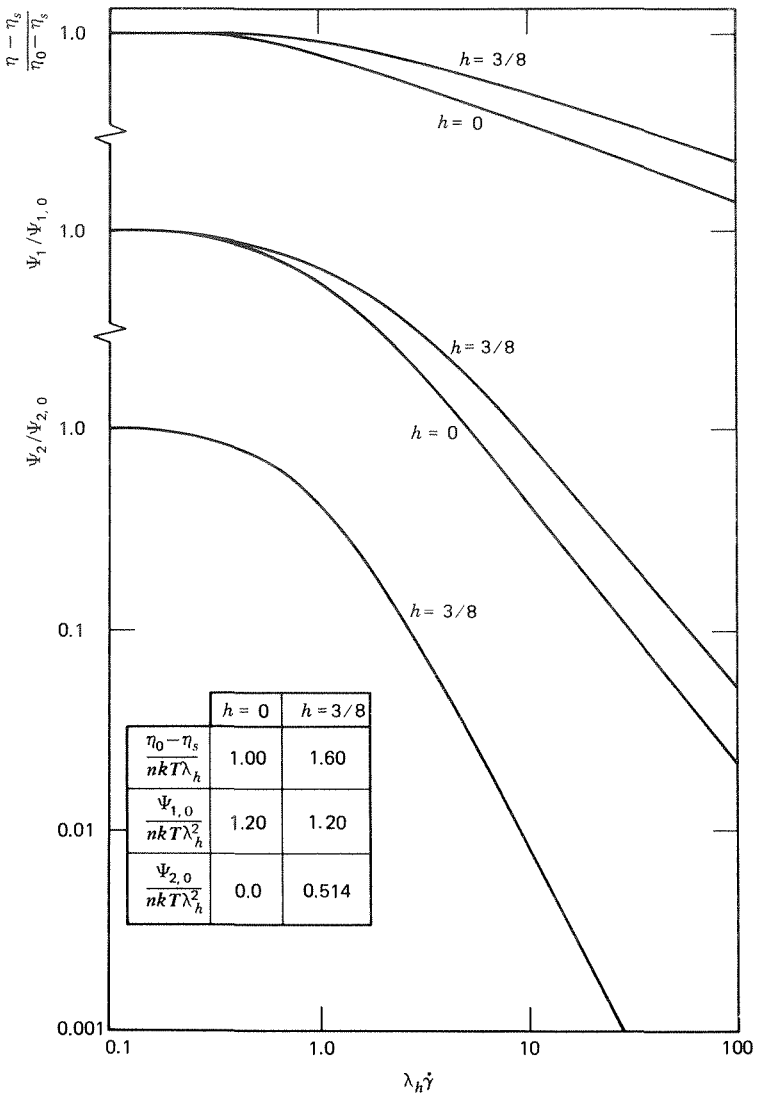


FIGURE 14.6-1. Viscometric functions for a dilute suspension of rigid dumbbells with complete hydrodynamic interaction. The quantity h is a hydrodynamic interaction parameter: $h = 0$ represents no hydrodynamic interaction, and $h = 3/8$ represents maximum hydrodynamic interaction. It is interesting to note that the η-curve approaches its asymptote from above, crossing it at $\lambda_h\dot{\gamma} = 0.3$, and is 13% higher than its asymptote at $\lambda_h\dot{\gamma} = 1$ (for the $h = 0$ curve). The normal-stress-coefficient curves approach their asymptotes from below. [W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1–13 (1972)].

If the external force acting on both beads is the same, so that $\boldsymbol{F}_1^{(e)} = \boldsymbol{F}_{-1}^{(e)} = \boldsymbol{F}^{(e)}$, then the solution of Eq. 14.6-42 for $\boldsymbol{J}$ is

$$\boldsymbol{J} = [1 + (A + B)h][\boldsymbol{uu}\cdot\boldsymbol{F}^{(e)}] + (1 + Ah)[(\boldsymbol{\delta} - \boldsymbol{uu})\cdot\boldsymbol{F}^{(e)}] \tag{14.6-43}$$

According to Eq. 14.6-4, for a system at rest $\boldsymbol{J} = \zeta[\![\dot{\boldsymbol{r}}_c]\!]$. When Eq. 14.6-43 is multiplied by $(1/\zeta)f_{eq}$ and integrated over all $\boldsymbol{u}$ we get $\langle\dot{\boldsymbol{r}}_c\rangle_{eq}$, which is the average velocity of the center of mass that results from

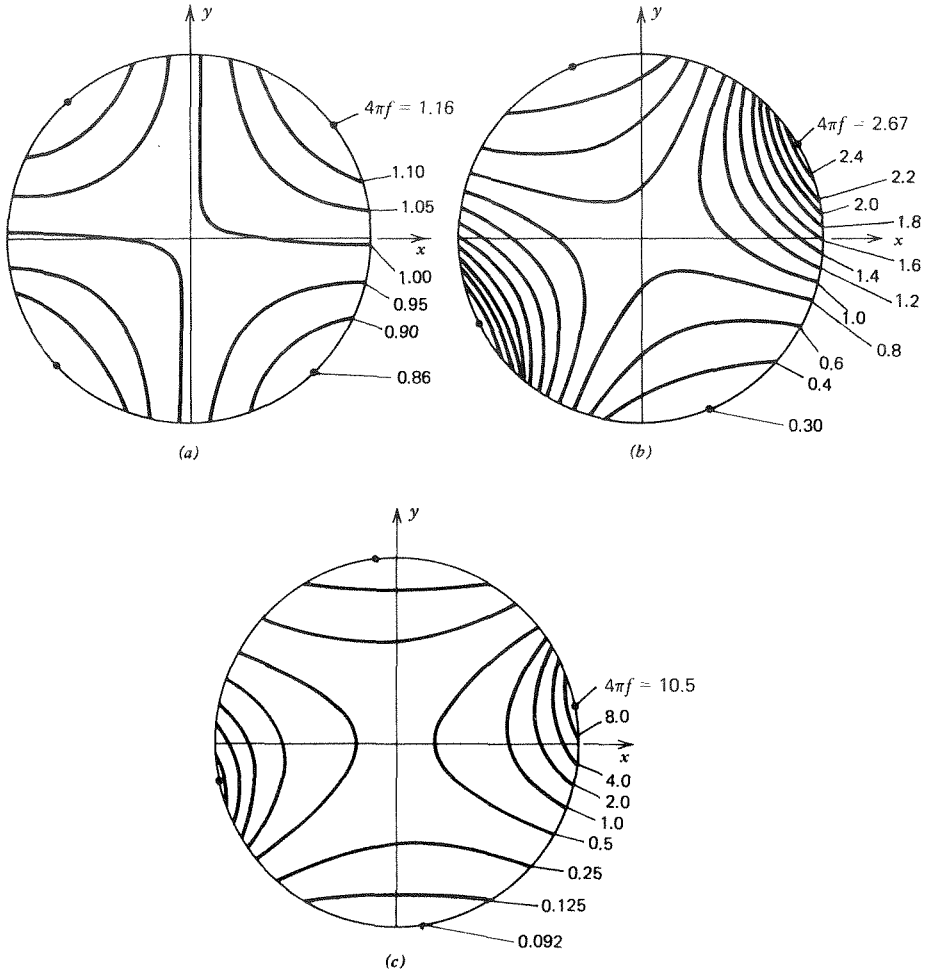


FIGURE 14.6-2. The distribution function f (multiplied by 4π) for a rigid dumbbell suspension undergoing steady shear flow. Contours of constant f are plotted on a unit sphere, and the resulting diagram projected onto the xy-plane (the unit sphere is viewed along the z-axis from infinity). Plots are shown for three different shear shear rates: (*a*) $\lambda_h\dot{\gamma} = 0.1$, (*b*) $\lambda_h\dot{\gamma} = 1.0$, and (*c*) $\lambda_h\dot{\gamma} = 10.0$. Notice that the peak in f at $\phi = 90°$ and $\theta \doteq$ (*a*) 40°, (*b*) 27°, and (*c*) 13° approaches the x-axis as $\lambda_h\dot{\gamma}$ increases. If there were no flow ($\lambda_h\dot{\gamma} = 0$), then f would be $1/4\pi$ everywhere on the surface of the unit sphere. [W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1-13 (1972)].

an applied external force. The result is

$$\langle \dot{\boldsymbol{r}}_c \rangle_{\text{eq}} = \frac{1}{\zeta}[1 + (A + \tfrac{1}{3}B)h]\boldsymbol{F}^{(e)} \tag{14.6-44}$$

But the friction coefficient Z for the dumbbell is defined by $2\boldsymbol{F}^{(e)} = Z\langle \dot{\boldsymbol{r}}_c \rangle$ (Eq. 13.6-19) and the translational diffusivity is related to Z by $D_{\text{tr}} = kT/Z$ (Eq. 13.6-15), so that for Rotne-Prager-Yamakawa hydrodynamic interaction

$$D_{\text{tr}} = \frac{kT}{2\zeta}[1 + (A + \tfrac{1}{3}B)h] = \frac{kT}{2\zeta}(1 + \tfrac{4}{3}h) \tag{14.6-45}$$

In obtaining this result we have used the equilibrium value of $\langle \dot{\boldsymbol{r}}_c \rangle$ since the fluid as a whole is very nearly in a state of rest. We have also used the values of A and B given just below Eq. 14.6-2. For Oseen–Burgers hydrodynamic interaction ($A = B = 1$) the same result is obtained; for no hydrodynamic interaction D_{tr} is just $kT/2\zeta$.

PROBLEMS

14A.1 Viscosity of a Tobacco Mosaic Virus Solution

For the tobacco mosaic virus solution shown in Fig. 14.4-1, the zero-shear-rate intrinsic viscosity is $[\eta]_0 = 28\ \text{cm}^3/\text{g}$. Compute the viscosity of a $5.1 \times 10^{-4}\ \text{g/cm}^3$ aqueous solution of tobacco mosaic virus at a temperature of 300 K and at a shear rate $\dot{\gamma} = 0.15\ \text{s}^{-1}$. Compare the size of the macromolecule contribution to τ_{yx} to the magnitude of the solvent contribution.

14A.2 Distribution Function for Steady Shear Flow

a. A dilute suspension of rodlike macromolecules is undergoing steady shear flow. Using the perturbation solution for the distribution function given in Eqs. 14.4-7, 14.4-11, and 14.4-13, construct a plot showing contours of constant f for a dimensionless shear rate $\lambda\dot{\gamma} = 0.1$. The graph should be patterned after Fig. 14.6-2. Compare the plot from the perturbation solution to that based on the exact numerical solution, Fig. 14.6-2*a*. How well does the perturbation expansion describe the dumbbell suspension at these low shear rates?

b. Next use the terms through ϕ_3 in the perturbation solution to locate a few points on Fig. 14.6-2*b* for which $f = 1.4$ and $\lambda\dot{\gamma} = 1.0$. How well does the expansion do at the higher shear rate?

14A.3 Elongational Viscosity of a Poly-γ-benzyl-L-glutamate Solution

It is desired to estimate the behavior of the solution of poly-γ-benzyl-L-glutamate in *m*-cresol shown in Fig. 14.4-2 in an elongational flow. Pertinent data for the solution are $[\eta]_0 = 2.90\ \text{dL/g}$; $T = 293\ K$; $\bar{M}_w = 208{,}000$; $c = 0.51\ \text{g/dL}$.

a. What is the zero-elongation-rate elongational viscosity for this solution?

b. What is the slope of the $\bar{\eta}$ versus $\dot{\varepsilon}$ curve at $\dot{\varepsilon} = 0$?

c. What is the maximum value of $\bar{\eta}$ at large elongation rates (see Problem 14B.3)?

d. At a reduced elongation rate $\lambda\dot{\varepsilon} = \frac{1}{2}$, what is the value of $\bar{\eta}$? Compare this result with the prediction of the Hookean dumbbell.

14B.1 Stress Tensor for Steady, Homogeneous Potential Flow

Show that for rigid dumbbells in a fluid undergoing steady, homogeneous potential flow

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - 3nkT\lambda \frac{\int_0^{2\pi}\int_0^{\pi} \{\boldsymbol{\kappa}\cdot\boldsymbol{uu} + \boldsymbol{uu}\cdot\boldsymbol{\kappa}\} \exp(3\lambda\boldsymbol{\kappa}:\boldsymbol{uu}) \sin\theta\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\pi} \exp(3\lambda\boldsymbol{\kappa}:\boldsymbol{uu}) \sin\theta\, d\theta\, d\phi} \tag{14B.1-1}$$

What is the corresponding result for elastic dumbbells?

14B.2 Obtaining Rigid Dumbbell Results from an Elastic Dumbbell Model

Show that the stress tensor for rigid dumbbell suspensions undergoing steady, homogeneous irrotational flow (Eq. 14B.1-1) may be obtained from the corresponding result for Fraenkel dumbbells by taking the limit as $H \to \infty$. (HINT: see Eq. E.4-1.) What is the physical significance of this limiting process? Although this procedure works for dumbbell models it does not for three-bead, two-spring (rod) systems. (See §16.5.)

14B.3 Elongational Viscosity by Viscous Dissipation Arguments[1]

The limiting value of the elongational viscosity for a rigid dumbbell suspension at high elongation rates may be evaluated using a simple viscous dissipation argument. This is possible because in the limit as $\dot{\varepsilon} \to \infty$, all of the dumbbells will have a fixed orientation parallel to the z-axis (see Fig. 14B.3).

a. By computing the rate at which a bead does work on the solvent moving past it, show that the rate of viscous dissipation due to the presence of the dumbbells is $\frac{1}{2}n\zeta L^2\dot{\varepsilon}^2$, if there are n dumbbells per unit volume.

b. Next show that the rate of energy dissipation in the solvent flow field is $3\eta_s\dot{\varepsilon}^2$. In doing this it is assumed that the solvent flow field is not disturbed by the presence of the dumbbells.

c. Use Eq. 9.6-21 to obtain the rate of viscous dissipation in a viscoelastic continuum undergoing an elongational flow in terms of the components of the solution stress tensor and the velocity gradient tensor; then use Eq. D.5-14 to rewrite this result in terms of the elongational viscosity $\bar{\eta}$ and the elongation rate $\dot{\varepsilon}$. Equate this result to the sum of the dissipation rates in (a) and (b) and show that

$$\bar{\eta}(\infty) = 3\eta_s + 6nkT\lambda \tag{14B.3-1}$$

d. Show that Eq. 14B.3-1 is in agreement with $\bar{\eta}(\infty)$ found from Eq. 14.4-32.

14B.4 Oldroyd Model and Rigid Dumbbell Solution

a. Insert the expressions in Eq. 14.5-29 for the b's into the corresponding expression for the six-constant Oldroyd model given in Table 6.2-2. Show that the Oldroyd model constants are given in terms of the rigid-dumbbell kinetic theory parameters by:

$$\eta_0 = \eta_s + nkT\lambda \tag{14B.4-1}$$

$$\lambda_1 = \lambda \tag{14B.4-2}$$

$$\lambda_2 = \lambda\left(1 - \frac{3}{5}\frac{nkT\lambda}{\eta_s + nkT\lambda}\right) \tag{14B.4-3}$$

$$\lambda_3 = \tfrac{8}{7}\lambda \tag{14B.4-4}$$

$$\lambda_4 = \tfrac{8}{7}\lambda \tag{14B.4-5}$$

$$\lambda_5 = -\tfrac{2}{7}\lambda \tag{14B.4-6}$$

b. Show that when the above constants are substituted into Eq. A of Table 7.3-3 we get

$$\frac{\eta - \eta_s}{nkT\lambda} = \frac{1 + (124/245)(\lambda\dot{\gamma})^2}{1 + (50/49)(\lambda\dot{\gamma})^2} \tag{14B.4-7}$$

How does this compare with the exact numerical calculations of Stewart and Sørensen (§14.6)?

c. Compare Eq. 14B.4-7 with Eq. 14.4-18. [NOTE: The six-constant Oldroyd model with the constants given in (a) describes the steady shear flow properties through the third order in $\lambda\dot{\gamma}$ exactly

[1] R. I. Tanner and W. Stehrenberger, *J. Chem. Phys.*, **55**, 1958-1964 (1971).

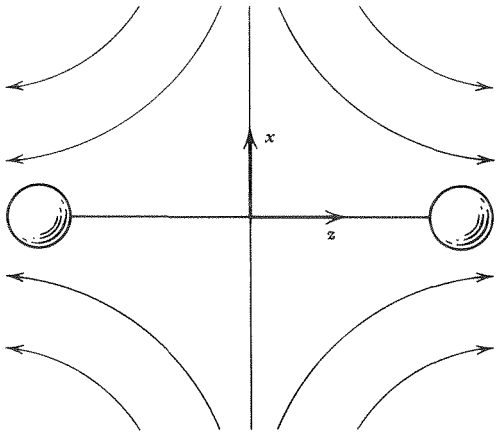


FIGURE 14B.3. Orientation of a dumbbell in an elongational flow as $\dot{\varepsilon} \to \infty$.

and almost all transient phenomena through the second order; in order to get a complete second-order description it is necessary to include additional nonlinear terms[2] in Eq. 7.3-2].

d. Use the six-constant Oldroyd model parameters determined above together with Eq. F of Table 7.3-3 to show that

$$\frac{\bar{\eta} - 3\eta_s}{3nkT\lambda} = \frac{1 + (26/35)\lambda\dot{\varepsilon} + (104/245)(\lambda\dot{\varepsilon})^2}{1 + (1/7)\lambda\dot{\varepsilon} + (4/49)(\lambda\dot{\varepsilon})^2} \tag{14B.4-8}$$

Compare this result with the exact solution for $\bar{\eta}$ with regard to predictions at both low and high elongation rates.

14B.5 Stress Relaxation after Cessation of Steady Shear Flow[3]

A dilute solution of rigid dumbbells undergoes a steady shear flow, $v_x = \dot{\gamma}_0 y$, $v_y = v_z = 0$, for $t < 0$. Then at time $t = 0$, the flow is suddenly stopped. We wish to use the formalism of §14.4 to develop expressions for the decaying shear and normal stresses after the fluid is brought to rest.

a. For $t < 0$, we denote the flow contribution to the distribution function by $f(t < 0) \equiv f^< (\theta, \phi)$. What is $f^<$ for this problem?

b. Likewise, $f(t \geq 0) \equiv f^> (\theta, \phi, t)$. Show that the differential equation for $f^>$ is

$$6\lambda \frac{\partial f^>}{\partial t} = \Lambda f^> \tag{14B.5-1}$$

What are the initial and final conditions that $f^>$ must satisfy?

[2] This has been attempted by R. B. Bird, *Zeits. für angew. Math. u. Phys.*, **23**, 157–159 (1972), but the resulting viscosity equation is less realistic than Eq. 14B.4-7 [see note added in proof in S. I. Abdel-Khalik, O. Hassager, and R. B. Bird, *J. Chem. Phys.*, **61**, 4312–4316 (1974)].

[3] This flow was first analyzed by H. Giesekus, *Rheol. Acta*, **1**, 2–20 (1958). Many other time dependent flow problems are discussed by R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971); the coefficient 4/7 in Eq. 14B.5-4 is given incorrectly as 15/14 in this review.

c. Verify that the solution to Eq. 14B.5-1 is

$$f^{>}(0, \phi, t) = \sum_{n=0}^{\infty} \sum_{m=0}^{n} P_n^m (A_{mn} c_m + B_{mn} s_m) e^{-n(n+1)t/6\lambda} \tag{14B.5-2}$$

where the A_{mn} and B_{mn} are constants that may depend on the shear rate.

d. Apply the initial condition to show that up through third-order terms $f^{>}$ is given by

$$\begin{aligned} 4\pi f^{>}(0, \phi, t) = 1 &+ (6\lambda\dot{\gamma}_0)\left[\frac{1}{12} P_2^2 s_2 e^{-t/\lambda}\right] + (6\lambda\dot{\gamma}_0)^2\left[\left(-\frac{1}{84} P_2^0 + \frac{1}{72} P_2^2 c_2\right)e^{-t/\lambda}\right. \\ &\left. + \left(\frac{1}{280} P_4^0 - \frac{1}{6720} P_4^4 c_4\right)e^{-10t/3\lambda}\right] + (6\lambda\dot{\gamma}_0)^3\left[\left(-\frac{19}{7560} P_2^2 e^{-t/\lambda} - \frac{1}{18480} P_4^2 e^{-10t/3\lambda}\right.\right. \\ &\left.\left. + \frac{1}{221760} P_6^2 e^{-7t/\lambda}\right)s_2 + \frac{1}{25200} P_4^4 s_4 e^{-10t/3\lambda} - \frac{1}{15966720} P_6^6 s_6 e^{-7t/\lambda}\right] + \cdots \end{aligned} \tag{14B.5-3}$$

e. Finally use $f^{>}$ to determine the following time-dependent stress components (actually, with $f^{>}$ known through terms of order $(\lambda\dot{\gamma}_0)^3$, the terms of order $(\lambda\dot{\gamma}_0)^2$ in Ψ_1^- and Ψ_2^- cannot be obtained):

$$\frac{\eta^-}{\eta(\dot{\gamma}_0) - \eta_s} = \frac{3}{5}\left[1 - \frac{4}{7}(\lambda\dot{\gamma}_0)^2 + \cdots\right]e^{-t/\lambda} \tag{14B.5-4}$$

$$\frac{\Psi_1^-}{\Psi_1(\dot{\gamma}_0)} = \left[1 - \frac{8}{35}(\lambda\dot{\gamma}_0)^2 + \cdots\right]e^{-t/\lambda} \tag{14B.5-5}$$

$$\Psi_2^- = -\frac{12}{35} nkT\lambda^2\left[1 - \frac{157}{110}(\lambda\dot{\gamma}_0)^2 + \cdots\right]e^{-t/\lambda} \tag{14B.5-6}$$

where the functions η^-, Ψ_1^-, and Ψ_2^- are defined in Eqs. D.5-11, D.5-12, and D.5-13, and $\eta(\dot{\gamma}_0)$ and $\Psi_1(\dot{\gamma}_0)$ are the steady shear flow values of η and Ψ_1 for a shear rate $\dot{\gamma}_0$. Comment on the qualitative shapes of these functions.

f. Verify that the rigid dumbbell results above satisfy

$$(\tau_{xx} - \tau_{yy})^{<} = 2\dot{\gamma}_0 \int_0^{\infty} \tau_{yx}^{>} dt \tag{14B.5-7}$$

See Problem 14C.1 for a derivation of this equation.

14B.6 Vortex Inhibition[4]

In this problem we wish to investigate the effect of dilute polymer solutions in vortex inhibition (see §2.5(g)). The following procedure is suggested:

a. The flow in the draining tank is assumed to be

$$\boldsymbol{v} = -\frac{\dot{\varepsilon}}{2} r\boldsymbol{\delta}_r + \frac{\Omega}{r}\boldsymbol{\delta}_\theta + \dot{\varepsilon} z\boldsymbol{\delta}_z \tag{14B.6-1}$$

[4] R. C. Armstrong, Ph.D. Thesis, University of Wisconsin, Madison (1973). A more detailed description of the vortex flow, including numerical simulations and measurements of velocity fields, is given by S. Ishikawa, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge (1979). Also given here are numerical computations of stretching of nonlinear elastic dumbbells (cf. Eq. 13.5-56c) in the bottom boundary layer region of the vortex flow.

when referred to cylindrical coordinates. The coordinate system is chosen so that the z-axis coincides with the centerline of the tank, the positive direction being in the direction of the exiting fluid. For our purposes we can assume that the free surface is at $z = 0$ and that the level in the tank remains constant. This velocity seems reasonable for small values of r, the region of interest in vortex inhibition. Show that the assumed profile satisfies the continuity equation.

b. Assuming that the dilute polymer solution is adequately described by the second-order fluid model Eq. D.4-3, determine the normal stress differences $(\tau_{rr} - \tau_{zz})$ and $(\tau_{\theta\theta} - \tau_{rr})$ for the postulated flow in terms of the expansion coefficients b_1, b_2, and b_{11}.

c. Using the b's for rigid dumbbells, find the normal stresses.

d. In order to see the effects of these stresses in inhibiting vortex formation, use the radial component of the equation of motion together with the answer in **(c)** to find the pressure distribution over the fluid required to keep a level surface.

$$\text{Answer:} \quad p = -\frac{2b_2\Omega^2}{r^4} + \text{constant} \qquad \text{(for small } r\text{)}$$

The result **(d)** says that in order to maintain a flat fluid surface, which we assumed we would have, the pressure over the solution must be unbounded at $r = 0$ and decrease as r^{-4} near the center. In an actual experiment, of course, the pressure above the fluid is simply atmospheric pressure. If we remove the required pressure distribution, we would expect the liquid to "bulge out" at $r = 0$ rather than "dip in" as occurs in the vortex.

14B.7 Steady Elongational Viscosity for Multibead Dumbbells with Hydrodynamic Interaction

Show that Eq. 14.4-32 can be modified for multibead dumbbells as follows:

$$\frac{\bar{\eta} - 3\eta_s}{3nkT\lambda_N^{(2)}} = \left[\frac{1}{2} \mp \frac{3}{4X} \pm \frac{3}{4}\frac{\exp(\pm X)}{\sqrt{X}\int_0^{\sqrt{X}} \exp(\pm y^2)dy}\right] \tag{14B.7-1}$$

in which $X = (9/2)\lambda_N^{(1)} \mid \dot{\varepsilon} \mid$.

14B.8 Rigid-Dumbbell Diffusion Equation for Shear Flows

Show how to obtain Eq. 14.4-1 from Eq. 14.2-8. Information in §§E.5 and E.6 may be helpful. Also note that for the shear flow being considered in §14.4(a), $\boldsymbol{\kappa} = \boldsymbol{\delta}_x\boldsymbol{\delta}_y\,\dot{\gamma}$. Use Appendix A to show that this tensor can also be written as

$$\begin{aligned}\boldsymbol{\kappa} = &(\sin\theta\cos\phi\,\boldsymbol{u} + \cos\theta\cos\phi\,\boldsymbol{s} \\ &- \sin\phi\,\boldsymbol{t})(\sin\theta\sin\phi\,\boldsymbol{u} + \cos\theta\sin\phi\,\boldsymbol{s} + \cos\phi\,\boldsymbol{t})\dot{\gamma}\end{aligned} \tag{14B.8-1}$$

14C.1 A Theorem for Stress Relaxation[5]

Consider the problem of stress relaxation in a dilute suspension of rigid dumbbells after cessation of a steady homogeneous flow. Before $t = 0$ we take the transpose of the velocity gradient tensor to be a constant $\boldsymbol{\kappa} = \boldsymbol{\kappa}_0$; for $t \geq 0$, $\boldsymbol{\kappa} = \mathbf{0}$. If the stress tensor for $t < 0$ and $t \geq 0$ is denoted by $\boldsymbol{\tau}^<$ and $\boldsymbol{\tau}^>$, respectively, then show that

$$\boldsymbol{\tau}^< + (\eta_s + nkT\lambda)(\boldsymbol{\kappa}_0 + \boldsymbol{\kappa}_0^\dagger) = \left\{\boldsymbol{\kappa}_0 \cdot \int_0^\infty \boldsymbol{\tau}^> dt + \int_0^\infty \boldsymbol{\tau}^> dt \cdot \boldsymbol{\kappa}_0^\dagger\right\} \tag{14C.1-1}$$

[5] O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498–2501 (1972).

Furthermore, show that if the flow for $t < 0$ is a simple shear flow with $v_x = \dot{\gamma}_0 y$, $v_y = v_z = 0$, then the above simplifies to Eq. 14B.5-7.

14C.2 Properties of Mixtures of Rigid Dumbbells

In the text we have taken the rigid dumbbell suspension to be monodisperse, since we have assumed all dumbbells have the same length L Here we extend the results for the steady-shear-flow material functions to polydisperse solutions by allowing the suspension to contain dumbbells of m different lengths.

a. Show that if the fraction of dumbbells of length L_j is x_j, then

$$(\eta - \eta_s)_{\text{mix}} = nkT \sum_{j=1}^{m} x_j \lambda_j \left[1 - \frac{18}{35} (\lambda_j \dot{\gamma})^2 + \frac{1326}{1925} (\lambda_j \dot{\gamma})^4 - \cdots \right] \tag{14C.2-1}$$

$$\Psi_{1\,\text{mix}} = \tfrac{6}{5} nkT \sum_{j=1}^{m} x_j \lambda_j^2 \left[1 - \frac{38}{35} (\lambda_j \dot{\gamma})^2 + \cdots \right] \tag{14C.2-2}$$

where $\lambda_j = \zeta L_j^2 / 12kT$.

b. We now restrict our attention to mixtures for which the zero-shear-rate viscosity is the same as for a monodisperse solution of dumbbells of length L. With this additional restriction show that the above results can be written

$$\left(\frac{\eta - \eta_s}{\eta_0 - \eta_s} \right)_{\text{mix}} = \sum_{j=1}^{m} x_j \left(\frac{L_j}{L} \right)^2 \left[1 - \frac{18}{35} \left(\frac{L_j}{L} \right)^4 (\lambda \dot{\gamma})^2 + \frac{1326}{1925} \left(\frac{L_j}{L} \right)^8 (\lambda \dot{\gamma})^4 - \cdots \right] \tag{14C.2-3}$$

$$\left(\frac{\Psi_1}{\Psi_{1,0}} \right)_{\text{mix}} = \frac{\sum_{j=1}^{m} x_j (L_j/L)^4 [1 - \frac{38}{35} (L_j/L)^4 (\lambda \dot{\gamma})^2 + \cdots]}{\sum_{j=1}^{m} x_j (L_j/L)^4} \tag{14C.2-4}$$

Figures 14C.2 *a* and *b* show the viscometric functions of the mixture found using the scheme outlined here but computed numerically following the procedure of Example 14.6-2.

14D.1 Time-Dependent Elongational Flows of Rigid Dumbbell Suspensions[6]

Consider the unsteady elongational flow field $v_z = \dot{\varepsilon} z$, $v_x = -(\dot{\varepsilon}/2)x$, and $v_y = -(\dot{\varepsilon}/2)y$, where $\dot{\varepsilon} = \dot{\varepsilon}_0 f(t)$. Here $\dot{\varepsilon}_0$ is a constant used to order results, and $f(t)$ specifies the time dependence of the velocity field.

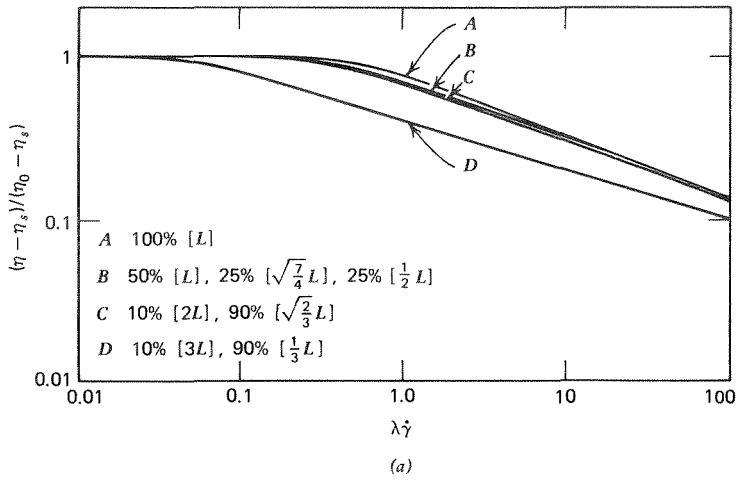
a. Show that the distribution function for this flow is

$$\begin{aligned} f = \frac{1}{4\pi} \Bigg\{ & 1 + (6\lambda\dot{\varepsilon}_0) \left[\frac{1}{2} P_2^0(1; t) \right] + (6\lambda\dot{\varepsilon}_0)^2 \left[\frac{1}{28} P_2^0(0, 1; t) + \frac{3}{14} P_4^0\left(\frac{7}{3}, 1; t \right) \right] \\ & + (6\lambda\dot{\varepsilon}_0)^3 \left[P_2^0\left(\frac{1}{392} (0, 0, 1; t) - \frac{1}{49} \left(-\frac{7}{3}, \frac{7}{3}, 1; t \right) \right) \right. \\ & \left. + \text{terms containing } P_4^0 \text{ and } P_6^0 \right] + \cdots \Bigg\} \end{aligned} \tag{14D.1-1}$$

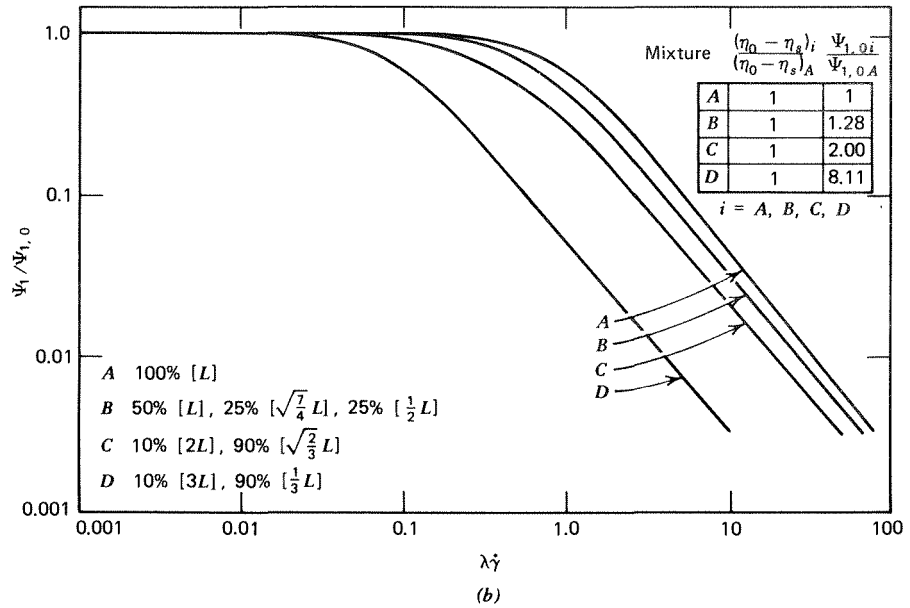
We have used the abbreviated notation $(a, b, c, \ldots; t)$ which is illustrated by

$$(a, b, c; t) = \frac{1}{\lambda^3} \int_{-\infty}^{t} \int_{-\infty}^{t'} \int_{-\infty}^{t''} e^{-a(t-t')/\lambda} e^{-b(t-t'')/\lambda} e^{-c(t-t''')/\lambda} f(t') f(t'') f(t''') \, dt''' \, dt'' \, dt' \tag{14D.1-2}$$

[6] R. B. Bird and R. C. Armstrong, *J. Chem. Phys.*, **56**, 3680–3682 (1972).



(a)



(b)

FIGURE 14C.2. (*a*) Viscosity and (*b*) first normal stress coefficient for various mixtures of rigid dumbbells. For a rigid linear molecule, the molecular weight is proportional to the length. Thus, the mixtures shown here have $\bar{M}_w/\bar{M}_n$ equal to A, 1; B, 1.093; C, 1.145; and D, 2.780. From these curves we see that (i) the shapes and displacements are sensitive to $\bar{M}_w/\bar{M}_n$ (ii) that the displacements are governed primarily by the length of the longest dumbbell in the mixture, and (iii) the first normal stress coefficient is more affected than viscosity by polydispersity. [R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1-90 (1971)].

b. Use the result in **(a)** to find

$$\left(\frac{\tau_{xx}-\tau_{zz}}{nkT}\right)-\left(\frac{3\eta_s\dot{\varepsilon}}{nkT}\right)=(\lambda\dot{\varepsilon}_0)\left[\frac{9}{5}(1;t)+\frac{6}{5}f(t)\right]$$
$$+(\lambda\dot{\varepsilon}_0)^2\left[\frac{27}{35}(0,1;t)+\frac{36}{35}f(t)(1;t)\right]$$
$$+(\lambda\dot{\varepsilon}_0)^3\left[\frac{81}{245}(0,0,1;t)+\frac{108}{245}f(t)(0,1;t)\right.$$
$$\left.-\frac{648}{245}\left(-\frac{7}{3},\frac{7}{3},1;t\right)+\frac{648}{245}f(t)\left(\frac{7}{3},1;t\right)\right]+\cdots \qquad (14D.1\text{-}3)$$

c. Show that the kernels G_1 and G_2 for the memory integral expansion can be obtained from D.1-3.

CHAPTER 15

THE BEAD-SPRING CHAIN MODELS

In Chapter 13 the kinetic theory of polymers was introduced by using the elastic dumbbell models to describe the polymer molecule. These models are the simplest ones for flexible macromolecules and contain the main physical ideas normally incorporated in dilute-solution theories. The dumbbell models are, of course, oversimplified models, accounting for polymer-solvent interaction only at two points. We now consider the more realistic chain models composed of N beads and $N - 1$ springs connected linearly; this model was introduced in §11.4, and some of the equilibrium properties of the model were examined in Chapter 12. In the Rouse and Zimm models the springs are taken to be Hookean. When hydrodynamic interaction is neglected the bead-spring chain model is called the Rouse model,[1] and when hydrodynamic interaction is included it is referred to as the Zimm model.[2]

The Rouse and Zimm models have been widely used by polymer chemists for interpreting linear viscoelastic measurements and have had considerable influence on the direction of experimental programs.[3] They are mathematically more complicated than the dumbbell models because they have N beads instead of two. Consequently much of this chapter has to deal with questions of coordinate transformations and normal coordinates;[4,5,6] this requires the use of some elementary notions from the theory of matrices.

The two principal parts of the kinetic theory are given in the first two sections: the diffusion equation for the chain distribution function is given in §15.1, and the expression for the stress tensor is given in §15.2. Then in §15.3 we specialize to chains with Hookean springs and obtain the constitutive equation; from the latter we obtain expressions for some of the rheological properties. Up to this point the development does not include hydrodynamic interaction; that is, we are concerned with the Rouse theory for "freely draining" chains. In §15.4 we consider the Zimm theory for chains with equilibrium averaged hydrodynamic interaction.

It must be emphasized that neither the Rouse nor the Zimm theory describes the decrease of viscosity with increasing shear rate. The models have been used primarily in the description of linear viscoelastic phenomena. The Rouse and Zimm theories illustrate the

[1] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272-1280 (1953); R. Takserman-Krozer, *J. Polym. Sci.*, **C16**, 2855-2865 (1967).

[2] B. H. Zimm, *J. Chem. Phys.*, **24**, 269-278 (1956); errors in Zimm's paper have been pointed out by M. C. Williams [*J. Chem. Phys.*, **42**, 2988-2989 (1965)], who also obtained expressions for the normal stresses.

[3] J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 3rd ed. (1980).

[4] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539-553 (1971).

[5] P. H. van Wiechen and H. C. Booij, *J. Eng. Math.*, **5**, 89-98 (1971).

[6] D. H. King and D. F. James, *J. Chem. Phys.*, **78**, 4743-4748, 4749-4754 (1983); see also H. C. Booij, *ibid.*, **80**, 4571-4572 (1984).

use of normal coordinates in coupled mechanical systems, and in addition provide useful background for the study of the chapters that follow.

§15.1 THE "DIFFUSION EQUATION" FOR THE CONFIGURATION-SPACE DISTRIBUTION FUNCTION

The discussion of §13.1 on modeling of polymer solutions can be taken over directly in this chapter, except that there are now N beads rather than 2. We make the same assumption regarding the factoring of the single-molecule phase-space distribution function that we made in Eq. 13.1-1, and we assume that the velocity distribution is Maxwellian about the fluid velocity at the center of mass of the polymer chain, exactly as we did in Eq. 13.1-3. We now obtain the partial differential equation for the configuration-space distribution function by combining the force balances on the beads with the equation of continuity in configuration space.

a. The Equations of Motion for the Beads of the Chain

If the acceleration terms in the equations of motion are omitted then these reduce to force balances, one for each bead; these are generalizations of Eqs. 13.2-1 to 13.2-4 with $\nu = 1, 2$ being replaced by $\nu = 1, 2, \ldots, N$. When we use Stokes' law with a scalar friction coefficient and a Maxwellian velocity distribution in the Brownian force term, the equations of motion for the beads become (cf. Eq. 13.2-5):

$$-\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu]) - kT\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi + \boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)} = \boldsymbol{0} \qquad (\nu = 1, 2, \ldots, N) \quad (15.1\text{-}1)$$

These equations of motion for the N beads can be transformed into equations of motion for the center of mass $\boldsymbol{r}_c = (1/N)\sum_\nu \boldsymbol{r}_\nu$ and for the connector vectors $\boldsymbol{Q}_k = \boldsymbol{r}_{k+1} - \boldsymbol{r}_k$ by using the relations in Table 15.1-1. In this way we obtain (see Problem 15B.5)

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_c] + \frac{1}{N\zeta}\sum_\nu \boldsymbol{F}_\nu^{(e)} \qquad (15.1\text{-}2)$$

$$[\![\dot{\boldsymbol{Q}}_j]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{Q}_j] - \frac{1}{\zeta}\sum_k A_{jk}\left(kT\frac{\partial}{\partial \boldsymbol{Q}_k}\ln\psi + \boldsymbol{F}_k^{(c)}\right) + \frac{1}{\zeta}\sum_\nu \bar{B}_{j\nu}\boldsymbol{F}_\nu^{(e)} \qquad (15.1\text{-}3)$$

Here $\boldsymbol{F}_k^{(c)} = -\sum_\nu B_{\nu k}\boldsymbol{F}_\nu^{(\phi)}$ is the tension in the kth connector, and the A_{jk} are the elements of the Rouse matrix defined in Eq. 11.6-8. Clearly the equations of motion for the $\boldsymbol{Q}_j$ are coupled, the motion of each link depending on the movement of the adjacent links in the chain.

b. Equation of Continuity for $\psi(\boldsymbol{Q}^{N-1}, t)$

By means of a derivation similar to that in §13.2(b) we obtain for the bead-spring chain model

$$\frac{\partial\Psi}{\partial t} = -\sum_\nu\left(\frac{\partial}{\partial \boldsymbol{r}_\nu}\cdot[\![\dot{\boldsymbol{r}}_\nu]\!]\Psi\right) \qquad (15.1\text{-}4)$$

TABLE 15.1-1[a]

Relations Involving $\bar{B}_{kv}$ and B_{vk}

Algebraic relations

$$\sum_v \bar{B}_{kv} = 0 \tag{A}$$

$$\sum_v B_{vk} = 0 \tag{B}$$

$$\sum_v \bar{B}_{jv} B_{vk} = \delta_{jk} \tag{C}$$

$$\sum_k B_{vk} \bar{B}_{k\mu} = \delta_{v\mu} - \frac{1}{N} \tag{D}$$

$$B_{v+1,k} - B_{vk} = \delta_{vk} \tag{E}$$

Derivatives of arbitrary functions of the configurational vectors $f(\boldsymbol{r}_c, \boldsymbol{Q}_1, \boldsymbol{Q}_2, \ldots, \boldsymbol{Q}_{N-1}) = g(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$:

$$\frac{\partial f}{\partial \boldsymbol{r}_c} = \sum_v \frac{\partial g}{\partial \boldsymbol{r}_v}; \quad \frac{\partial f}{\partial \boldsymbol{Q}_k} = \sum_v B_{vk} \frac{\partial g}{\partial \boldsymbol{r}_v} \tag{F}$$

$$\frac{\partial g}{\partial \boldsymbol{r}_v} = \frac{1}{N} \frac{\partial f}{\partial \boldsymbol{r}_c} + \sum_k \bar{B}_{kv} \frac{\partial f}{\partial \boldsymbol{Q}_k} \tag{G}$$

Jacobian relation for the configurational vectors

$$\left| \frac{\partial(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)}{\partial(\boldsymbol{r}_c, \boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_{N-1})} \right| = 1 \tag{H}$$

Relations between the net spring force $\boldsymbol{F}_v^{(\phi)}$ acting on bead v and the force $\boldsymbol{F}_k^{(c)}$ on bead $v = k$ due to the tension in the kth connector.

$$\boldsymbol{F}_v^{(\phi)} = -\sum_k \bar{B}_{kv} \boldsymbol{F}_k^{(c)} = -\frac{\partial \phi}{\partial \boldsymbol{r}_v} \tag{I}$$

$$\boldsymbol{F}_k^{(c)} = -\sum_v B_{vk} \boldsymbol{F}_v^{(\phi)} = +\frac{\partial \phi}{\partial \boldsymbol{Q}_k} \tag{J}$$

[a] For additional information on chain geometry and the definitions of the Rouse matrix (A_{ij}) and the Kramers matrix (C_{ij}) see §11.6.

By applying the chain rule of partial differentiation and using the relations in Table 15.1-1 we get

$$\frac{\partial \Psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{r}_c} \cdot [\![\dot{\boldsymbol{r}}_c]\!]\Psi\right) - \sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}_j} \cdot [\![\dot{\boldsymbol{Q}}_j]\!]\Psi\right) \tag{15.1-5}$$

Next we use Eq. 15.1-2, the fact that there are no concentration gradients, and the fact that $\boldsymbol{\kappa}$ is traceless (a consequence of $(\nabla \cdot \boldsymbol{v}) = 0$) in order to simplify Eq. 15.1-5 to

$$\frac{\partial \psi}{\partial t} = -\sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}_j} \cdot [\![\dot{\boldsymbol{Q}}_j]\!]\psi\right) \tag{15.1-6}$$

Note that we do not evaluate the average in velocity space appearing in this equation.

c. The Diffusion Equation for $\psi(\boldsymbol{Q}^{N-1}, t)$

We now substitute $[\![\dot{\boldsymbol{Q}}_j]\!]$ from Eq. 15.1-3 into the equation of continuity to get the diffusion equation:

$$\boxed{\frac{\partial \psi}{\partial t} = -\sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}_j} \cdot \left\{[\boldsymbol{\kappa} \cdot \boldsymbol{Q}_j]\psi - \frac{1}{\zeta}\sum_k A_{jk}\left[kT\frac{\partial}{\partial \boldsymbol{Q}_k}\psi + \boldsymbol{F}_k^{(c)}\psi\right] + \frac{1}{\zeta}\sum_v \bar{B}_{jv}\boldsymbol{F}_v^{(e)}\psi\right\}\right)} \tag{15.1-7}$$

This equation has to be solved to get the distribution function. For the Rouse model, for which $\boldsymbol{F}_j^{(c)} = H\boldsymbol{Q}_j$, the solution is known for any choice of the flow field (i.e., for any choice of $\boldsymbol{\kappa}(t)$), as is shown in §15.3. For steady-state, homogeneous, potential flow of a dilute solution of bead-spring chains with any kind of spring force law and no external forces, the diffusion equation has a solution similar to that shown in Eq. 13.2-14:

$$\psi(\boldsymbol{Q}^{N-1}) = \frac{1}{J}\exp[-\phi(\boldsymbol{Q}^{N-1})/kT]\exp\left[(\zeta/2kT)(\boldsymbol{\kappa} : \sum_i \sum_j C_{ij}\boldsymbol{Q}_i\boldsymbol{Q}_j)\right] \tag{15.1-8}$$

where J is a normalization constant, and $\phi(\boldsymbol{Q}^{N-1})$ is the total potential energy of the bead-spring chain. This can be used for getting the distribution of orientations in elongational flow, for example.

Next we derive an equation of change for the average value of any scalar function of the connector vectors, $B(\boldsymbol{Q}^{N-1})$. We multiply the diffusion equation, Eq. 15.1-7, by B and then integrate over the entire configuration space. This leads to the following relation:[1]

$$\begin{aligned}\frac{d}{dt}\langle B\rangle = &\left(\boldsymbol{\kappa} : \left\langle \sum_j \boldsymbol{Q}_j \frac{\partial}{\partial \boldsymbol{Q}_j} B\right\rangle\right) + \frac{kT}{\zeta}\left\langle \sum_j \sum_k A_{jk}\left(\frac{\partial}{\partial \boldsymbol{Q}_k} \cdot \frac{\partial}{\partial \boldsymbol{Q}_j} B\right)\right\rangle \\ &- \frac{1}{\zeta}\left\langle \sum_j \sum_k A_{jk}\left(\boldsymbol{F}_k^{(c)} \cdot \frac{\partial}{\partial \boldsymbol{Q}_j} B\right)\right\rangle + \frac{1}{\zeta}\sum_j \sum_v \bar{B}_{jv}\left\langle\left(\boldsymbol{F}_v^{(e)} \cdot \frac{\partial}{\partial \boldsymbol{Q}_j} B\right)\right\rangle\end{aligned} \tag{15.1-9}$$

[1] O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498–2501 (1972), erratum, *ibid.*, **57**, 1368 (1972).

A similar relation is valid for any tensor function of the $\boldsymbol{Q}_j$. In particular we let $\mathbf{B}(\boldsymbol{Q}^{N-1})$ be the second-order tensor $\sum_j \sum_k C_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k$, where the C_{jk} are the elements of the Kramers matrix defined in Eq. 11.6-7. When this choice is made one gets:[1]

$$\left\langle \sum_j \sum_k C_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k \right\rangle_{(1)} = \frac{2kT}{\zeta}(N-1)\boldsymbol{\delta} - \frac{2}{\zeta}\left\langle \sum_k \boldsymbol{F}_k^{(c)}\boldsymbol{Q}_k \right\rangle + \frac{1}{\zeta}\sum_\nu \sum_k B_{\nu k}\left\langle \boldsymbol{F}_\nu^{(e)}\boldsymbol{Q}_k + \boldsymbol{Q}_k\boldsymbol{F}_\nu^{(e)} \right\rangle \tag{15.1-10}$$

which is the analog of Eq. 13.2-17 for elastic dumbbells. The subscript (1) denotes the convected time derivative. Finally we note that at equilibrium ($\boldsymbol{\kappa} = \mathbf{0}$), Eq. 15.1-10 gives

$$\sum_k \langle \boldsymbol{F}_k^{(c)}\boldsymbol{Q}_k \rangle_{\text{eq}} = (N-1)kT\boldsymbol{\delta} \tag{15.1-11}$$

a result that we need in the next section.

§15.2 EXPRESSIONS FOR THE STRESS TENSOR

In §13.3 we derived an expression for the stress tensor for a dilute polymer solution in which the polymers were modeled as elastic dumbbells. In getting the polymer contribution to the stress tensor, we accounted for three major effects: the contribution resulting from the tensions in the springs, that resulting from external forces, and that associated with the momentum transport by the beads. These elementary physical arguments led us to the expression for the stress tensor in Eq. 13.3-14. An analogous derivation for the bead-spring chain model would lead us to the following expressions for the stress tensor, one in terms of the tensions in the connectors, and the other in terms of the hydrodynamic forces:

$$\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\sum_{k=1}^{N-1}\langle \boldsymbol{Q}_k\boldsymbol{F}_k^{(c)} \rangle + n\sum_{\nu=1}^{N}\sum_{k=1}^{N-1} B_{\nu k}\langle \boldsymbol{Q}_k\boldsymbol{F}_\nu^{(e)} \rangle + nm\sum_{\nu=1}^{N}\langle (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rangle$$

Solvent contribution	Contribution of intramolecular forces	Contribution of external forces	Contribution of the bead motion

(15.2-1)

$$\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\sum_{\nu=1}^{N}\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)} \rangle + Nnm\langle (\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v}) \rangle \tag{15.2-2}$$

The only assumption made in going from Eq. 15.2-1 to Eq. 15.2-2 is that the velocity distribution function is an even function of $(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})$. Both of these equations are applicable whether or not hydrodynamic interaction is included, and whether the friction coefficient is a second-order tensor or a scalar.

In most kinetic theories of polymers it is assumed that the velocity distribution is Maxwellian; in this chapter we adopt this same assumption henceforth, so that the last term of Eq. 15.2-1 becomes $NnkT\boldsymbol{\delta}$, and the last term of Eq. 15.2-2 becomes $nkT\boldsymbol{\delta}$. Then the stress

TABLE 15.2-1

Expressions for the Stress Tensor for Bead-Spring Chains[a,b] (Maxwellian Velocity Distribution Assumed)

Kramers:[c]
$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\sum_{k=1}^{N-1}\langle \boldsymbol{Q}_k\boldsymbol{F}_k^{(c)}\rangle + n\sum_{\nu=1}^{N}\sum_{k=1}^{N-1}B_{\nu k}\langle \boldsymbol{Q}_k\boldsymbol{F}_\nu^{(e)}\rangle + (N-1)nkT\boldsymbol{\delta} \tag{A}$$

Modified Kramers:
$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + n\sum_{\nu=1}^{N}\langle \boldsymbol{R}_\nu(\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)})\rangle + (N-1)nkT\boldsymbol{\delta} \tag{B}$$

Kramers-Kirkwood:[d]
$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\sum_{\nu=1}^{N}\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)}\rangle \tag{C}$$

Giesekus:[e]
$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + \tfrac{1}{2}n\zeta\left\langle\sum_{j=1}^{N-1}\sum_{k=1}^{N-1}C_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k\right\rangle_{(1)} + \tfrac{1}{2}n\sum_{\nu=1}^{N}\sum_{k=1}^{N-1}B_{\nu k}\langle \boldsymbol{Q}_k\boldsymbol{F}_\nu^{(e)} - \boldsymbol{F}_\nu^{(e)}\boldsymbol{Q}_k\rangle \tag{D}$$

[a] R. B. Bird and C. F. Curtiss, *J. Polym. Sci.: Polym. Symp.*, **73**, 187-199 (1985).
[b] See §15.4 for inclusion of hydrodynamic interaction.
[c] H. A. Kramers, *Physica*, **11**, 1-19 (1944).
[d] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).
[e] H. Giesekus, *Rheol. Acta*, **2**, 50-62 (1962); O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498-2501 (1972).

tensor may be expressed in terms of $\boldsymbol{\tau}$ by subtracting the corresponding expression at equilibrium. This leads to the expressions in Table 15.2-1. Once again we attach names to these various forms for the stress tensor in order to distinguish among them. Equations A and B in this table are obtained directly from Eq. 15.2-1, and Eq. C is a simplification of Eq. 15.2-2; Eq. D is obtained from Eq. A by making use of Eq. 15.1-10 to eliminate the spring force law.

§15.3 THE BEAD-SPRING CHAIN WITH HOOKEAN SPRINGS (ROUSE MODEL)

The first two sections of this chapter apply to bead-spring chains with any kind of spring force law. In this section we specialize the results for chains with Hookean springs (the Rouse chain). First we obtain a solution to the diffusion equation for any kind of flow pattern. Then we obtain the constitutive equation for the fluid.

a. Introduction of Normal Coordinates

In the diffusion equation, Eq. 15.1-7, we note that there is coupling among the various connector vectors because of the Rouse matrix. This coupling can be removed by

introducing a new set of variables called "normal coordinates".[1] Specifically we introduce the $\boldsymbol{Q}'_k$ (the Cartesian components Q'_{kn} with $n = 1, 2, 3$ are the normal coordinates) by

$$\boldsymbol{Q}_j = \sum_k \Omega_{jk} \boldsymbol{Q}'_k \tag{15.3-1}$$

Here the Ω_{jk} are the elements of an $(N-1) \times (N-1)$ orthogonal matrix ($\Omega_{jk}^{-1} = \Omega_{kj}$) chosen to diagonalize the Rouse matrix. That is, the Ω_{ij} have the following properties:[2]

$$\sum_i \Omega_{ij}\Omega_{ik} = \delta_{jk} \tag{15.3-2}$$

$$\sum_j \sum_k \Omega_{ji} A_{jk} \Omega_{kl} = a_l \delta_{il} \tag{15.3-3}$$

where the $a_l = 4 \sin^2(l\pi/2N)$ are the eigenvalues of the Rouse matrix (see Eq. 11.6-9). The elements of the rotation matrix Ω_{jk} are known to be[3]

$$\Omega_{jk} = \sqrt{\frac{2}{N}} \sin \frac{jk\pi}{N} \tag{15.3-4}$$

In addition it can be shown that the derivatives transform as follows:

$$\frac{\partial}{\partial \boldsymbol{Q}_j} = \sum_k \Omega_{jk} \frac{\partial}{\partial \boldsymbol{Q}'_k} \tag{15.3-5}$$

by using the relation among the coordinates, Eq. 15.3-1, and the orthogonality property of the Ω_{jk}.

When the diffusion equation in Eq. 15.1-7 is now written in terms of the normal coordinates, it becomes

$$\frac{\partial \psi}{\partial t} = -\sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}'_j} \cdot \left\{ [\boldsymbol{\kappa} \cdot \boldsymbol{Q}'_j]\psi - \frac{a_j}{\zeta} \left[kT \frac{\partial}{\partial \boldsymbol{Q}'_j} \psi + H \boldsymbol{Q}'_j \psi \right] \right\} \right) \tag{15.3-6}$$

This form of the diffusion equation is somewhat simpler inasmuch as only a single summation appears on the right side.

b. Separation of Variables in the Transformed Diffusion Equation[4,5,6]

Next we postulate that Eq. 15.3-6 has a solution of the form

$$\psi(\boldsymbol{Q}'^{N-1}, t) = \prod_{k=1}^{N-1} \psi_k(\boldsymbol{Q}'_k, t) \tag{15.3-7}$$

[1] For an elementary discussion of normal coordinates in polymer kinetic theory see B. H. Zimm, in F. R. Eirich, ed., *Rheology*, Vol. 3, Academic Press, New York (1960), Chapter 1, pp. 1–16.

[2] Note that Eqs. 15.3-2 and 15.3-3 are sufficient to determine all the Ω_{jk} (of which there are $(N-1) \times (N-1)$) and the a_j (of which there are $N-1$), that is a total of $N(N-1)$ unknowns. The relations in Eq. 15.3-2 are a set of $(1/2)N(N-1)$ equations, and, since the A_{jk} are symmetric, Eq. 15.3-3 contains $(1/2)N(N-1)$ equations.

[3] P. H. Verdier, *J. Chem. Phys.*, **45**, 2118–2121 (1966); J. Kovac and M. Fixman, *ibid.*, **63**, 935–941 (1975); D. H. King and D. F. James, *ibid.*, **78**, 4743–4748 (1983).

[4] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539–553 (1971).

[5] P. H. van Wiechen and H. C. Booij, *J. Eng. Math.*, **5**, 89–98 (1971).

[6] D. H. King and D. F. James, *J. Chem. Phys.*, **78**, 4743–4748, 4749–4754 (1983); erratum: *ibid.* **80**, 4573 (1984). See also H. C. Booij, *J. Chem. Phys.*, **80**, 4571–4572 (1984).

with $\int \psi_k(\boldsymbol{Q}'_k, t)d\boldsymbol{Q}'_k = 1$ giving the normalization. Substitution of this postulated solution into Eq. 15.3-6 then gives

$$\sum_j \left(\prod_{\substack{k=1 \\ k\neq j}}^{N-1} \psi_k \right) \frac{\partial \psi_j}{\partial t} = -\sum_j \left(\left(\prod_{\substack{k=1 \\ k\neq j}}^{N-1} \psi_k \right) \frac{\partial}{\partial \boldsymbol{Q}'_j} \cdot \left\{ [\boldsymbol{\kappa} \cdot \boldsymbol{Q}'_j]\psi_j - \frac{a_j}{\zeta} \left[kT \frac{\partial}{\partial \boldsymbol{Q}'_j} \psi_j + H\boldsymbol{Q}'_j \psi_j \right] \right\} \right) \tag{15.3-8}$$

Next we divide by $\prod_k \psi_k = \psi_1 \psi_2 \cdots \psi_{N-1}$, and this gives us terms containing only $\boldsymbol{Q}'_1$, terms containing only $\boldsymbol{Q}'_2$, and so on. The only way that this equation can be satisfied is if each of these groups of terms is equal to $E_j(t)$, a function of t (with $\sum_j E_j(t) = 0$). That is,

$$\frac{\partial \psi_j}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}'_j} \cdot \left\{ [\boldsymbol{\kappa} \cdot \boldsymbol{Q}'_j]\psi_j - \frac{a_j}{\zeta} \left[kT \frac{\partial}{\partial \boldsymbol{Q}'_j} \psi_j + H\boldsymbol{Q}'_j \psi_j \right] \right\} \right) + E_j(t)\psi_j \tag{15.3-9}$$

If this equation is integrated over all $\boldsymbol{Q}'_j$, then according to the normalization condition the left side is zero; the first term on the right side is also zero, because of the vanishing of ψ_j as $\boldsymbol{Q}'_j \to \infty$. We conclude, therefore, that all the $E_j(t)$ must be zero. Then Eq. 15.3-9, for the jth normal mode, has the same form as the elastic dumbbell equation in Eq. 13.2-13 (with $\boldsymbol{F}^{(c)}$ set equal to $H\boldsymbol{Q}$). We also point out that when Eq. 15.3-9 is multiplied by $\boldsymbol{Q}'_j\boldsymbol{Q}'_j$ and integrated over all $\boldsymbol{Q}'_j$, we get

$$\langle \boldsymbol{Q}'_j\boldsymbol{Q}'_j \rangle_{(1)} = \frac{2a_j}{\zeta} (kT\boldsymbol{\delta} - H\langle \boldsymbol{Q}'_j\boldsymbol{Q}'_j \rangle) \tag{15.3-10}$$

a result that we need presently.

c. Development of the Constitutive Equation

Next we specialize Eq. A of Table 15.2-1 for Hookean springs by inserting $\boldsymbol{F}^{(c)}_j = H\boldsymbol{Q}_j$; then we write both Eqs. A and D in terms of the normal coordinates. Note that the spring contribution in the Kramers expression can be written thus:

$$\begin{aligned} -nH \sum_i \langle \boldsymbol{Q}_i\boldsymbol{Q}_i \rangle &= -nH \sum_i \sum_k \sum_l \Omega_{ik}\Omega_{il} \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_l \rangle \\ &= -nH \sum_k \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_k \rangle \end{aligned} \tag{15.3-11}$$

and that the polymer contribution in the Giesekus expression can be transformed as follows:

$$\begin{aligned} \frac{n\zeta}{2} \sum_i \sum_j C_{ij} \langle \boldsymbol{Q}_i\boldsymbol{Q}_j \rangle_{(1)} &= \frac{n\zeta}{2} \sum_i \sum_j \sum_k \sum_l C_{ij}\Omega_{ik}\Omega_{jl} \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_l \rangle_{(1)} \\ &= \frac{n\zeta}{2} \sum_k c_k \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_k \rangle_{(1)} \end{aligned} \tag{15.3-12}$$

in which $c_k = 1/a_k$ is the kth eigenvalue of the Kramers matrix. As a result the Kramers and Giesekus expressions can be written finally as

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + \sum_j \boldsymbol{\tau}_j \tag{15.3-13}$$

with

$$\text{Kramers:} \quad \tau_j = -nH\langle Q'_j Q'_j\rangle + nkT\delta \tag{15.3-14}$$

$$\text{Giesekus:} \quad \tau_j = +\frac{n\zeta c_j}{2}\langle Q'_j Q'_j\rangle_{(1)} \tag{15.3-15}$$

Then because of Eq. 15.3-10 we can obtain the following differential equation for the jth contribution to the stress tensor:

$$\tau_j + \lambda_j \tau_{j(1)} = -nkT\lambda_j \dot{\gamma} \tag{15.3-16}$$

in which the quantities $\lambda_j = \zeta/2Ha_j = \zeta c_j/2H$ are the time constants. Hence we have demonstrated that each of the partial stress tensors satisfies a constitutive equation that is exactly of the same form as the equation satisfied by the polymer contribution to the stress tensor of a Hookean dumbbell. That is, each of the "normal modes" is given by a convected Maxwell model (see Table 7.3-2). Therefore, the constitutive equation can be put into an integral form, thus:[4]

$$\boxed{\tau = -\eta_s \dot{\gamma} + \int_{-\infty}^{t} \left\{ nkT \sum_j \frac{1}{\lambda_j} e^{-(t-t')/\lambda_j} \right\} \gamma_{[0]}(t, t')dt'} \tag{15.3-17}$$[7]

in which $\gamma_{[0]}$ is the finite strain tensor discussed in §8.1 and §9.2 (see also Appendix D); the quantity within the braces is called the "memory function." We have thus succeeded in getting the complete constitutive equation for the dilute solution of Hookean chains without actually getting the solution to the diffusion equation.

Any flow problem for a solution of Rouse chains can be solved (at least in principle) by using Eq. 15.3-17 and the hydrodynamic equations of continuity and motion. Furthermore, when the flow field is specified [i.e., $\gamma_{[0]}(t, t')$ is known] the expression for $\tau + \eta_s\dot{\gamma}$ for the Rouse model is just a linear superposition of similar results for the Hookean dumbbells (see Eq. 13.4-9) with relaxation times given by

$$\lambda_j = \frac{\zeta c_j}{2H} = \frac{\zeta/2H}{4\sin^2(j\pi/2N)} = \frac{3M[\eta]\eta_s}{2(N^2-1)\tilde{N}kT\sin^2(j\pi/2N)} \tag{15.3-18}$$

In the last line we have eliminated ζ and H by using the expression for intrinsic viscosity given ahead in Eq. 15.3-28. We note further that for large N and small j (i.e., the largest time constants)[8]

$$\lambda_j \sim \frac{\zeta/2H}{4(j\pi/2N)^2} = \frac{6[\eta]M\eta_s}{\pi^2\tilde{N}kT}\left(\frac{1}{j^2}\right) \tag{15.3-19}$$

[7] Note that Eq. 15.3-17 has the same form as the first term in Eq. D.4-1.
[8] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272–1280 (1953), Eq. 33.

d. Solution to the Diffusion Equation

For many purposes it is desirable to have the complete solution to the diffusion equation. This means we have to go back and solve Eq. 15.3-9 (with $E_j(t)$ set equal to zero). This can be done by taking the three-dimensional Fourier transform[6,9] of this equation:

$$\frac{\partial \bar{\psi}_j}{\partial t} = \left(\boldsymbol{\kappa} : \left(\frac{\partial \bar{\psi}}{\partial \boldsymbol{P}} \boldsymbol{P}\right)\right) - \frac{a_j H}{\zeta}\left[\frac{kT}{H}(\boldsymbol{P}\cdot\boldsymbol{P})\bar{\psi}_j + \left(\boldsymbol{P}\cdot\frac{\partial}{\partial \boldsymbol{P}}\bar{\psi}_j\right)\right] \tag{15.3-20}$$

We now try a solution of the form

$$\bar{\psi}_j = \exp\left[-\frac{kT}{2H}(\boldsymbol{\alpha}_j : \boldsymbol{P}\boldsymbol{P})\right] \tag{15.3-21}$$

When this is substituted into the preceding equation we get

$$\boldsymbol{\alpha}_j + \lambda_j \boldsymbol{\alpha}_{j(1)} = \boldsymbol{\delta} \tag{15.3-22}$$

for the differential equation for $\boldsymbol{\alpha}_j$. We note, however, that this is just the same differential equation as that for $\langle H\boldsymbol{Q}_j'\boldsymbol{Q}_j'/kT\rangle$ as may be seen from Eq. 15.3-10. Therefore, from Eqs. 15.3-14, 15.3-16, and 15.3-17 we see that[4]

$$\boldsymbol{\alpha}_j = \boldsymbol{\delta} - \frac{1}{\lambda_j}\int_{-\infty}^{t} e^{-(t-t')/\lambda_j}\boldsymbol{\gamma}_{[0]}(t, t')dt' \tag{15.3-23}$$

[9] We follow the conventions of A. Erdélyi (Ed.), *Tables of Integral Transforms*, Vol. I, McGraw-Hill, New York (1954) and define

$$\bar{\psi}(\boldsymbol{P}, t) \equiv \mathscr{F}\{\psi(\boldsymbol{Q}, t)\} = \int_{-\infty}^{+\infty} \psi(\boldsymbol{Q}, t)\exp[-i(\boldsymbol{P}\cdot\boldsymbol{Q})]d\boldsymbol{Q} \tag{15.3-20a}$$

$$\psi(\boldsymbol{Q}, t) \equiv \mathscr{F}^{-1}\{\bar{\psi}(\boldsymbol{P}, t)\} = (2\pi)^{-3}\int_{-\infty}^{+\infty} \bar{\psi}(\boldsymbol{P}, t)\exp[+i(\boldsymbol{P}\cdot\boldsymbol{Q})]d\boldsymbol{P} \tag{15.3-20b}$$

With these conventions we can derive the following relations:

$$\mathscr{F}\left\{\frac{\partial}{\partial \boldsymbol{Q}}\psi\right\} = i\boldsymbol{P}\bar{\psi} \tag{15.3-20c}$$

$$\mathscr{F}\{\boldsymbol{Q}\psi\} = i\frac{\partial}{\partial \boldsymbol{P}}\bar{\psi} \tag{15.3-20d}$$

$$\mathscr{F}\left\{\boldsymbol{Q}\frac{\partial}{\partial \boldsymbol{Q}}\psi\right\} = -\left(\frac{\partial}{\partial \boldsymbol{P}}\bar{\psi}\right)\boldsymbol{P} - \boldsymbol{\delta}\bar{\psi} \tag{15.3-20e}$$

$$\mathscr{F}\left\{\frac{\partial}{\partial \boldsymbol{Q}}\frac{\partial}{\partial \boldsymbol{Q}}\psi\right\} = -\boldsymbol{P}\boldsymbol{P}\bar{\psi} \tag{15.3-20f}$$

These are used to get Eq. 15.3-20.

When Eq. 15.3-21 is inverted and ψ_j is normalized to unity, we get the solution of Eq. 15.3-9 as[4,5]

$$\boxed{\psi_j(\mathbf{Q}'_j, t) = \frac{(H/2\pi kT)^{3/2}}{\sqrt{\det \boldsymbol{\alpha}_j}} e^{-(H/2kT)(\boldsymbol{\alpha}_j^{-1}:\mathbf{Q}_j\mathbf{Q}_j)}} \tag{15.3-24}$$

Equations 15.3-24 and 15.3-23, along with Eq. 15.3-7, then give the configuration-space distribution function for the Rouse chain with Hookean springs. This result is a generalization of that given in Eqs. 13.4-12 and 13.4-13 for Hookean dumbbells. As in Chapter 13 we note that, since the combination $\boldsymbol{\delta} - \boldsymbol{\gamma}_{[0]}$ is positive definite, the $\boldsymbol{\alpha}_j^{-1}$ all exist.

EXAMPLE 15.3-1 Material Functions from the Rouse Model

Obtain the material functions for the Rouse model for (**a**) steady-state shear flow, and (**b**) small-amplitude oscillatory shearing motion. Show that the Rouse model gives $[\eta]$ proportional to molecular weight (Staudinger's rule). Show further how the Rouse theory suggests a way to plot η' data taken at different temperatures so that all the data fall on a single curve (the method of reduced variables).

SOLUTION (**a**) Steady-State Shear Flow

In Eqs. 13.4-17 to 13.4-19 we obtained the steady-state shear flow material functions for the elastic dumbbell with a Hookean spring connector. A superposition of solutions then gives for the Rouse model

$$\eta - \eta_s = nkT \sum_{j=1}^{N-1} \lambda_j = nkT\left(\frac{\zeta}{4H}\right)\left[\frac{N^2 - 1}{3}\right] \tag{15.3-25}$$

$$\Psi_1 = 2nkT \sum_{j=1}^{N-1} \lambda_j^2 = 2nkT\left(\frac{\zeta}{4H}\right)^2\left[\frac{(N^2 - 1)(2N^2 + 7)}{45}\right] \tag{15.3-26}$$

$$\Psi_2 = 0 \tag{15.3-27}$$

in which use has been made of the sums in Eqs. 11.6-10 and 11.6-12 and the definitions of the material functions in Eqs. D.5-1 to D.5-3. The quantities in brackets are both unity for $N = 2$. We note that none of the material functions depend on the shear rate.[10]

[10] F. Bueche, *J. Chem. Phys.*, **22**, 1570–1576 (1954), using the Rouse model (but with the springs restricted to being aligned in the x-, y-, and z-directions) obtained a result analogous to Eq. 15.3-25, in which, however, the viscosity decreases dramatically with increasing shear rate. This result, which has often been quoted and used, is incorrect, probably because the kinetic theory was improperly formulated in a corotating coordinate frame. Other polymer researchers have expressed doubts about Bueche's expression for steady-shear flow viscosity, for example, H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 316, and A. Peterlin, *Adv. Macr. Chem.*, **1**, 225–281 (1968), p. 252.

In another paper [*J. Chem. Phys.*, **22**, 603–609 (1954)] Bueche derived expressions for η' and η'' which are not in agreement with the Rouse results in Eqs. 15.3-29 and 30. R. E. DeWames, W. F. Hall, and M. C. Shen, *J. Chem. Phys.*, **46**, 2782–2794 (1961) reported that they could resolve the discrepancy between Bueche and Rouse by correcting an error in the Bueche paper. For further discussion, see M. C. Williams, *AIChE J.*, **21**, 1–25 (1975), p. 6, footnote.

From Eq. 15.3-25 we can get the dependence of the intrinsic viscosity $[\eta]$ on molecular weight M, if we recognize that the number of beads is related to the molecular weight and bead mass by $N = M/m$. Then for large N we get

$$[\eta] = \lim_{c \to 0} \frac{(\eta - \eta_s)}{c\eta_s} = \lim_{n \to 0} \frac{(\eta - \eta_s)\tilde{N}}{n\eta_s M}$$

$$= \frac{kT}{\eta_s} \frac{\zeta \tilde{N}}{12Hm^2} M \tag{15.3-28}$$

where $\tilde{N}$ is Avogadro's number and c is the mass concentration. The proportionality of $[\eta]_0$ to M is known as the Staudinger rule.[11] However for most dilute polymer solutions it is found[12] that $[\eta]_0 = K'M^a$, where a is in the range from 0.5 to 0.8 (see §3.6). In §15.4 we shall find that the inclusion of hydrodynamic interaction does indeed provide a more realistic relation between $[\eta]_0$ and M; it also leads to a more accurate portrayal of the shapes of the $[\eta']$ and $[\eta'']$ curves.

(b) Small-Amplitude Oscillatory Shearing

By superposing the results given for Hookean dumbbells in Eqs. 13.4-21 and 13.4-22 we get directly

$$\eta' - \eta_s = nkT \sum_{j=1}^{N} \frac{\lambda_j}{1 + (\lambda_j \omega)^2} \tag{15.3-29}$$

$$\eta'' = nkT \sum_{j=1}^{N-1} \frac{\lambda_j^2 \omega}{1 + (\lambda_j \omega)^2} \tag{15.3-30}$$

According to the Rouse theory η' should approach η_s in the limit of very high frequencies, but experimental data indicate that the high frequency limit is higher than η_s. If the approximate expression for λ_j in Eq. 15.3-19 is used, then Eqs. 15.3-29 and 15.3-30 give η' and η'' in terms of molecular weight, (zero-shear-rate) intrinsic viscosity, and temperature. The model parameters ζ, H, and N, all difficult to relate precisely to molecular structure, have thus been eliminated.

It can be seen from Eq. 15.3-18 that all the λ_j have the same dependence on temperature. One can therefore define a function $a_T(T_0)$ by

$$a_T(T_0) = \frac{\lambda_j(T)}{\lambda_j(T_0)} \tag{15.3-31}$$

where T_0 is some arbitrary reference temperature. One can then show from Eq. 15.3-29 that data taken at various temperatures plotted as

$$\frac{\eta' - \eta_s}{a_T} \frac{T_0 n_0}{Tn} \quad \text{versus} \quad a_T \omega \tag{15.3-32}$$

should superpose on the curve corresponding to T_0. Here n_0 is the number density of macromolecules at T_0. Hence if a_T is known, then an $\eta'(\omega)$ curve over a wide frequency range at temperature T_0 can be

[11] H. Staudinger and W. Heuer, Ber. der deutschen chem. Gesellschaft, **63**, 222-234 (1930); see also F. W. Billmeyer, Jr., *Textbook of Polymer Science*, Wiley Interscience, New York (1984), 3rd ed.

[12] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953), pp. 310-314; W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.*, **11**, 37-51 (1953); M. Kurata and W. H. Stockmayer, *Adv. Polym. Sci.*, **3**, 196-312 (1963).

generated by taking η' data at various temperatures over a modest frequency range. The above procedure is known as the *method of reduced variables*[13] (the term *time-temperature superposition principle* is also widely used). The function $a_T(T_0)$ has been successfully fitted by the empirical WLF equation:[14]

$$\log a_T = \frac{-c_1^0(T - T_0)}{c_2^0 + (T - T_0)} \tag{15.3-33}$$

in which T_0 is an arbitrary reference temperature, and c_1^0 and c_2^0 are experimentally determined constants. Although the method of reduced variables was developed empirically, it is useful to see how the molecular approach justifies the method.

EXAMPLE 15.3-2 Chain Extension in Steady Shear Flow[15]

In Example 11.4-1 we obtained $\langle r^2\rangle_{eq}$, the average value of the square of the end-to-end distance of a Rouse chain in a dilute solution at equilibrium. Obtain the analogous expression for a Rouse chain in an arbitrary flow field; then obtain $\langle r^2\rangle$ for a steady-state shear flow $v_x = \dot{\gamma}y$, $v_y = v_z = 0$.

SOLUTION First we express $\langle r^2\rangle$ in terms of the normal coordinates introduced in Eq. 15.3-1:

$$\begin{aligned}\langle r^2\rangle &= \langle (\boldsymbol{r}_N - \boldsymbol{r}_1)^2\rangle \\ &= \text{tr} \sum_j \sum_k \langle \boldsymbol{Q}_j \boldsymbol{Q}_k\rangle \\ &= \text{tr} \sum_{jkmn} \Omega_{jm}\Omega_{kn}\langle \boldsymbol{Q}'_m \boldsymbol{Q}'_n\rangle\end{aligned} \tag{15.3-34}$$

From Eq. 15.3-24 we see that

$$\text{tr}\langle \boldsymbol{Q}'_m \boldsymbol{Q}'_n\rangle = \delta_{mn}\,\text{tr}\langle \boldsymbol{Q}'_m \boldsymbol{Q}'_m\rangle \tag{15.3-35}$$

and from Eq. 15.3-14 we get

$$\text{tr}\langle \boldsymbol{Q}'_m \boldsymbol{Q}'_n\rangle = \delta_{mn}\left(\frac{3kT}{H} - \frac{1}{nH}\,\text{tr}\,\boldsymbol{\tau}_m\right) \tag{15.3-36}$$

Next it follows from the integral of Eq. 15.3-16 that $\boldsymbol{\tau}_m$ is given in terms of the flow field by

$$\boldsymbol{\tau}_m = nkT \int_{-\infty}^{t} \frac{1}{\lambda_m} e^{-(t-t')/\lambda_m} \boldsymbol{\gamma}_{[0]}(t, t')dt' \tag{15.3-37}$$

[13] J. D. Ferry, *J. Amer. Chem. Soc.*, **72**, 3746–3752 (1950).

[14] M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701–3707 (1955); for an extensive discussion of the WLF equation see J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York (1980), 3rd ed., Chapter 11, Sections B and C, pp. 273–290. It has been found that for many polymer solutions, if T_0 is taken to be the glass-transition temperature T_g, then $c_1^0 = 17.44$ and $c_2^0 = 51.6$; these constants should not be used above $T_g + 100$.

[15] R. B. Bird, H. H. Saab, P. J. Dotson, and X. J. Fan, *J. Chem. Phys.*, **79**, 5729–5730 (1983).

For steady shear flow tr $\tau_m = -2nkT\lambda_m^2\dot{\gamma}^2$ (see Eq. 13.4-15) so that

$$\begin{aligned}\frac{\langle r^2\rangle}{\langle r^2\rangle_{\text{eq}}} &= 1 - \frac{1}{3(N-1)nkT}\sum_{jkm}\Omega_{jm}\Omega_{km}\,\text{tr}\,\tau_m \\ &= 1 + \frac{2}{3(N-1)}\left(\sum_{jkm}\Omega_{jm}\Omega_{km}\lambda_m^2\right)\dot{\gamma}^2 \\ &= 1 + \frac{2}{3(N-1)}\left(\frac{\zeta}{2H}\right)^2\left(\sum_{jkm}\Omega_{jm}\Omega_{km}c_m^2\right)\dot{\gamma}^2 \\ &= 1 + \frac{2}{3(N-1)}\left(\frac{\zeta}{2H}\right)^2\left(\sum_{ijk}C_{ik}C_{kj}\right)\dot{\gamma}^2 \\ &= 1 + \frac{1}{45}N(N+1)(N^2+1)\lambda_H^2\dot{\gamma}^2 \end{aligned} \tag{15.3-38}$$

where $\lambda_H = \zeta/4H$; here Eq. 11.6-13 has been used, as well as a relation for C_{jk} and c_j similar to Eq. 15.3-3 (see Problem 15D.3). Equation 15.3-38 has been used to check Brownian-dynamics simulations.[16]

§15.4 THE BEAD-SPRING CHAIN WITH HOOKEAN SPRINGS AND EQUILIBRIUM-AVERAGED HYDRODYNAMIC INTERACTION (ZIMM MODEL)

Up to this point in this chapter we have considered "free draining" chains—that is, we have not included the hydrodynamic interactions among the various beads in one chain. In this section we show how this hydrodynamic interaction can be accounted for approximately, by using the equilibrium-averaged Oseen–Burgers tensor, as was originally done by Zimm[1] who was guided by the formalism developed earlier by Kirkwood and collaborators.[2]

We begin by modifying the equations of motion for the beads (Eq. 15.1-1) by including an extra contribution $\boldsymbol{v}'_\nu$ to the fluid velocity at bead ν:

$$-\zeta(\llbracket \dot{\boldsymbol{r}}_\nu \rrbracket - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu] - \boldsymbol{v}'_\nu) - kT\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi + \boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)} = \boldsymbol{0} \tag{15.4-1}$$

The hydrodynamic interaction contribution $\boldsymbol{v}'_\nu$ is presumed to depend linearly on the hydrodynamic forces acting on all the other beads in the chain, the coefficients being the hydrodynamic interaction tensors $\boldsymbol{\Omega}_{\nu\mu}$:

$$\begin{aligned}\boldsymbol{v}'_\nu &= -\sum_\mu [\boldsymbol{\Omega}_{\nu\mu}\cdot\boldsymbol{F}_\mu^{(h)}] \\ &= \sum_\mu\left[\boldsymbol{\Omega}_{\nu\mu}\cdot\left\{-kT\frac{\partial}{\partial \boldsymbol{r}_\mu}\ln\Psi + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}_\mu^{(e)}\right\}\right]\end{aligned} \tag{15.4-2}$$

[16] P. J. Dotson, *J. Chem. Phys.*, **79**, 5730–5731 (1983); H. H. Saab and P. J. Dotson, Univ. of Wisconsin Rheology Research Center Rept. No. 97 (Nov. 1984).

[1] B. H. Zimm, *J. Chem. Phys.*, **24**, 269–278 (1956); for a tabulation of the errata in this paper see J. J. Hermans (Ed.), *Polymer Solutions Properties, Part II, Hydrodynamics and Light Scattering*, Dowdon, Hutchinson, and Ross, Stroudsburg, PA (1978), pp. 83–84.

[2] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).

In the Zimm theory the $\boldsymbol{\Omega}_{\nu\mu}$ are taken to be the Oseen-Burgers tensors:

$$\boldsymbol{\Omega}_{\nu\mu} = \frac{1}{8\pi\eta_s r_{\mu\nu}}\left(\boldsymbol{\delta} + \frac{\boldsymbol{r}_{\mu\nu}\boldsymbol{r}_{\mu\nu}}{r_{\mu\nu}^2}\right) \text{ for } \mu \neq \nu;\ \boldsymbol{\Omega}_{\nu\nu} = \mathbf{0} \tag{15.4-3}$$

Note that the indices on $\boldsymbol{\Omega}_{\nu\mu}$ are labels for the pairs of beads, whose relative locations are given by the vectors $\boldsymbol{r}_{\mu\nu} = \boldsymbol{r}_\nu - \boldsymbol{r}_\mu$. Equations 15.4-1 to 15.4-3 are generalizations of the equations for elastic dumbbells given in Eqs. 13.6-1, 13.6-2, 13.6-4, and 13.6-5.

Combination of the above three equations then gives for the velocity of the νth bead

$$[\![\dot{\boldsymbol{r}}_\nu]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu] + \frac{1}{\zeta}\sum_\mu\left[\boldsymbol{\Upsilon}_{\nu\mu}\cdot\left(-kT\frac{\partial}{\partial\boldsymbol{r}_\mu}\ln\Psi + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}_\mu^{(e)}\right)\right] \tag{15.4-4}$$

in which we have introduced[3] the *dimensionless diffusion tensors* $\boldsymbol{\Upsilon}_{\nu\mu}$:

$$\boldsymbol{\Upsilon}_{\nu\mu} = \delta_{\nu\mu}\boldsymbol{\delta} + \zeta\boldsymbol{\Omega}_{\nu\mu} \tag{15.4-5}$$

Note that both $\boldsymbol{\Omega}_{\nu\mu}$ and $\boldsymbol{\Upsilon}_{\nu\mu}$ are symmetric tensors and in addition symmetric with respect to the indices ν and μ.

The discussion here is restricted to the use of equilibrium-averaged Oseen-Burgers tensors. That is, in Eq. 15.4-5 we replace $\boldsymbol{\Omega}_{\nu\mu}$ by

$$\langle\boldsymbol{\Omega}_{\nu\mu}\rangle_{\text{eq}} = \frac{\int\boldsymbol{\Omega}_{\nu\mu}\Psi_{\text{eq}}\,d\boldsymbol{r}^N}{\int\Psi_{\text{eq}}\,d\boldsymbol{r}^N} = \frac{1-\delta_{\nu\mu}}{6\pi\eta_s}\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{\text{eq}}\boldsymbol{\delta} \tag{15.4-6}$$

Then the dimensionless diffusion tensors become $\boldsymbol{\Upsilon}_{\nu\mu} = H_{\nu\mu}\boldsymbol{\delta}$, where

$$H_{\nu\mu} = \delta_{\nu\mu} + (1-\delta_{\nu\mu})\zeta\frac{1}{6\pi\eta_s}\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{\text{eq}} \tag{15.4-7}$$

are the components of the $N \times N$ *Zimm hydrodynamic interaction matrix*, which is symmetric and nonsingular. The use of equilibrium averaging then allows us to rewrite the expressions for the bead velocities as

$$[\![\dot{\boldsymbol{r}}_\nu]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu] + \frac{1}{\zeta}\sum_\mu H_{\nu\mu}\left[-kT\frac{\partial\ln\Psi}{\partial\boldsymbol{r}_\mu} + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}_\mu^{(e)}\right] \tag{15.4-8}$$

This equation is more complicated than the corresponding "free draining" equation (Eq. 15.1-1), because now the velocity of the νth bead depends on the various forces acting on all of the beads in the chain. This extra coupling can, however, be taken care of without too much difficulty.

[3] The *diffusion tensors* are generally defined as $\boldsymbol{D}_{\nu\mu} = (kT/\zeta)\boldsymbol{\Upsilon}_{\nu\mu}$ but we prefer to use the dimensionless quantities defined in Eq. 15.4-5.

We now want to transform the N equations for the bead velocities to $N-1$ equations for the connector vectors and an additional equation for the motion of the bead-spring chain as a whole (cf. Eqs. 15.1-2 and 15.1-3). The situation is somewhat more complicated than that in §15.1, since when hydrodynamic interaction is included it is found that the center of mass moves relative to the solvent even when there are no external forces acting. Hence, it is conventional to introduce a "(hydrodynamic) center of resistance,"[4] $\boldsymbol{r}_h$, which is defined as that weighted mean of the bead position vectors that has no relative motion with respect to the solvent when there are no external forces. That is, we define:

$$\boldsymbol{r}_h = \sum_v l_v \boldsymbol{r}_v \qquad \left(\sum_v l_v = 1\right) \tag{15.4-9}$$

and then determine the weight factors l_v so that $\boldsymbol{r}_h$ satisfies the definition above. Clearly $l_v = 1/N$ when hydrodynamic interaction is neglected.

We now replace Eqs. 11.6-3 and 11.6-4 by

$$\boldsymbol{Q}_k = \sum_v \bar{B}_{kv} \boldsymbol{r}_v \tag{15.4-10}$$

$$\boldsymbol{r}_v - \boldsymbol{r}_h = \sum_k \tilde{B}_{vk} \boldsymbol{Q}_k \tag{15.4-11}$$

where

$$\bar{B}_{kv} = \delta_{k+1,v} - \delta_{kv} \tag{15.4-12}$$

$$\tilde{B}_{vk} = \begin{cases} \sum_{\mu=1}^{k} l_\mu & k < v \\ -\sum_{\mu=k+1}^{N} l_\mu & k \geq v \end{cases} \tag{15.4-13}$$

Various relations involving the $\bar{B}_{kv}$ and $\tilde{B}_{vk}$ are given in Table 15.4-1. In addition to the above quantities we shall need the $(N-1) \times (N-1)$ modified Kramers and Rouse matrices whose components are

$$\tilde{C}_{ij} = \sum_v \sum_\mu \tilde{B}_{vi} H_{v\mu}^{-1} \tilde{B}_{\mu j} \tag{15.4-14}$$

$$\tilde{A}_{ij} = \sum_v \sum_\mu \bar{B}_{iv} H_{v\mu} \bar{B}_{j\mu} \tag{15.4-15}$$

These matrices become identical to the Kramers and Rouse matrices of Eqs. 11.6-7 and 8 when hydrodynamic interaction is neglected. They are not, however, inverse to one another until we make a particular choice for the l_v after Eq. 15.4-17.

[4] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539–553 (1971); O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498–2501 (1972). In §16.1 and §18.4 a more general discussion is given in which a set of tensors $\boldsymbol{\lambda}_v$ plays a role somewhat related to that of the l_v here.

TABLE 15.4-1[a]

Relations Involving $\bar{B}_{kv}$ and $\tilde{B}_{vk}$

Algebraic relations

$$\sum_v \bar{B}_{kv} = 0 \tag{A}$$

$$\sum_v l_v \tilde{B}_{vk} = 0 \tag{B}$$

$$\sum_v \bar{B}_{jv} \tilde{B}_{vk} = \delta_{jk} \tag{C}$$

$$\sum_k \tilde{B}_{vk} \bar{B}_{k\mu} = \delta_{v\mu} - l_\mu \tag{D}$$

Derivatives of arbitrary functions of the configurational vectors $f(\boldsymbol{r}_h, \boldsymbol{Q}_1, \boldsymbol{Q}_2, \ldots, \boldsymbol{Q}_{N-1}) = g(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$:

$$\frac{\partial f}{\partial \boldsymbol{r}_h} = \sum_v \frac{\partial g}{\partial \boldsymbol{r}_v}; \qquad \frac{\partial f}{\partial \boldsymbol{Q}_k} = \sum_v \tilde{B}_{vk} \frac{\partial g}{\partial \boldsymbol{r}_v} \tag{E}$$

$$\frac{\partial g}{\partial \boldsymbol{r}_v} = l_v \frac{\partial f}{\partial \boldsymbol{r}_h} + \sum_k \bar{B}_{kv} \frac{\partial f}{\partial \boldsymbol{Q}_k} \tag{F}$$

Jacobian relation for the configurational vectors

$$\left| \frac{\partial(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)}{\partial(\boldsymbol{r}_h, \boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_N)} \right| = 1 \tag{G}$$

Relations between the net spring force $\boldsymbol{F}_v^{(\phi)}$ acting on bead v and the force $\boldsymbol{F}_k^{(c)}$ on bead $v = k$ due to the tension in the kth connector.

$$\boldsymbol{F}_v^{(\phi)} = -\sum_k \bar{B}_{kv} \boldsymbol{F}_k^{(c)} = -\frac{\partial \phi}{\partial \boldsymbol{r}_v} \tag{H}$$

$$\boldsymbol{F}_k^{(c)} = -\sum_v \tilde{B}_{vk} \boldsymbol{F}_v^{(\phi)} = +\frac{\partial \phi}{\partial \boldsymbol{Q}_k} \tag{I}$$

[a] For the definitions of the modified Rouse matrix $(\tilde{A}_{ij})$ and the modified Kramers matrix $(\tilde{C}_{ij})$ see Eqs. 15.4-14 and 15.4-15.

With the above definitions and with the help of Table 15.4-1 we may now get an expression for the velocity of the center of resistance and the time rate change of the connector vectors:

$$[\![\dot{\boldsymbol{r}}_h]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_h] - \frac{kT}{\zeta}\sum_\mu\sum_\nu l_\mu l_\nu H_{\nu\mu}\frac{\partial}{\partial \boldsymbol{r}_h}\ln\Psi$$
$$- \frac{1}{\zeta}\sum_k\left\{\sum_\mu\sum_\nu l_\nu H_{\nu\mu}\bar{B}_{k\mu}\right\}\left[kT\frac{\partial}{\partial \boldsymbol{Q}_k}\ln\Psi + \boldsymbol{F}_k^{(c)}\right] + \frac{1}{\zeta}\sum_\nu\sum_\mu l_\nu H_{\nu\mu}\boldsymbol{F}_\mu^{(e)} \quad (15.4\text{-}16)$$

$$[\![\dot{\boldsymbol{Q}}_j]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{Q}_j] - \frac{kT}{\zeta}\left\{\sum_\mu\sum_\nu l_\mu H_{\nu\mu}\bar{B}_{j\nu}\right\}\frac{\partial}{\partial \boldsymbol{r}_h}\ln\Psi$$
$$- \frac{1}{\zeta}\sum_k \tilde{A}_{jk}\left[kT\frac{\partial}{\partial \boldsymbol{Q}_k}\ln\Psi + \boldsymbol{F}_k^{(c)}\right] + \frac{1}{\zeta}\sum_\nu\sum_\mu H_{\nu\mu}\bar{B}_{j\nu}\boldsymbol{F}_\mu^{(e)} \quad (15.4\text{-}17)$$

In these equations the derivatives with respect to $\boldsymbol{Q}_k$ are understood to be taken at constant $\boldsymbol{r}_h$. Since it is assumed that $\Psi(\boldsymbol{r}^N, t) = n\psi(\boldsymbol{Q}^{N-1}, t)$, the derivatives with respect to $\boldsymbol{r}_h$ in the above equations vanish. Then in order that the center of resistance move with the fluid in the absence of any external forces, it is necessary to select the l_ν in such a way that the quantity inside the braces $\{\ \}$ in Eq. 15.4-16 be zero for all values of the index k. With this choice for the l_ν the modified Kramers and Rouse matrices become inverse to one another. The dashed-underlined terms in Eqs. 15.4-16 and 15.4-17 can now be omitted.

The equation of continuity for the distribution function, Eq. 15.1-4, may also be rewritten in terms of the variables $\mathbf{r}_h$ and $\boldsymbol{Q}_k$:

$$\frac{\partial\Psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{r}_h}\cdot[\![\dot{\boldsymbol{r}}_h]\!]\Psi\right) - \sum_j\left(\frac{\partial}{\partial \boldsymbol{Q}_j}\cdot[\![\dot{\boldsymbol{Q}}_j]\!]\Psi\right) \quad (15.4\text{-}18)$$

The term involving the derivative with respect to $\boldsymbol{r}_h$ can be omitted as explained above.

When $[\![\dot{\boldsymbol{Q}}_j]\!]$ from Eq. 15.4-17 is now substituted into Eq. 15.4-18 we obtain the diffusion equation; if we omit the external force terms we get

$$\boxed{\frac{\partial}{\partial t}\psi = -\sum_j\left(\frac{\partial}{\partial \boldsymbol{Q}_j}\cdot\left\{[\boldsymbol{\kappa}\cdot\boldsymbol{Q}_j]\psi - \frac{1}{\zeta}\sum_k\tilde{A}_{jk}\left(kT\frac{\partial}{\partial \boldsymbol{Q}_k}\psi + \boldsymbol{F}_k^{(c)}\psi\right)\right\}\right)} \quad (15.4\text{-}19)$$

This equation is the same as Eq. 15.1-7 except that the Rouse matrix elements A_{jk} have been replaced by the corresponding modified Rouse matrix elements $\tilde{A}_{jk}$ that contain information about the hydrodynamic interaction between the beads.

When the diffusion equation is multiplied by $\sum_j\sum_k \tilde{C}_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k$ and integrated over all the connector vectors $\boldsymbol{Q}_j$, we obtain

$$\left\langle\sum_j\sum_k \tilde{C}_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k\right\rangle_{(1)} = \frac{2kT}{\zeta}(N-1)\boldsymbol{\delta} - \frac{2}{\zeta}\left\langle\sum_k \boldsymbol{F}_k^{(c)}\boldsymbol{Q}_k\right\rangle \quad (15.4\text{-}20)$$

which is analogous to Eq. 15.1-10. Up to this point no assumption has been made regarding the spring force law.

All of the development in §15.3 for the free-draining Rouse chains can now be taken over just by replacing the Rouse and Kramers matrices by the corresponding modified matrices in Eqs. 15.4-14 and 15.4-15, and by making similar replacements for the eigenvalues of the matrices. As a consequence the constitutive equation for the chain with Hookean springs and equilibrium-averaged hydrodynamic interaction can be obtained by making a slight modification of Eq. 15.3-17:[4]

$$\boxed{\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + \int_{-\infty}^{t} \left\{ nkT \sum_j \frac{1}{\tilde{\lambda}_j} e^{-(t-t')/\tilde{\lambda}_j} \right\} \boldsymbol{\gamma}_{[0]}(t, t')dt'} \tag{15.4-21}$$

in which the modified time constants are

$$\tilde{\lambda}_j = \frac{\zeta \tilde{c}_j}{2H} = \frac{\zeta}{2H\tilde{a}_j} \tag{15.4-22}$$

the $\tilde{c}_j$ and $\tilde{a}_j$ being the eigenvalues of the modified Kramers and Rouse matrices respectively.

The only remaining problem is then that of evaluating the eigenvalues of the matrix in Eq. 15.4-15, which in turn contains the Zimm hydrodynamic interaction matrix $H_{\nu\mu}$. From the definition in Eq. 15.4-7 and the expression for $\langle 1/r_{\nu\mu} \rangle_{eq}$ worked out in Eq. 12.5-11 we have

$$H_{\mu\nu} = \delta_{\mu\nu} + (1 - \delta_{\mu\nu})h^* \sqrt{\frac{2}{|\mu - \nu|}} \tag{15.4-23}$$

in which h^* is the dimensionless hydrodynamic interaction parameter[5] given by

$$h^* = \frac{\zeta}{\eta_s} \sqrt{\frac{H}{36\pi^3 kT}} \tag{15.4-24}$$

Next we have to use the above expression for $H_{\nu\mu}$ and the definition of the $\bar{B}_{k\nu}$ from Eq. 15.4-12 in order to construct the elements of the modified matrix $\tilde{A}_{jk}$. Then we have to determine the eigenvalues of this matrix. For $N = 2$ and 3 the eigenvalues can be found analytically (see Problem 15B.2):

$$\begin{aligned} N = 2: \quad & \tilde{a}_1 = 2(1 - \sqrt{2}h^*) \\ N = 3: \quad & \tilde{a}_1 = 1 - h^* \\ & \tilde{a}_2 = 3 + (1 - 4\sqrt{2})h^* \end{aligned} \tag{15.4-25}$$

[5] This h^*, first used by G. B. Thurston and A. Peterlin [*J. Chem. Phys.*, **46**, 4881–4885 (1967)] is related to Zimm's h by $h = \sqrt{N-1}\,h^*$.

For higher values of N the eigenvalues are given in tabular form for various values of N and h^*; for example, for $N = 5$:

$h^* = 0.075$	$h^* = 0.150$	$h^* = 0.250$	
$\tilde{a}_1 = 0.375$	0.367	0.357	
$\tilde{a}_2 = 1.274$	1.166	1.022	(15.4-26)
$\tilde{a}_3 = 2.333$	2.047	1.667	
$\tilde{a}_4 = 3.170$	2.722	2.125	

Several groups of investigators have compiled eigenvalue tables,[6] the most extensive table being that of Sammler, Schrag, and Lodge.[7] For some purposes it is convenient to have available an approximate expression for the eigenvalues, such as Thurston's equation,[8] which reproduces the exact numerical values to within 10% or better:

$$\tilde{a}_j = a_j b\left(\frac{j}{N}\right)^{\sigma} \tag{15.4-27}$$

in which

$$b = 1 - 1.66h^{*0.78} \tag{15.4-28}$$

$$\sigma = -1.40h^{*0.78} \tag{15.4-29}$$

and the a_j are the eigenvalues for the Rouse model given in Eq. 11.6-9.

The inclusion of the equilibrium-averaged hydrodynamic interaction still leads to the method of reduced variables, and furthermore it gives $[\eta] = K'M^a$ with a less than unity in agreement with experimental data (see Problem 15A.2). This noticeable improvement over the Rouse theory is taken as one bit of evidence to support the notion that hydrodynamic interaction is an important effect in the kinetic theory of macromolecular solutions. Other evidence of the importance of hydrodynamic interaction is in the comparison between the Zimm theory and experimental linear viscoelastic data as shown[9] in Fig. 15.4-1. It can be seen that the Zimm theory gives curves that have the same shapes as the curves obtained experimentally. In addition, the inclusion of hydrodynamic interaction gives nearly the correct dependence of translational diffusivity on molecular weight (see Example 15.4-2).

There seems to be general agreement among polymer chemists that the measured oscillatory linear viscoelastic material functions (G' and G'', or η' and η'') have shapes very similar to those computed by the Zimm theory for very dilute solutions in poor solvents. However, as the concentration or solvent power increases, the measured material functions acquire shapes that are more nearly of the form given by the Rouse theory (even though the Rouse theory was intended for dilute solutions). The reason for this unexpected success of

[6] B. H. Zimm, G. M. Roe, and L. F. Epstein, *J. Chem. Phys.*, **24**, 279-280 (1956); G. B. Thurston and J. D. Morrison, *Polymer*, **10**, 421-438 (1969); K. Osaki, *Adv. Polym. Phys.*, **12**, 1-64 (1973); *Macromolecules*, **5**, 141-144 (1972); A. S. Lodge and Y. Wu, University of Wisconsin Rheology Research Center Report No. 16 (1972); A. S. Lodge, University of Wisconsin Rheology Research Center Report No. 19 (1972).

[7] R. L. Sammler, J. L. Schrag, and A. S. Lodge, "Exact Eigenvalue Spectra for Calculation of Dynamic Functions for Dilute Polymer Solutions Based on the Bead-Spring Model: Part I. Linear Homopolymers," Univ. of Wisconsin Rheology Research Center Report No. 82, June 1982.

[8] G. B. Thurston, *Polymer*, **15**, 569-572 (1974).

[9] K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 144-147 (1972).

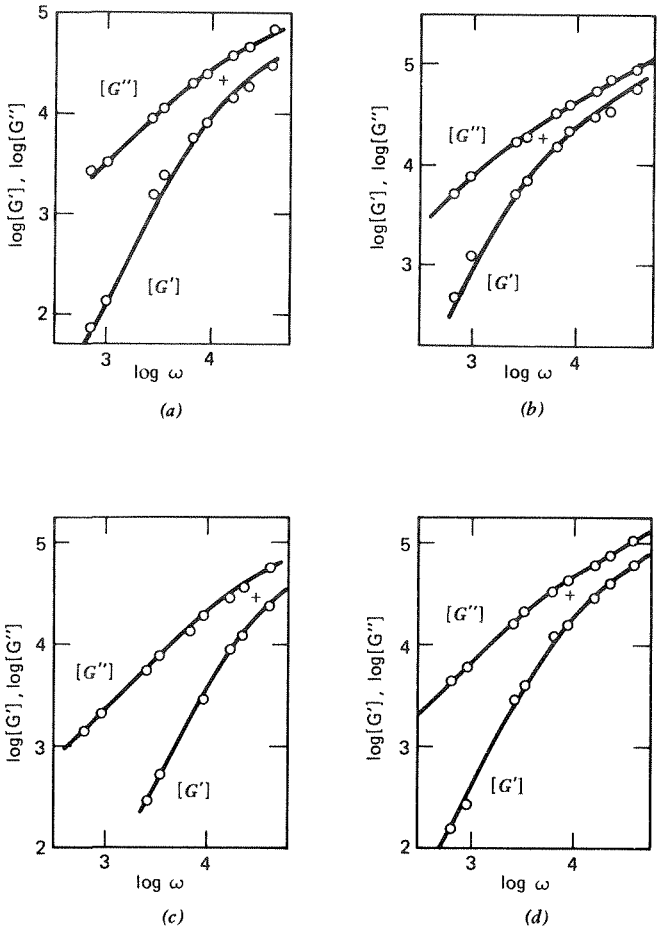


FIGURE 15.4-1. Comparison of the Zimm theory (Eqs. 15.3-29 and 30, with λ_j replaced by the $\tilde{\lambda}_j$ of Eq. 15.4-22) with experimental data. The data are presented in terms of $[G'] = \omega\eta_s[\eta'']$ and $[G''] = \omega\eta_s[\eta']$. In each case N is taken to be 200. The data in (*a*) and (*b*) are those of K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **3**, 144–147 (1972); those in (*c*) and (*d*) were taken from R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Polymer J.*, **1**, 742–749 (1970). On each graph the + sign corresponds to the coordinates λ_1^{-1}, $\tilde{N}kT/M$. The theoretical curves were calculated from the eigenvalues computed by Lodge and Wu.[6] [Reprinted with permission from K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 144–147 (1972). Copyright by the American Chemical Society.]

Graph	Solute	Solvent	Temperature	h^*
(a)	Poly-α-methylstyrene ($M = 1.43 \times 10^6$)	Decalin	298°K	0.2
(b)	Poly-α-methylstyrene ($M = 1.43 \times 10^6$)	α-chloro-naphthalene	298°K	0.1
(c)	Polystyrene ($M = 8.6 \times 10^5$)	Decalin	289°K	0.2
(d)	Polystyrene ($M = 8.6 \times 10^5$)	α-chloro-naphthalene	298°K	0.15

the Rouse theory in concentrated solutions may be because the various parts of one chain are "shielded" from each other by the surrounding polymer molecules.[10]

There have been many modifications of the Rouse–Zimm theory, which are outside the scope of this text. The reviews of Yamakawa,[11] Osaki,[9] Fixman and Stockmayer,[12] and Williams[13] provide convenient guides to the research literature. We just mention here some of the refinements that have been considered:

1. Elimination of the assumption of preaveraging the Oseen tensor.[14,15]
2. Inclusion of the "excluded volume effect.[15,16,17]
3. Modification for polymers that are not chainlike, for example branched polymers[18,19] and ring-shaped polymers.[20,21,22,23,24]
4. Inclusion of "stiffness" by adding a term to the chain potential energy that describes a resistance against the bending of two adjacent links.[25]
5. Inclusion of "internal viscosity" by incorporating dashpots into the molecular model.[5,26,27,28]
6. Inclusion of nonlinear springs in the chain.[29]

[10] K. F. Freed and S. F. Edwards, *J. Chem. Phys.*, **61**, 3626–3633 (1974); F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1619–1637 (1974).

[11] H. Yamakawa, *Modern Theories of Polymer Solutions*, Harper and Row, New York (1971); *Ann. Revs. Phys. Chem.*, **25**, 179–200 (1974).

[12] M. Fixman and W. H. Stockmayer, *Ann. Revs. Phys. Chem.*, **21**, 407–428 (1970).

[13] M. C. Williams, *AIChE J.*, **21**, 1–25 (1975).

[14] This work has been done primarily by Fixman and collaborators: M. Fixman, *J. Chem. Phys.*, **45**, 785–792, 793–803 (1966); C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **42**, 3838–3844 (1965), **44**, 2107–2115 (1966); H. D. Stidham and M. Fixman, *J. Chem. Phys.*, **48**, 3092–3095 (1968). A comparison of theory with experiment has been presented by H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 317; Yamakawa concludes that the Fixman theory underestimates the shear rate dependence of the viscosity. Another comparison between theory and experiment has been given by G. C. Berry and E. F. Casassa, *Macromolecular Reviews*, **4**, 1–66 (1970), pp. 36–38.

[15] R. H. Shafer [*Macromolecules*, **9**, 895–898 (1976)] calculated the normal stress differences in steady shear flow, without preaveraging the Oseen–Burgers tensors, and found that $\Psi_2 = -0.01\,\Psi_1$; this should be compared with the relation $\Psi_2 = -(1/7)\Psi_1$ obtained for rigid rods [T. Kotaka, *J. Chem. Phys.*, **30**, 1566–1567 (1959); see also §16.4]. Experimental data of M. Keentok, A. G. Georgescu, A. A. Sherwood, and R. I. Tanner [*J. Non-Newtonian Fluid Mech.*, **6**, 303–324 (1980)] for 0.2%–7% (by weight) polydisperse polymer solutions give values of $-\Psi_2/\Psi_1$ between 0.065 and 0.30.

[16] A. Peterlin, *J. Chem. Phys.*, **23**, 2464–2465 (1955).

[17] N. W. Tschoegl, *J. Chem. Phys.*, **40**, 473–479 (1964).

[18] J. S. Ham, *J. Chem. Phys.*, **26**, 625–633 (1957).

[19] B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19–42 (1959).

[20] B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301–1314 (1949); V. Bloomfield and B. H. Zimm, *J. Chem. Phys.*, **44**, 315–323 (1966).

[21] J. M. Wiest, S. R. Burdette, T. W. Liu, and R. B. Bird, *J. Non-Newtonian Fluid Mech.* (1987).

[22] M. Kurata, *Bull. Inst. Chem. Res. Kyōto Univ.*, **44**, 150–154 (1966); M. Fukatsu, *loc. cit.*, **43**, 156–166 (1965); M. Fukatsu and M. Kurata, *J. Chem. Phys.*, **44**, 4539–4545 (1966).

[23] G. Tanaka and H. Yamakawa, *Polym. Journal*, **4**, 446–451 (1973).

[24] S. Imai, *J. Chem. Phys.*, **51**, 1732–1741 (1969).

[25] R. A. Harris and J. E. Hearst, *J. Chem. Phys.*, **44**, 2595–2602 (1966); J. E. Hearst, R. A. Harris, and E. Beals, *J. Chem. Phys.*, **45** 3106–3113 (1966). I. Noda and J. E. Hearst, *J. Chem. Phys.*, **54**, 2342–2354 (1971).

[26] R. Cerf, *Adv. Polym. Phys.*, **1**, 382–450 (1959).

[27] A. Peterlin, *J. Polym. Sci.*, **A2**, **5**, 179–193 (1967); A. Peterlin and C. Reinhold, *Trans. Soc. Rheol.*, **11**, 15–37 (1967).

[28] E. R. Bazúa and M. C. Williams, *J. Chem. Phys.*, **59**, 2858–2868 (1973); *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 825–848 (1974).

[29] R. B. Bird, P. J. Dotson, and N. L. Johnson, *J. Non-Newtonian Fluid Mech.*, **7**, 213–235 (1980); errata: *ibid.* (1984) Eq. 58 is incorrect, and all subsequent results are in error; A. Peterlin, *Pure Appl. Chem.*, **12**, 563–586 (1966).

Some of these modifications are taken into account only approximately, and there are points of controversy regarding the nature of the assumptions. These points of disagreement are discussed in the review articles cited earlier. All of the above modifications of the basic theory introduce additional parameters and, consequently, better fitting of the experimental data is claimed. It is probably not possible at the present time to decide whether the alleged more accurate description is a result of a fundamental improvement in the model or simply a result of the greater flexibility of the theoretical functions.

EXAMPLE 15.4-1 Stress Relaxation after Cessation of Steady Homogeneous Flows (Non-Hookean Springs)[4]

Consider a flow system for which $\boldsymbol{v}_0 = \boldsymbol{0}$ and

$$\begin{aligned} \boldsymbol{\kappa} &= \boldsymbol{\kappa}_0 \qquad t \leq 0 \\ \boldsymbol{\kappa} &= \boldsymbol{0} \qquad t > 0 \end{aligned} \tag{15.4-30}$$

Obtain the Hassager-Bird relation between the stresses prior to $t = 0$ and an integral over the stresses from $t = 0$ to $t = \infty$.

SOLUTION We start with Eq. D of Table 15.2-1 with C_{ij} replaced by $\tilde{C}_{ij}$. For $t > 0$ this simplifies to

$$\boldsymbol{\tau} = \frac{n\zeta}{2} \frac{\partial}{\partial t} \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle \tag{15.4-31}$$

When the latter is integrated with respect to time from $t = 0$ to $t = \infty$ we get

$$\int_0^\infty \boldsymbol{\tau}\, dt = -\frac{n\zeta}{2} \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle_{t=0} + A\boldsymbol{\delta} \tag{15.4-32}$$

in which A is a constant. The isotropic term arises from the evaluation of the $\langle\ \rangle$ quantity at $t = \infty$. Then for $t \leq 0$, Eq. D of Table 15.2-1 gives

$$\boldsymbol{\tau} = -\eta_s(\boldsymbol{\kappa}_0 + \boldsymbol{\kappa}_0^\dagger) - \frac{n\zeta}{2} \left\{ \boldsymbol{\kappa}_0 \cdot \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle_{t=0} + \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle_{t=0} \cdot \boldsymbol{\kappa}_0^\dagger \right\} \tag{15.4-33}$$

Since the distribution function is continuous at $t = 0$, the $\langle\ \rangle_{t=0}$ expressions are equal in Eqs. 15.4-32 and 15.4-33. Therefore,

$$(\boldsymbol{\tau})_{t\leq 0} + (\eta_s + A)(\boldsymbol{\kappa}_0 + \boldsymbol{\kappa}_0^\dagger) = \left\{ \boldsymbol{\kappa}_0 \cdot \int_0^\infty \boldsymbol{\tau}(t)dt + \int_0^\infty \boldsymbol{\tau}(t)dt \cdot \boldsymbol{\kappa}_0^\dagger \right\} \tag{15.4-34}$$

For the shearing flow $v_x = \dot{\gamma}_0 y$ between two parallel planes, Eq. 15.4-34 yields[30]

$$(\tau_{xx} - \tau_{yy})_{t\leq 0} = 2\dot{\gamma}_0 \int_0^\infty \tau_{yx}(t)dt \tag{15.4-35}$$

[30] B. D. Coleman and H. Markovitz, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2195-2207 (1974), have shown by continuum mechanics arguments that Eq. 15.4-35 is valid for any incompressible, simple fluid with fading memory, within an error of $O(\dot{\gamma}_0^4)$.

Note that no assumptions have been made about the nature of the spring force $\boldsymbol{F}_k^{(c)}$; hence the springs could be nonlinear. Equation 15.4-35 has not been tested experimentally for dilute polymer solutions.[31]

EXAMPLE 15.4-2 Translational Diffusion for Bead-Spring Chains

Obtain an expression for the average velocity of the center of mass of a polymer molecule moving under the influence of an external force in a fluid that is otherwise at rest. Use the Nernst-Einstein equation to obtain the expression for the translational diffusivity of a bead-spring chain.

SOLUTION Begin by summing Eq. 15.4-8, with $\boldsymbol{\kappa} = \boldsymbol{0}$ and $v_0 = \boldsymbol{0}$ over all beads, and then divide by the total number of beads in the chain to get

$$[\![\dot{\boldsymbol{r}}_c]\!] = \frac{1}{N\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu}\left[-kT\frac{\partial \ln \Psi}{\partial \boldsymbol{r}_\mu} + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}^{(e)}\right] \tag{15.4-36}$$

Here all the forces $\boldsymbol{F}_\mu^{(e)}$ are taken to be the same and equal to $\boldsymbol{F}^{(e)}$. Next use Eqs. G and I of Table 15.1-1 to get

$$[\![\dot{\boldsymbol{r}}_c]\!] = \frac{1}{N\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu}\left[-kT\sum_k \bar{\boldsymbol{B}}_{k\mu}\frac{\partial \ln \Psi}{\partial \boldsymbol{Q}_k} - \sum_k \bar{\boldsymbol{B}}_{k\mu}\boldsymbol{F}_k^{(c)} + \boldsymbol{F}^{(e)}\right] \tag{15.4-37}$$

where $\boldsymbol{F}_k^{(c)}$ is a function of the scalar Q_k multiplied by the vector $\boldsymbol{Q}_k$. Then average over all configurations using the distribution function for a system at equilibrium; when this is done the terms involving the connector vectors $\boldsymbol{Q}_k$ drop out, and we are left with

$$\langle \dot{\boldsymbol{r}}_c \rangle_{eq} = \frac{1}{N\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu}\boldsymbol{F}^{(e)} \tag{15.4-38}$$

If we now define the friction coefficient Z for the entire polymer chain by

$$N\boldsymbol{F}^{(e)} = Z\langle \dot{\boldsymbol{r}}_c \rangle_{eq} \tag{15.4-39}$$

then use of the Nernst-Einstein equation (Eq. 13.6-15) and the equations for $H_{\nu\mu}$ (Eq. 15.4-7) gives for any spring law:

$$\boxed{D_{tr} = \frac{kT}{N^2\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu} = \frac{kT}{N\zeta}\left[1 + \frac{\zeta}{6\pi\eta_s N}\sum_{\substack{\nu}}\sum_{\substack{\mu \\ \nu\neq\mu}}\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{eq}\right]} \tag{15.4-40}$$

[31] E. K. Harris, Jr., Ph.D. Thesis, University of Wisconsin, Madison (1970), found that the experimental values of the right side of Eq. 15.4-35 were 20-100% larger than the experimental values of the left side for 7.5% solutions of polystyrene of various molecular weights in Aroclor. Later measurements on polystyrene melts and concentrated solutions of polyisobutylene in a mineral oil by P. Attane, P. LeRoy, J. M. Pierrard, and G. Turrel [*J. Non-Newtonian Fluid Mech.*, **3**, 1-12 (1977)] and for concentrated solutions of polystyrene in *n*-butylbenzene by H. W. Gao, S. Ramachandran, and E. B. Christiansen [*J. Rheol.*, **25**, 213-235 (1981)] show average deviations from Eq. 15.4-35 of about 5%.

TABLE 15.4-2

Molecular Weight Dependence of Diffusion Coefficient for Very Dilnte Solntions[a,b]

Reference	System	Comments	Exponent b in $D_{tr} \propto M^{-b}$
1.	Polystyrene in cyclohexane	Θ-condition	0.497 ± 0.006
2.	Polystyrene in cyclohexane	Θ-condition	0.49
3.	Polystyrene in benzene	Good solvent	0.55 ± 0.02
4.	Polystyrene in tetrahydrofuran	Good solvent	0.564 ± 0.004
5.	Polystyrene in toluene	Good solvent	0.577
6.	Polystyrene in tetrahydrofuran	Good solvent	0.58
7.	Polystyrene in 2-butanone	Good solvent	0.53 ± 0.02
8.	Polystyrene in tetrahydrofuran	Good solvent	0.533[c]
9.	Poly-α-methylstyrene in toluene and benzene	Good solvent	0.59 ± 0.01

[a] The molecular weight in $D_{tr} \propto M^{-b}$ is the weight-averaged molecular weight.
[b] For a general survey see D. W. Schaefer and C. C. Han, "Quasielastic Light Scattering from Dilute and Semidilute Polymer Solutions", in R. Pecora, ed., *Dynamic Light Scattering: Applications of Photon Spectroscopy*, Plenum Press, New York (1984).
[c] See Problem 15A.3.
1. T. A. King, A. Knox, W. I. Lee, and J. D. G. McAdam, *Polymer*, **14**, 151–155 (1973).
2. H. J. Cantow, *Makromol. Chemie*, **30**, 169–188 (1959).
3. M. Adam and M. Delsanti, *Macromolecules*, **10**, 1229–1237 (1977).
4. W. Mandema and H. Zeldenrust, *Polymer*, **18**, 835–839 (1977).
5. P. N. Pusey, J. M. Vaughan, and G. Williams, *J. Chem. Soc., Faraday Trans. II*, **70**, 1696–1704 (1974).
6. M. E. McDonnell and A. M. Jamieson, *J. Macromol. Sci.-Phys.*, **B13**, 67–88 (1977).
7. N. C. Ford, F. E. Karasz, and J. E. M. Owen, *Disc. Faraday Soc.*, **49**, 228–237 (1970).
8. B. Appelt and G. Meyerhoff, *Macromolecules*, **13**, 657–662 (1980).
9. T. L. Yu, H. Reihanian, and A. M. Jamieson, *Macromolecules*, **13**, 1590–1594 (1980).

This is the Kirkwood expression for the translational diffusivity of chainlike polymers in dilute solution.[32] For very large values of N and Hookean springs it may be shown (see Problem 15D.2) that the translational diffusivity becomes proportional to $N^{-1/2}$. Some sample experimental results are shown in Table 15.4-2. Generalizations of Eq. 15.4-40 are developed in §18.4c.

PROBLEMS

15A.1 Slope of $\log(\eta' - \eta_s)$ vs. $\log \omega$ Curves for Rouse and Zimm Models

Review the discussion leading up to Eqs. 5.3-8 and 9, and the use of Eqs. 5.2-16 and 5.2-17 to give the high-frequency expressions in Eqs. 5.3-14 and 5.3-15.

a. Use the appropriate time constants from the Rouse theory (in Eq. 15.3-19) in Eq. 15.3-29 and obtain the slope of the $\log(\eta' - \eta_s)$ vs. $\log \omega$ curve at high frequency.

b. Use the approximate eigenvalues for the Zimm theory (in Eq. 15.4-27) in Eq. 15.3-29 to obtain the high-frequency slope of the $\log(\eta' - \eta_s)$ vs. $\log \omega$ curve. What value is obtained for $h^* = 0.25$?

[32] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967), pp. 13, 25, 41, 76–77, 95, 101–102; see also H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), pp. 261–262, 273–280. An equation for D_{tr} different from that in Eq. 15.4-40 was obtained by P. Brunn, *J. Chem. Phys.*, **80**, 5821–5826 (1984).

c. Compare the results in **(a)** and **(b)** with the data on $[G'']$ in Fig. 15.4-1 and with η' data for dilute and concentrated solutions in Chapter 3. What do you conclude?

Answers: a. Slope $= -\frac{1}{2}$
b. Slope $= -(1+\sigma)/(2+\sigma)$;
approximately $-\frac{1}{3}$

15A.2 Hydrodynamic Interaction and Deviations from Staudinger's Rule

a. Show that use of Thurston's eigenvalue expression in Eq. 15.4-27 (with a_j given by Eq. 11.6-9) in the Zimm formula for $[\eta]$ (i.e., Eq. 15.3-28 with λ_j replaced by $\tilde{\lambda}_j$) leads to

$$[\eta] = \left(\frac{\zeta \tilde{N} kT}{2\pi^2 H \eta_s b m^{\sigma+2}} \sum_j \frac{1}{j^{2+\sigma}}\right) M^{\sigma+1} \tag{15A.2-1}$$

b. Show that as h^* varies from 0 to 0.25 the molecular-weight dependence[1] of $[\eta]$ varies from M to $\sqrt{M}$. Compare this with Osaki's result[1] that $[\eta] \propto \sqrt{M}$ as $M \to \infty$ for all $h^* > 0$.

15A.3 Molecular Weight Dependence of Translational Diffusivity

The following experimental data[2] were obtained by quasi-elastic light scattering for the translational diffusivity of linear polystyrenes in dilute solutions of tetrahydrofuran at 30°C:

Molecular Weight	D_{tr} ($cm^2 s^{-1}$)
1.8×10^5	3.25×10^{-7}
3.9×10^5	2.48×10^{-7}
3.0×10^6	8.13×10^{-8}
1.0×10^7	4.35×10^{-8}

From these data obtain a power-law expression for diffusivity as a function of molecular weight. Compare the exponent so obtained with that obtained from Eq. 15.4-40.

15B.1 The Configurational Matrices for $N = 3$

a. In §11.6 a number of relations involving matrix elements were given. For the special case that $N = 3$ show that

$$\bar{B}_{kv} = \begin{pmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \end{pmatrix} \tag{15B.1-1}$$

$$B_{vk} = \begin{pmatrix} -\frac{2}{3} & -\frac{1}{3} \\ \frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{2}{3} \end{pmatrix} \tag{15B.1-2}$$

Then verify that Eqs. 11.6-3 through 11.6-15 are correct for $N = 3$, and that all entries in Table 15.1-1 are valid for $N = 3$.

[1] In θ-solvents $[\eta]$ has been found to be proportional to $\sqrt{M}$. For better solvents $[\eta] \propto M^a$ where $a > 0.5$. See the references cited after Eq. 15.3-28 and also I. Noda, K. Mizutani, T. Kato, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 787–794 (1970) and K. Osaki, *Macromolecules*, **5**, 141–144 (1972).

[2] T. L. Yu, H. Reihanian, and A. M. Jamieson, *Macromolecules*, **13**, 1590–1594 (1980).

b. Then show that for $N = 3$

$$\tilde{B}_{vk} = \begin{pmatrix} -l_2 - l_3 & -l_3 \\ l_1 & -l_3 \\ l_1 & l_1 + l_2 \end{pmatrix} \tag{15B.1-3}$$

Show that Eq. D of Table 15.4-1 is valid for $N = 3$. Then show that $\sum_k \tilde{A}_{ik}\tilde{C}_{kj} = \delta_{ij}$ if the $\{\ \}$-factor in Eq. 15.4-16 is zero.

15B.2 Calculation of the Time Constants and Viscosity in the Zimm Model for a Chain with Three Beads

a. Calculate the $\tilde{\lambda}_j$ of Eq. 15.4-22 for the chain with $N = 3$. Use the result in Eq. 15B.1-1 to find

$$(\tilde{A}_{ij}) = \begin{pmatrix} 2(1 - \sqrt{2}h^*) & (2\sqrt{2} - 1)h^* - 1 \\ (2\sqrt{2} - 1)h^* - 1 & 2(1 - \sqrt{2}h^*) \end{pmatrix} \tag{15B.2-1}$$

Then obtain the eigenvalues $\tilde{a}_j$ of this matrix and use them to find the time constants $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$.

b. Are these time constants larger or smaller than the corresponding quantities for the Rouse model where hydrodynamic interaction is neglected? Can one get the Rouse results by setting $h^* = 0$? Is this a legitimate operation?

c. Obtain the expression for the viscosity of a three-bead chain with hydrodynamic interaction in terms of ζ, H, and h^*.

d. Obtain an expression for $\eta'(\omega)$ in terms of $[\eta]$, η_s, M, $\tilde{N}kT$, and h^*.

15B.3 Estimation of Maximum Value of h^* in the Zimm Theory[3]

In the expression for h^* given in Eq. 15.4-24, ζ can be estimated by using Stokes' law $\zeta = 6\pi\eta_s a$, where a is the bead radius. Show further that from the expression in Eq. 11.4-2, the average extension b of a single spring will be approximately $\sqrt{3kT/H}$; what restrictions are placed on this result? Show then that the introduction of a and b into the expression for h^* gives

$$h^* = 0.977(a/b) \tag{15B.3-1}$$

Next require $a < \frac{1}{2}b$ (where does this come from?), and thus obtain an approximate upper limit for the magnitude of h^*.

15B.4 Equilibrium-Averaged Hydrodynamic Interaction and the Hydrodynamic Interaction Center of Resistance

The hydrodynamic interaction center of resistance is defined in Eq. 15.4-9. The l_ν are determined just after Eq. 15.4-17. That is the l_ν must satisfy

$$\sum_\nu l_\nu = 1 \tag{15B.4-1}$$

$$\sum_\mu \sum_\nu l_\nu H_{\nu\mu} \bar{B}_{j\nu} = 0 \tag{15B.4-2}$$

[3] This problem is based on an analysis given by K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 144–147 (1972).

Verify that this set of N equations is satisfied by

$$l_\nu = \frac{\sum_\mu H^{-1}_{\mu\nu}}{\sum_\mu \sum_\eta H^{-1}_{\mu\eta}} \tag{15B.4-3}$$

15B.5 Transformation of the Force-Balance Equations

The equation of motion for bead ν (or force-balance equation) is given in Eq. 15.1-1.

a. Use Eq. 15.1-1 to get Eq. 15.1-2 for the mean motion of the center of mass by summing on ν and dividing by N. This leads directly to the $[\![\dot{r}_c]\!]$, v_0, $[\kappa \cdot r_c]$, and external force terms in Eq. 15.1-2. The Brownian motion terms drop out by the use of $\Psi = n\psi$ and Eqs. A and G of Table 15.1-1. Why do the $F_\nu^{(\phi)}$ terms drop out?

b. Next in Eq. 15.1-1 substitute $r_\nu = r_c + \sum_k B_{\nu k} Q_k$ and use Eqs. G and I of Table 15.1-1. This gives after using the result of (**a**):

$$\sum_k B_{\nu k}[\![\dot{Q}_k]\!] = \left[\kappa \cdot \sum_k B_{\nu k} Q_k\right] - \frac{1}{\zeta}\sum_k \bar{B}_{k\nu}\left[kT\frac{\partial \ln \psi}{\partial Q_k} + F_k^{(c)}\right] + \frac{1}{\zeta}F_\nu^{(e)} - \frac{1}{N\zeta}\sum_\nu F_\nu^{(e)} \tag{15B.5-1}$$

Then multiply by $\bar{B}_{j\nu}$ and sum on ν to get Eq. 15.1-3, after using Eq. 11.6-8 and Eq. C of Table 15.1-1.

15C.1 Derivation of the Flory-Fox Equation from the Zimm Model

For many polymer-solvent systems the Flory-Fox relation[4]

$$[\eta]_0 = \Phi \frac{\langle r^2\rangle_{eq}^{3/2}}{M} \tag{15C.1-1}$$

holds, provided that $M > 10^6$. The constant Φ is nearly a universal constant, equal to about 2.5×10^{23} or $0.42\,\tilde{N}$ (where $\tilde{N}$ is Avogadro's number), when the root-mean-square end-to-end distance $\langle r^2\rangle^{1/2}$ is given in cm and $[\eta_0]$ is in cm^3/g.

Show that the Flory-Fox equation can be obtained from the bead-spring chain model of Zimm if h^* is taken to be 0.267. To do this use Eq. 15.3-25 with the $\tilde{\lambda}_j$ of Eq. 15.4-22, and Eq. 15.4-27 describing the $\tilde{a}_j$. If the exact Zimm eigenvalues are used (instead of Eq. 15.4-27), then it can be shown[5] that $\Phi \doteq 0.474\tilde{N}$ for all values of h^* in the limit as $M \to \infty$.

15D.1 Single-Link Distribution Function for the Rouse Chain[6]

a. The configurational distribution function $\psi(Q^{N-1}, t)$ for a Rouse chain is given by Eqs. 15.3-7, 15.3-23, and 15.3-24. By integrating as described in Eq. 12.5-2 obtain the single-link distribution function $\psi_j(Q, t)$ for link j:

$$\psi_j(Q, t) = \frac{(H/2\pi kT)^{3/2}}{\sqrt{\det \sigma_j}} \exp\left[-\left(\frac{H}{2kT}\right)(\sigma_j^{-1} : QQ)\right] \tag{15D.1-1}$$

[4] P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904–1908 (1951); P. J. Flory, *op. cit.*, pp. 616–620; W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1–179 (1974); H. Yamakawa, *Modern Theories of Polymer Solutions*, Harper and Row, New York (1971), p. 365.

[5] H. C. Öttinger, to be published (1987).

[6] H. H. Saab, X. J. Fan, P. J. Dotson, and R. B. Bird, University of Wisconsin Rheology Research Center Report No. 97 (November 1984).

where

$$\sigma_j = \sum_k \Omega_{jk}^2 \alpha_k \tag{15D.1-2}$$

and α_k is given in terms of the finite strain tensor in Eq. 15.3-23. *Caution*: The distribution function $\psi_j(Q, t)$ is not to be confused with the $\psi_j(Q'_j, t)$ introduced in Eq. 15.3-7.

b. How do the results in (**a**) simplify at equilibrium?

c. Use (**a**) to get an expression for the average value of the square of the end-to-end distance of link j.

15D.2 Derivation of the Molecular-Weight Dependence of the Translational Diffusivity

Verify the statement after Eq. 15.4-40 that the Zimm theory predicts that the translational diffusivity is inversely proportional to the square root of the molecular weight. Use Eq. 12.5-11 for $\langle 1/r_{\mu\nu}\rangle_{eq}$ and then replace the double sum in Eq. 15.4-40 by a double integral. Consider chains with very large N, and retain only the terms containing the highest powers of N. Show that this leads to

$$\sum_\nu \sum_\mu \left\langle \frac{1}{r_{\mu\nu}} \right\rangle_{eq} \doteq \frac{8}{3}\sqrt{\frac{2H}{\pi kT}}\, N^{3/2} \tag{15D.2-1}$$

and that $D_{tr} \propto M^{-1/2}$.

15D.3 Relations Involving Matrices and Eigenvalues

Verify that for the Kramers matrix (C_{ij}) with eigenvalues c_j:

$$\sum_j C_{jj} = \sum_j c_j \tag{15D.3-1}$$

$$\sum_j C_{ij} C_{jk} = \sum_j c_j^2 \Omega_{ij} \Omega_{jk}^{-1} \tag{15D.3-2}$$

To get the second of these write Eq. 15.3-3 (in terms of C_{jk} and c_j) twice: once for free indices ip, and once for iq. When the two equations are multiplied together one gets

$$\sum_j \sum_k \sum_m \sum_n \Omega_{ij}^{-1} C_{jk} \Omega_{kp} \Omega_{im}^{-1} C_{mn} \Omega_{nq} = c_i^2 \delta_{ip} \delta_{iq} \tag{15D.3-3}$$

Perform the sum on i; then multiply by $\Omega_{rp}\Omega_{qs}^{-1}$ and sum on p and q to get the desired result. Equation 15D.3-2 is used in Eq. 15.3-38.

CHAPTER 16

GENERAL BEAD-ROD-SPRING MODELS

In Chapter 13 we set up the kinetic theory equations for elastic dumbbells, explaining thoroughly the origins of the terms in the diffusion equation for the configurational distribution function as well as the various forms for the stress-tensor expression. In Chapter 15 the kinetic theory was extended to linear bead-spring chains, the main new idea being the introduction of normal coordinates; the latter was systematized by the introduction of several sets of matrices that facilitated coordinate transformations and other operations. In Chapter 14 we dealt with the kinetic theory of rigid dumbbells and multibead-rods; we did not show in detail how to set up the kinetic theory equations, pointing out only that since the models in that chapter involved constraints (fixed interbead distances), special techniques would have to be developed later (in Chapters 17 and 18) to handle such models.

We have thus seen examples of models with and without constraints. In each of these chapters we have also seen modeling both with and without hydrodynamic interaction (the latter having received attention in §§13.6, 14.6, and 15.4). Most of the time we took the Stokes' law friction coefficient to be a scalar, but in §13.7 we examined the possibility of tensor friction coefficients. In the preceding three chapters we took the beads to be identical (as to mass and friction coefficient), but an obvious generalization would be to allow each bead in the model to have a different mass m_ν and friction coefficient ζ_ν. Thus far we have considered only linear arrangements of beads, and we have considered fluids containing only one polymer species, which, in addition, is monodisperse.

In Chapters 17 and 18 we set up the kinetic theory equations for mixtures and we include polydispersity. We allow for much more general models, with beads different, nonlinear bead arrangements, tensor friction coefficients, and beads of finite size in space; we also allow for hydrodynamic interaction. The development of the kinetic theory to that degree of generality is a long and arduous process. Since some readers will not wish to work through the details, we give in this chapter some of the key kinetic theory results for dilute solutions including (a) arbitrary bead-rod-spring models, (b) mixtures, (c) hydrodynamic interactions, and (d) structureless beads (i.e., point masses) that may have different masses and (scalar) friction coefficients. That is, the kinetic theory results we cite here are somewhat less general than those developed in Chapters 17 and 18 but much more general than those of the preceding three chapters. All of the key kinetic theory equations—diffusion equations and stress tensor expressions—given for the simple models of Chapters 13-15 (except for §13.7) are special cases of general equations summarized here.

In §16.1 we begin by systematizing the notation that we need in this chapter for handling complex molecular models and for including hydrodynamic interaction. In §§16.2 and 3 we present, respectively, the diffusion equation and the stress-tensor expressions. Then in §16.4 we show how to get the second-order fluid constants for arbitrary bead-rod-spring models (with and without hydrodynamic interaction). Next, in §§16.5 and 6, we

discuss the two important bead-rod-chain models: the freely jointed (Kramers) chain and the freely rotating (Kirkwood–Riseman) chain. Finally in §16.7 we discuss other kinds of bead-rod models.

§16.1 SUMMARY OF NOTATION

In this section we deal with three types of notational problems: (a) the development of systematic notation appropriate for describing the geometry of bead-rod-spring models when the first three generalized coordinates are the Euler angles, which specify the overall orientation of the model in space; (b) the presentation of some matrices and tensors that facilitate the formulation of kinetic theory equations for bead-rod-spring models including hydrodynamic interaction (complete or equilibrium averaged); and (c) the notation for various kinds of forces—generalized, effective, and true forces—that will be used in Chapters 17–19 and that allow some kinetic theory results to be written in more concise forms.

a. Use of Euler Angles

As discussed in §12.1, the configuration of an arbitrary molecular model made up of mass points may be described by a set of generalized coordinates Q_s. The number of coordinates required is determined by the model, but the particular choice of coordinates is arbitrary. For some molecular models the evaluation of the base vectors $\boldsymbol{b}_{vs}$, defined by Eq. 12.1-6, and the matrix components g_{st}, defined by Eq. 12.1-7, can be simplified somewhat by treating the overall orientation in space separately. To do this we introduce a coordinate system embedded in the model in an arbitrary but well-defined manner, with a set of orthogonal unit vectors $\check{\boldsymbol{\delta}}_1, \check{\boldsymbol{\delta}}_2, \check{\boldsymbol{\delta}}_3$ in the directions of the axes $\check{x}, \check{y}, \check{z}$ of the embedded frame. The orientation of this frame with respect to the fixed frame with unit vectors $\boldsymbol{\delta}_1, \boldsymbol{\delta}_2, \boldsymbol{\delta}_3$ is described by

$$\check{\boldsymbol{\delta}}_m = \sum_n \Omega_{mn} \boldsymbol{\delta}_n \tag{16.1-1}$$

where the Ω_{mn} are given in terms of the Euler angles α, β, γ in matrix form as follows:

$$(\Omega_{mn}) = \begin{pmatrix} cC\phi - s\$ & sC\phi + c\$ & -S\phi \\ -cC\$ - s\phi & -sC\$ + c\phi & S\$ \\ cS & sS & C \end{pmatrix} \tag{16.1-2}$$[1]

with s, S, \$ denoting $\sin\alpha$, $\sin\beta$, $\sin\gamma$ and c, C, ϕ denoting $\cos\alpha$, $\cos\beta$, $\cos\gamma$. The geometrical interpretation of the Euler angles is discussed in §E.11.

The Euler angles may then be taken to be the first three generalized coordinates. If this is done, then, $Q_1 = \alpha$, $Q_2 = \beta$, $Q_3 = \gamma$ describe the orientation of the model in space and $Q_4, Q_5, Q_6, \ldots, Q_d$ are the remaining coordinates needed to specify the configuration of the model in the embedded coordinate system. The bead locations are then given by the three

[1] Note that the Ω_{mn} are the components of a 3×3 matrix describing rotations in a 3-dimensional space, whereas the Ω_{jk} of Eq. 15.3-1 are the components of an $(N-1) \times (N-1)$ matrix. Note further that the $\boldsymbol{\Omega}_{v\mu}$ of Eq. 15.4-2 form an $N \times N$ matrix of tensors (the "hydrodynamic interaction tensors"); when these tensors are equilibrium averaged, we write $\langle \boldsymbol{\Omega}_{v\mu} \rangle_{eq} = \Omega_{v\mu}\, \boldsymbol{\delta}$, where the $\Omega_{v\mu}$ form an $N \times N$ matrix of scalars.

Euler angles and the components R_{vm}, of $\boldsymbol{R}_v$, with respect to the embedded frame defined by $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$, so that

$$\boldsymbol{R}_v = \sum_m R_{vm}\check{\boldsymbol{\delta}}_m \tag{16.1-3}$$

and thus

$$\boldsymbol{R}_v = \sum_m \sum_n R_{vm}\Omega_{mn}\boldsymbol{\delta}_n \tag{16.1-4}$$

Note that the Ω_{mn} are functions only of Q_1, Q_2, and Q_3, whereas the R_{vm} depend only on Q_4, Q_5, Q_6, ... It is this separation that is important.

The systematization of the formulas for the various configurational quantities is then made possible by the introduction of the (Λ_{ut}) matrix defined by:[2]

$$\Lambda_{ut} = \begin{cases} \frac{1}{2}\sum_m \sum_n \sum_p \varepsilon_{umn}\Omega_{np}\dfrac{\partial \Omega_{mp}}{\partial Q_t} & t, u \leq 3 \\ \delta_{ut} & t, u \geq 4 \\ 0 & \text{otherwise} \end{cases} \tag{16.1-5}$$

This matrix and its inverse are given as follows[3] in terms of the Euler angles β and γ:

$$(\Lambda_{ut}) = \left(\begin{array}{ccc:ccccc} -S\not{c} & \$ & 0 & & & & & \\ S\$ & \not{c} & 0 & & & 0 & & \\ C & 0 & 1 & & & & & \\ \hdashline & & & 1 & 0 & 0 & \cdots & \\ & 0 & & 0 & 1 & 0 & \cdots & \\ & & & 0 & 0 & 1 & \cdots & \\ & & & \vdots & \vdots & \vdots & & \end{array}\right) \tag{16.1-6}$$

$$(\Lambda_{ut}^{-1}) = \left(\begin{array}{ccc:ccccc} -S^{-1}\not{c} & S^{-1}\$ & 0 & & & & & \\ \$ & \not{c} & 0 & & & 0 & & \\ S^{-1}C\not{c} & -S^{-1}C\$ & 1 & & & & & \\ \hdashline & & & 1 & 0 & 0 & \cdots & \\ & 0 & & 0 & 1 & 0 & \cdots & \\ & & & 0 & 0 & 1 & \cdots & \\ & & & \vdots & \vdots & \vdots & & \end{array}\right) \tag{16.1-7}$$

[2] The permutation symbol ε_{mnp} is 1 if mnp is a cyclic permutation of 123; -1 if mnp is a cyclic permutation of 321; and 0 otherwise. See §A.2 for additional information.

[3] Λ_{ut} means the ut-component of the matrix, and (Λ_{ut}) stands for the matrix. Λ_{ut}^{-1} means the ut-component of the inverse matrix.

The (Λ_{ut})-matrix may now be used to develop a formula for the vectors $\boldsymbol{b}_{vt}$

$$
\begin{aligned}
\boldsymbol{b}_{vt} &= \sqrt{m_v}\,\frac{\partial}{\partial Q_t}\boldsymbol{R}_v \\
&= \sqrt{m_v}\,\frac{\partial}{\partial Q_t}\sum_m\sum_n R_{vm}\Omega_{mn}\boldsymbol{\delta}_n \\
&= \begin{cases} \sqrt{m_v}\displaystyle\sum_m\sum_n R_{vm}\left(\frac{\partial \Omega_{mn}}{\partial Q_t}\right)\boldsymbol{\delta}_n & t \le 3 \\ \sqrt{m_v}\displaystyle\sum_m\sum_n \left(\frac{\partial R_{vm}}{\partial Q_t}\right)\Omega_{mn}\boldsymbol{\delta}_n & t \ge 4 \end{cases} \\
&= \begin{cases} \sqrt{m_v}\displaystyle\sum_m\sum_n R_{vm}\left(\sum_p\sum_u \varepsilon_{mpu}\Lambda_{ut}\Omega_{pn}\right)\boldsymbol{\delta}_n & t \le 3 \\ \sqrt{m_v}\displaystyle\sum_m\sum_n\sum_u \Lambda_{ut}\left(\frac{\partial R_{vm}}{\partial Q_u}\right)\Omega_{mn}\boldsymbol{\delta}_n & t \ge 4 \end{cases} \\
&= \begin{cases} \displaystyle\sum_m\sum_n\sum_u \Lambda_{ut}\left[\sqrt{m_v}\sum_p R_{vp}\varepsilon_{pmu}\right]\Omega_{mn}\boldsymbol{\delta}_n & t \le 3 \\ \displaystyle\sum_m\sum_n\sum_u \Lambda_{ut}\left[\sqrt{m_v}\left(\frac{\partial R_{vm}}{\partial Q_u}\right)\right]\Omega_{mn}\boldsymbol{\delta}_n & t \ge 4 \end{cases} \\
&= \sum_m\sum_n\sum_u \Lambda_{ut}b^{vum}\Omega_{mn}\boldsymbol{\delta}_n
\end{aligned}
\tag{16.1-8}
$$

where

$$
b^{vum} = \begin{cases} \sqrt{m_v}\displaystyle\sum_p R_{vp}\varepsilon_{pmu} & u \le 3 \\ \sqrt{m_v}\left(\dfrac{\partial R_{vm}}{\partial Q_u}\right) & u \ge 4 \end{cases}
\tag{16.1-9}
$$

Note that Λ_{ut} and Ω_{mn} depend only on the Euler angles, that is, Q_1, Q_2, Q_3, whereas the b^{vum} depend only on $Q_4, Q_5, Q_6, \ldots$. It may then be shown that

$$
g_{tu} = \sum_v\sum_w \Lambda_{vt}\Gamma_{vw}\Lambda_{wu}
\tag{16.1-10}
$$

where

$$
\Gamma_{uv} = \sum_v\sum_m b^{vum}b^{vvm}
\tag{16.1-11}
$$

are the elements of a generalized moment of inertia matrix. From this expression it follows that

$$
G_{tu} = \sum_v\sum_w \Lambda_{tv}^{-1}\Gamma_{vw}^{-1}\Lambda_{uw}^{-1}
\tag{16.1-12}
$$

where the Λ_{tv}^{-1} are the elements of the inverse matrix given by Eq. 16.1-7 and the Γ_{vw}^{-1} are the elements of the inverse of the generalized moment of inertia matrix. For some molecular models one may choose the embedded "body-fixed" coordinate system so that this (Γ_{vw}) matrix is diagonal and thus easily inverted. In the use of these models it is then particularly convenient to use the Euler angles as generalized coordinates.

In Table 16.1-1 we summarize the notation presented here; the general expressions are given, and also the special expressions when Q_1, Q_2, Q_3 are taken to be α, β, γ. The symbols in Table 16.1-1 are used to describe geometrical properties of a particular molecular species. Whenever it is necessary to distinguish among various species in a mixture, Greek superscripts are appended; for example, we write $\boldsymbol{R}_v^\alpha$, $\boldsymbol{b}_{vs}^\alpha$, g_{st}^α, and so on, for species α.

b. Hydrodynamic Interaction

The *hydrodynamic interaction tensors* $\boldsymbol{\Omega}_{v\mu}$ were introduced in Eq. 15.4-2 for bead-spring chains (and also earlier in Eq. 13.6-3 and below Eq. 14.6-1 for dumbbells). Specific forms for these tensors were also introduced: the Oseen–Burgers tensors, in Eqs. 13.6-5 and 15.4-3; and the Rotne–Prager–Yamakawa tensors, in Eq. 14.6-2. In §15.4 we also defined the dimensionless diffusion tensors $\boldsymbol{\Upsilon}_{v\mu}$, the Zimm hydrodynamic interaction matrix $H_{v\mu}$, and the weight factors l_v. In this section we define generalizations of these three quantities and some additional symbols that are helpful in systematizing the setting up of kinetic theory equations for mixtures, for more complex models, and for models with hydrodynamic interaction. The detailed development that leads to the notation summarized here is given in Chapters 17 and 18, and hence occasionally we refer ahead to equations where a fuller discussion is provided.

In the development of the kinetic theory the "hydrodynamic" force, $\boldsymbol{F}_v^{(h)\alpha}$, on bead v of a molecule of solute species α due to the surrounding solvent molecules is approximated by an expression similar to Stokes' law (Eq. 18.2-1) involving a set of friction tensors ζ_v^α. In this chapter the beads are taken to be mass points, and consequently we take these friction tensors to be isotropic, so that $\boldsymbol{\zeta}_v^\alpha = \zeta_v^\alpha \boldsymbol{\delta}$. In the expression for the hydrodynamic force, the effect of hydrodynamic interaction is described by a set of tensors, $\boldsymbol{\Omega}_{v\mu}^\alpha$. In the "free-draining" approximation (i.e., no hydrodynamic interaction) these tensors are taken to be the null tensor.

The *dimensionless diffusion tensors* are defined (Eq. 18.2-4, see also Eq. 15.4-5) as

$$\boldsymbol{\Upsilon}_{v\mu}^\alpha = \delta_{v\mu}\boldsymbol{\delta} + \zeta_v^\alpha \boldsymbol{\Omega}_{v\mu}^\alpha \tag{16.1-13}$$

and the *dimensionless mobility tensors*, $\mathbf{B}_{v\mu}^\alpha$, are defined by the condition that

$$\sum_\mu (\mathbf{B}_{v\mu}^\alpha \cdot \boldsymbol{\Upsilon}_{\mu\eta}^\alpha) = \delta_{v\eta}\boldsymbol{\delta} \tag{16.1-14}$$

The tensors $\boldsymbol{\Omega}_{v\mu}^\alpha$ and $\mathbf{B}_{v\mu}^\alpha$ are symmetric tensors and also invariant under the permutation of the subscripts. In the approximation that the hydrodynamic interaction tensors are equilibrium averaged, $\boldsymbol{\Omega}_{v\mu}^\alpha$ is replaced by $\langle \boldsymbol{\Omega}_{v\mu}^\alpha \rangle_{\text{eq}} = \Omega_{v\mu}^\alpha \boldsymbol{\delta}$, that defines the scalar quantities

TABLE 16.1-1

Notation for Coordinates and Related Quantities for Bead-Rod-Spring Models

m_v = mass of vth bead
$\boldsymbol{r}_v$ = position of vth bead
$\boldsymbol{r}_c$ = position vector of center of mass $= \sum_v m_v \boldsymbol{r}_v / \sum_v m_v$
$\boldsymbol{R}_v = \boldsymbol{r}_v - \boldsymbol{r}_c$ = position vector of vth bead with respect to the center of mass (with components X_{vn} in an arbitrary space-fixed coordinate system, and R_{vn} in an embedded coordinate system).
Q_s = sth generalized coordinate
Λ_{st} = components of the matrix defined in Eq. 16.1-5
Ω_{mn} = components of the matrix defined in Eq. 16.1-2

Quantity	General Expressions	Special Expressions When Q_1, Q_2, Q_3 Are Taken to be the Euler Angles α, β, γ
Position vectors	$\boldsymbol{R}_v = \sum_n X_{vn} \boldsymbol{\delta}_n$ (A)	$\boldsymbol{R}_v = \sum_m \sum_n R_{vm} \Omega_{mn} \boldsymbol{\delta}_n$ (F)
Base vectors	$\boldsymbol{b}_{vs} = \sqrt{m_v}\, \dfrac{\partial}{\partial Q_s} \boldsymbol{R}_v$ (B)	$\boldsymbol{b}_{vs} = \sum_m \sum_n \sum_t \Lambda_{ts} b^{vtm} \Omega_{mn} \boldsymbol{\delta}_n$ (G)
Configurational matrix components	...	$b^{vtm} = \begin{cases} \sqrt{m_v} \sum_n R_{vn} \varepsilon_{nmt} & t \le 3 \\ \sqrt{m_v}\, \dfrac{\partial}{\partial Q_t} R_{vm} & t \ge 4 \end{cases}$ (H)
Covariant metric matrix components	$g_{st} = \sum_v (\boldsymbol{b}_{vs} \cdot \boldsymbol{b}_{vt})$ (C)	$g_{st} = \sum_u \sum_v \Lambda_{us}\, \Gamma_{uv} \Lambda_{vt}$ (I)
Generalized moment of inertia tensor components	...	$\Gamma_{uv} = \sum_v \sum_n b^{vun} b^{vvn}$ (J)
Contravariant metric matrix components	$G_{st} = g_{st}^{-1}$ (D)	$G_{st} = \sum_u \sum_v \Lambda_{su}^{-1} \Gamma_{uv}^{-1} \Lambda_{tv}^{-1}$ (K)
Determinant of the covariant metric matrix	$g = \det(g_{st})$ (E)	$g = \sin^2\beta \det(\Gamma_{uv})$ (L)

Note: Λ_{st}^{-1} means the st-component of the matrix inverse to the matrix (Λ_{st}).

$\Omega^{\alpha}_{\nu\mu}$. Thus when equilibrium averaging is used, the dimensionless diffusion and mobility tensors are isotropic:

$$\text{Equilibrium Averaged H.I.: } \Upsilon^{\alpha}_{\nu\mu} = (\delta_{\nu\mu} + \zeta^{\alpha}_{\nu}\Omega^{\alpha}_{\nu\mu})\boldsymbol{\delta} = H^{\alpha}_{\nu\mu}\boldsymbol{\delta} \tag{16.1-15}$$

$$\text{Equilibrium Averaged H.I.: } \mathbf{B}^{\alpha}_{\nu\mu} = B^{\alpha}_{\nu\mu}\boldsymbol{\delta} \tag{16.1-16}$$

in which $(H^{\alpha}_{\nu\mu})$ is the *Zimm hydrodynamic interaction matrix* and $(B^{\alpha}_{\nu\mu})$ is the *dimensionless mobility matrix*. These matrices are inverse to one another; when hydrodynamic interaction is neglected, both of these matrices become the $N \times N$ unit matrix $(\delta_{\nu\mu})$. Note that in Eq. 16.1-13 we have written ζ^{α}_{ν}, indicating that the bead friction coefficients may depend on the bead number ν and the species α.

When complete hydrodynamic interaction is included the appropriate generalization of the scalar weight factors l_{ν} is a set of *weight tensors* $\boldsymbol{\lambda}^{\alpha}_{\nu}$ (Eq. 18.2-7) defined by

$$\boldsymbol{\lambda}^{\alpha}_{\nu} = \left\{(\mathbf{Z}^{\alpha})^{-1} \cdot \sum_{\mu} \boldsymbol{\zeta}^{\alpha}_{\mu\nu}\right\} \tag{16.1-17}$$

where $\mathbf{Z}^{\alpha}$ is the *total effective friction tensor*

$$\mathbf{Z}^{\alpha} = \sum_{\nu}\sum_{\mu} \boldsymbol{\zeta}^{\alpha}_{\nu\mu} = \sum_{\nu}\sum_{\mu} \zeta^{\alpha}_{\mu}\mathbf{B}^{\alpha}_{\nu\mu} \tag{16.1-18}$$

and the $\boldsymbol{\zeta}^{\alpha}_{\nu\mu}$ are the *effective friction tensors*. These quantities are summarized in Table 16.1-2, and simplified forms for equilibrium-averaged hydrodynamic interaction and no hydrodynamic interaction are given. In the table the species index α is omitted.

Along toward the end of Table 16.1-2 we give modifications of the metric matrix components g_{st} and G_{st} (see Table 16.1-1) that enable us to include hydrodynamic interaction formally in the diffusion equation. These *modified metric matrix components* $\tilde{g}^{\alpha}_{st}$ and $\tilde{G}^{\alpha}_{st}$ are given in terms of the *modified effective friction tensors* $\tilde{\boldsymbol{\zeta}}^{\alpha}_{\nu\mu}$. The latter quantities are also useful for obtaining a compact formula for the *coupling tensors* $\mathbf{M}^{\alpha}_{s}$, which, in the diffusion equation, appear "coupled" with the $\boldsymbol{\kappa}$-tensor through a double-dot product.

The notation summarized in Table 16.1-2 is very compact, and in §§16.2 and 16.3 it permits us to present some very general kinetic theory equations in an efficient way. Simplified equations for equilibrium-averaged or no hydrodynamic interaction are easily obtained by using the last two columns of Table 16.1-2. We conclude this discussion with two examples to illustrate the use of Table 16.1-1; Table 16.1-2 is used in Example 16.2-1.

EXAMPLE 16.1-1 Calculations of Configurational Quantities for the Multibead-Rod Model

Obtain the quantities listed in Eqs. A–E of Table 16.1-1 for the rigid multibead-rod model shown in Fig. 14.1-2. We need some of these quantities in Examples 16.2-1 and 16.3-1.

SOLUTION As generalized coordinates we take Q_1 and Q_2 to be θ and ϕ, the angles describing the direction of the unit vector along the rod. Then, as indicated in Fig. 14.1-2, the locations of the N beads are given by the following position vectors with respect to the center of mass:

$$\boldsymbol{R}_{\nu} = \tfrac{1}{2}a\nu\boldsymbol{u} \qquad (\nu = -(N-1), -(N-3), -(N-5), \ldots, +(N-1)) \tag{16.1-19}$$

Diffusion and Mobility Tensors and Related Quantites (With Complete Hydrodynamic Interaction and Equilibrium-Averaged Hydrodynamic Interaction)

The dimensionless diffusion and mobility tensors are related by $\sum_\eta \{\mathbf{B}_{\nu\eta} \cdot \boldsymbol{\Upsilon}_{\eta\mu}\} = \delta_{\nu\mu}\boldsymbol{\delta}$; the hydrodynamic interaction matrix and the mobility matrix are related by $\sum_\eta B_{\nu\eta}H_{\eta\mu} = \delta_{\nu\mu}$; and the modified metric matrix components are related by $\sum_t \tilde{g}_{st}\tilde{G}_{tu} = \delta_{su}$.

Quantity	Symbol	With Complete Hydrodynamic Interaction		With Equilibrium-Averaged Hydrodynamic Interaction		With no Hydrodynamic Interaction and Identical Beads	
Dimensionless diffusion tensors	$\boldsymbol{\Upsilon}_{\nu\mu}$	$\delta_{\nu\mu}\boldsymbol{\delta} + \zeta_\nu \boldsymbol{\Omega}_{\nu\mu}$	(A)	$(\delta_{\nu\mu} + \zeta_\nu \boldsymbol{\Omega}_{\nu\mu})\boldsymbol{\delta} = H_{\nu\mu}\boldsymbol{\delta}$	(I)	$\delta_{\nu\mu}\boldsymbol{\delta}$	(R)
Dimensionless mobility tensors	$\mathbf{B}_{\nu\mu}$	Definition given implicitly above		$B_{\nu\mu}\boldsymbol{\delta}$	(J)	$\delta_{\nu\mu}\boldsymbol{\delta}$	(S)
Effective friction tensors	$\boldsymbol{\zeta}_{\nu\mu}$	$\zeta_\mu \mathbf{B}_{\nu\mu}$	(B)	$\zeta_\mu B_{\nu\mu}\boldsymbol{\delta}$	(K)	$\zeta\delta_{\nu\mu}\boldsymbol{\delta}$	(T)
Total effective friction tensor	$\mathbf{Z}$	$\sum_\nu \sum_\mu \boldsymbol{\zeta}_{\nu\mu}$	(C)	$\sum_\nu \sum_\mu \zeta_\mu B_{\nu\mu}\boldsymbol{\delta} \equiv Z\boldsymbol{\delta}$	(L)	$N\zeta\boldsymbol{\delta}$	(U)
Weight tensors	$\boldsymbol{\lambda}_\nu$	$\left\{\mathbf{Z}^{-1} \cdot \sum_\mu \boldsymbol{\zeta}_{\mu\nu}\right\}$	(D)	$\dfrac{\sum_\mu \zeta_\mu B_{\nu\mu}}{\sum_\nu \sum_\mu \zeta_\mu B_{\nu\mu}}\boldsymbol{\delta} \equiv l_\nu\boldsymbol{\delta}$	(M)	$\dfrac{1}{N}\boldsymbol{\delta}$	(V)
Modified effective friction tensors	$\tilde{\boldsymbol{\zeta}}_{\nu\mu}$	$\boldsymbol{\zeta}_{\nu\mu} - \{\boldsymbol{\lambda}_\nu^\dagger \cdot \mathbf{Z} \cdot \boldsymbol{\lambda}_\mu\}$	(E)	$(B_{\nu\mu}\zeta_\mu - Zl_\nu l_\mu)\boldsymbol{\delta} \equiv \tilde{\zeta}_{\nu\mu}\boldsymbol{\delta}$	(N)	$\left(\delta_{\nu\mu} - \dfrac{1}{N}\right)\zeta\boldsymbol{\delta}$	(W)
Coupling tensors	$\mathbf{M}_s$	$\sum_\nu \sum_\mu \dfrac{1}{\sqrt{m_\nu}}\{\boldsymbol{R}_\mu \boldsymbol{b}_{\nu s} \cdot \tilde{\boldsymbol{\zeta}}_{\nu\mu}\}$	(F)	$\sum_\nu \sum_\mu \dfrac{\tilde{\zeta}_{\nu\mu}}{\sqrt{m_\nu}}\boldsymbol{R}_\mu \boldsymbol{b}_{\nu s}$	(O)	$\dfrac{\zeta}{\sqrt{m}}\sum_\nu \boldsymbol{R}_\nu \boldsymbol{b}_{\nu s}$	(X)
Modified covariant metric matrix components	$\tilde{g}_{st}$	$\sum_\nu \sum_\mu \dfrac{1}{\sqrt{m_\nu m_\mu}}(\boldsymbol{b}_{\nu s} \cdot \tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{b}_{\mu t})$	(G)	$\sum_\nu \sum_\mu \dfrac{\tilde{\zeta}_{\nu\mu}}{\sqrt{m_\nu m_\mu}}(\boldsymbol{b}_{\nu s} \cdot \boldsymbol{b}_{\mu t})$	(P)	$\dfrac{\zeta}{m}g_{st}$	(Y)
Modified contravarant metric matrix components	$\tilde{G}_{st}$	Definition given implicitly above		Definition given implicitly above		$\dfrac{m}{\zeta}G_{st}$	(Z)
Modified reciprocal base vectors	$\boldsymbol{a}_{\nu s}$	$\sum_t \sum_\mu \dfrac{1}{\sqrt{m_\nu m_\mu}}\tilde{G}_{st}[\tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{b}_{\mu t}]$	(H)	$\sum_t \sum_\mu \dfrac{1}{\sqrt{m_\nu m_\mu}}\tilde{G}_{st}\zeta_{\nu\mu}\boldsymbol{b}_{\mu t}$	(Q)	$\sum_t G_{st}\boldsymbol{b}_{\nu t}$	(AA)

Then the base vectors are obtained from Eq. B of Table 16.1-1 as

$$\boldsymbol{b}_{vs} = \sqrt{m}\frac{\partial}{\partial Q_s}(\tfrac{1}{2}av\boldsymbol{u}) = \tfrac{1}{2}\sqrt{m}\,av\boldsymbol{c}_s \tag{16.1-20}$$

in which the $\boldsymbol{c}_s$ are vectors defined in Table E.5-1. Next the matrices (g_{st}) and (G_{st}) are obtained from Eqs. C and D of Table 16.1-1

$$\begin{aligned}(g_{st}) &= \tfrac{1}{4}ma^2\left(\sum_{-(N-1)}^{+(N-1)} v^2\right)\begin{pmatrix}1 & 0\\ 0 & \sin^2\theta\end{pmatrix}\\ &= \tfrac{1}{12}ma^2N(N^2-1)\begin{pmatrix}1 & 0\\ 0 & \sin^2\theta\end{pmatrix}\end{aligned} \tag{16.1-21}$$

$$(G_{st}) = \frac{12}{ma^2N(N^2-1)}\begin{pmatrix}1 & 0\\ 0 & 1/\sin^2\theta\end{pmatrix} \tag{16.1-22}$$

Finally from Eq. E

$$g = \det(g_{st}) = (\tfrac{1}{12}ma^2N(N^2-1)\sin\theta)^2 \tag{16.1-23}$$

For the rigid dumbbell, $N = 2$, and $g = \frac{1}{4}m^2a^4\sin^2\theta$.

EXAMPLE 16.1-2 Calculation of Configurational Quantities for the Three-Bead-Two-Rod Model

Find the various configurational quantites for the short Kramers chain depicted in Fig. 16.1-1.

SOLUTION This model consists of three beads of equal masses and equal friction coefficients connected by two rigid rods of length a, freely jointed at the middle bead. To specify the location of the beads we introduce a set of orthogonal unit vectors $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$ with origin at the center of mass (Fig. 16.1-1). The vectors are oriented such that the plane of the three beads coincides with that given by $\check{\boldsymbol{\delta}}_2$ and $\check{\boldsymbol{\delta}}_3$ and such that $\check{\boldsymbol{\delta}}_3$ bisects the angle between the two links. As generalized coordinates for the description of the orientation and relative internal configuration of the model we use the three Euler angles $Q_1 \equiv \alpha$, $Q_2 \equiv \beta$, $Q_3 \equiv \gamma$ specifying the orientation of triad $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$ with respect to a space-fixed coordinate system, and the coordinate $Q_4 \equiv \chi$, the angle between the two links. The ranges of these coordinates are

$$\begin{aligned}0 \le \alpha < 2\pi \qquad & 0 \le \beta \le \pi\\ 0 \le \gamma < 2\pi \qquad & 0 \le \chi \le \pi\end{aligned}$$

The position vectors of the three beads may now be expressed by

$$\boldsymbol{R}_1 = a(\tfrac{1}{3}\mathrm{K}\check{\boldsymbol{\delta}}_3 - \Sigma\check{\boldsymbol{\delta}}_2) \tag{16.1-24}$$

$$\boldsymbol{R}_2 = -\tfrac{2}{3}a\mathrm{K}\check{\boldsymbol{\delta}}_3 \tag{16.1-25}$$

$$\boldsymbol{R}_3 = a(\tfrac{1}{3}\mathrm{K}\check{\boldsymbol{\delta}}_3 + \Sigma\check{\boldsymbol{\delta}}_2) \tag{16.1-26}$$

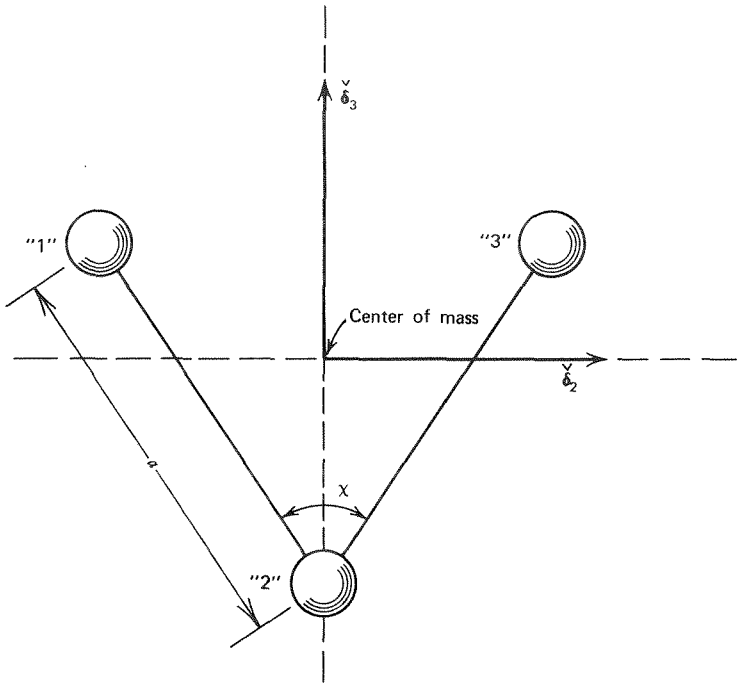


FIGURE 16.1-1. The unit vectors $\check{\delta}_2$ and $\check{\delta}_3$ embedded in the model of three beads and two rigid links. The center of mass is at the origin, and the plane given by $\check{\delta}_2$ and $\check{\delta}_3$ coincides with that determined by the three beads; $\check{\delta}_1$ is not shown, but is oriented such that $\check{\delta}_1, \check{\delta}_2, \check{\delta}_3$ form a right-handed set of orthonormal vectors.

where $\mathrm{K} = \cos(\chi/2)$ and $\Sigma = \sin(\chi/2)$. Hence the matrix with components $R_{\nu m}$ is

$$(R_{\nu m}) = a\begin{pmatrix} 0 & -\Sigma & \frac{1}{3}\mathrm{K} \\ 0 & 0 & -\frac{2}{3}\mathrm{K} \\ 0 & \Sigma & \frac{1}{3}\mathrm{K} \end{pmatrix} \tag{16.1-27}$$

The $R_{\nu m}$ are defined in Eq. F of Table 16.1-1.

Furthermore from Eq. H of Table 16.1-1 we find that

$$-3b^{112} = 3b^{121} = \tfrac{3}{2}b^{212} = -\tfrac{3}{2}b^{221} = -3b^{312} = 3b^{321}$$
$$= 2b^{342} = -2b^{142} = \sqrt{m}a\mathrm{K} \tag{16.1-28}$$

$$-b^{113} = b^{131} = b^{313} = -b^{331} = -6b^{143} = -6b^{343}$$
$$= 3b^{243} = \sqrt{m}a\Sigma \tag{16.1-29}$$

The 21 other $b^{\nu\mu m}$ are zero. It then follows from the definition of Γ_{uv} in Eq. J of Table 16.1-1 that

$$(\Gamma_{uv}) = ma^2\begin{pmatrix} \frac{2}{3}\mathrm{K}^2 + 2\Sigma^2 & 0 & 0 & 0 \\ 0 & \frac{2}{3}\mathrm{K}^2 & 0 & 0 \\ 0 & 0 & 2\Sigma^2 & 0 \\ 0 & 0 & 0 & \frac{1}{2}\mathrm{K}^2 + \frac{1}{6}\Sigma^2 \end{pmatrix} \tag{16.1-30}$$

The metric matrix components g_{tu} may then be found from Eq. I. From Eq. L it is found that the determinant is

$$g = \det(g_{tu})$$
$$= \tfrac{4}{27} m^4 a^8 (\sin^2 \chi)(1 - \tfrac{1}{4}\cos^2 \chi)\sin^2 \beta \tag{16.1-31}$$

Since in this example the generalized moment of inertia tensor in Eq. J is diagonal, it may easily be inverted. One then finds from Eq. K that the elements of the inverse metric matrix are

$$ma^2 G_{11} = \frac{3}{2}\frac{K^2 + 3\Sigma^2 \$^2}{K^2 S^2 (1 + 2\Sigma^2)} \tag{16.1-32}$$

$$ma^2 G_{22} = \frac{3}{2}\frac{K^2 + 3\Sigma^2 \not{c}^2}{K^2 (1 + 2\Sigma^2)} \tag{16.1-33}$$

$$ma^2 G_{33} = \frac{3}{2}\frac{C^2}{S^2}\frac{K^2 + 3\Sigma^2 \$^2}{K^2 (1 + 2\Sigma^2)} + \frac{1}{2\Sigma^2} \tag{16.1-34}$$

$$ma^2 G_{44} = \frac{6}{1 + 2K^2} \tag{16.1-35}$$

$$ma^2 G_{12} = \frac{9}{2}\frac{\Sigma^2 \$ \not{c}}{K^2 S (1 + 2\Sigma^2)} \tag{16.1-36}$$

$$G_{23} = -C G_{12} \tag{16.1-37}$$

$$G_{13} = -C G_{11} \tag{16.1-38}$$

$$G_{14} = G_{24} = G_{34} = 0 \tag{16.1-39}$$

The expressions developed in this example should be compared with those obtained in Example 12.1-1, in which the same molecular model is considered using a different set of configuration coordinates. In particular one may compare the determinants of the metric matrices, g, as given by Eqs. 12.1-17 and 16.1-31. The ratio of the square roots of these two expressions is the Jacobian of the transformation from one set of coordinates to the other set (see Eq. 12.3-4b).

c. Types of Forces

In §13.1 four kinds of forces acting on the beads were described, and in Eq. 13.2-1 these forces were combined in a "force balance." Explicit expressions for these forces were then given in Eqs. 13.2-2 to 4. No particular problems were encountered in writing the force balance or the expressions for the forces inasmuch as the system under consideration (the elastic-dumbbell model) contained no constraints.

In §14.2, on the other hand, we dealt with a system containing a constraint (the rigid-dumbbell model). There we had to be careful to "project out" the θ- and ϕ-components in writing the force balance.

In Chapters 17–19 in the formal kinetic theory for arbitrary models with constraints it is convenient and natural to work with *generalized forces* $\mathscr{F}_s^{(\ )}$, one associated with each

TABLE 16.1-3

Notation for Forces used in Chapters 16–19

	Forces in the Force Balance				
	(1) Hydrodynamic Forces	(2) Brownian Forces	(3) Intramolecular Forces	(4) External Forces	Sum of Forces in (1)–(4)
Generalized forces associated with degree of freedom s	$\mathscr{F}_s^{(h)}$	$\mathscr{F}_s^{(b)}$	$\mathscr{F}_s^{(\phi)}$	$\mathscr{F}_s^{(e)}$	0
Effective forces[a] associated with bead v	$\mathscr{F}_v^{(h)}$	$\mathscr{F}_v^{(b)}$	$\mathscr{F}_v^{(\phi)}$	$\mathscr{F}_v^{(e)}$	**0**
Effective total forces[b] exerted on bead v	$\boldsymbol{F}_v^{(h)}$	$\boldsymbol{F}_v^{(b)}$	$\boldsymbol{F}_v^{(\phi)}$	$\boldsymbol{F}_v^{(e)}$	**0**, if there are no constraints
True forces[c] on entire molecule	$\boldsymbol{F}^{(h)}$	$\boldsymbol{F}^{(b)}$	**0**	$\boldsymbol{F}^{(e)}$	**0**, for dilute solutions

[a] The effective forces, the effective total forces, and the generalized forces are related by

$$\begin{cases} \mathscr{F}_v^{(\ )} = \sqrt{m_v} \sum_s \sum_t \mathscr{F}_s^{(\ )} G_{st} \boldsymbol{b}_{vt} \\ \mathscr{F}_s^{(\ )} = \sum_v \dfrac{1}{\sqrt{m_v}} (\boldsymbol{b}_{vs} \cdot \boldsymbol{F}_v^{(\ )}) \end{cases} \tag{A}$$

[b] The effective total forces and the effective forces are related by

$$\boldsymbol{F}_v^{(h)} = \mathscr{F}_v^{(h)} + (m_v/m_p)\boldsymbol{F}^{(h)} \quad \text{(for dilute solutions of models with } \textit{no constraints} \text{ only; see Eq. 18.1-16 with } \bar{N} = 1) \tag{B}$$

$$\boldsymbol{F}_v^{(b)} = \mathscr{F}_v^{(b)} + (m_v/m_p)\boldsymbol{F}^{(b)} \quad \text{(cf. Eq. 18.3-13)} \tag{C}$$

$$\boldsymbol{F}_v^{(\phi)} = \mathscr{F}_v^{(\phi)} \quad \text{(because the total intramolecular force is zero)} \tag{D}$$

$$\boldsymbol{F}_v^{(e)} = \mathscr{F}_v^{(e)} + (m_v/m_p)\boldsymbol{F}^{(e)} \quad \text{(cf. Eq. 18.4-12)} \tag{E}$$

For models with no constraints the effective forces and the effective total forces, $\mathscr{F}_v^{(\phi)}$, $\mathscr{F}_v^{(e)}$, $\boldsymbol{F}_v^{(\phi)}$, $\boldsymbol{F}_v^{(e)}$ are true forces derivable from potentials (see Example 17.2-1), and the Brownian forces $\mathscr{F}_v^{(b)}$, $\boldsymbol{F}_v^{(b)}$ are derivable in an analogous sense from $\ln \Psi$.

[c] Note that $\boldsymbol{F}^{(\ )} = \sum_v \boldsymbol{F}_v^{(\ )}$, and that $\boldsymbol{F}^{(\phi)} \equiv \boldsymbol{0}$. Three of these relations follow immediately from Eqs. C, D, and E above; for the $\boldsymbol{F}_v^{(h)}$ relation see Eq. 18.1-9, which is true without the restrictions stated above for Eq. B.

internal degree of freedom, s, of the molecular model, where ( ) can stand for (h), (b), (ϕ), or (e), the forces associated with hydrodynamic drag, Brownian motion, intramolecular potentials, or external force fields. Closely associated with these generalized forces are the *effective forces* $\mathscr{F}_v^{(\ )}$, and the *effective total forces* $\boldsymbol{F}_v^{(\ )}$, one associated with each bead v.

In Table 16.1-3 we summarize the notation and give some of the most important relations connecting the various forces. In Chapters 17 and 18 precise definitions are given, and the notation for generalized and effective forces enables us to write many kinetic theory relations in compact forms that bring out the physical meanings of the equations. A few of these symbols are used in §§16.2 and 16.3.

§16.2 THE "DIFFUSION EQUATION" FOR THE CONFIGURATIONAL DISTRIBUTION FUNCTION

We recall from chapters 13, 14, and 15 that there are two main parts to the kinetic theory of macromolecular solutions: the establishment and solution of a partial differential equation for ψ, and the development of an expression for the stress tensor involving average values that are integrals containing ψ. For complex macromolecules the same two problems are confronted; in this section we deal with the diffusion equation for ψ, and in the following section we focus our attention on the stress-tensor expression.

In the foregoing chapters we made use of an *equation of continuity* in the configuration space: Eq. 13.2-12 for elastic dumbbells; Eq. 14.2-7 for rigid dumbbells; Eq. 15.1-6 for Rouse chains. All of these are special cases of a more general equation, derived in Chapter 17, and given there as Eq. 17.5-14. If the external forces depend only on the configuration coordinates Q_s^α (that is, they are independent of the center of mass coordinates r_c^α), then this equation becomes

$$\frac{\partial}{\partial t}\psi_\alpha = -\sum_s \frac{\partial}{\partial Q_s^\alpha}(\llbracket \dot{Q}_s \rrbracket^\alpha \psi_\alpha) \tag{16.2-1}$$

The index α indicates that the quantity pertains to solute species α in a multicomponent solution; the solute may be either a mixture of different chemical species or a polydisperse mixture of a single chemical species.

Next we need an expression for $\llbracket \dot{Q}_s \rrbracket^\alpha$, the momentum-space-averaged generalized velocity. It is shown later (see Eq. 18.2-42) that[1]

$$\llbracket \dot{Q}_s \rrbracket^\alpha = -\sum_t \tilde{G}_{st}^\alpha (\mathscr{F}_t^{(h)\alpha} - \mathbf{M}_t^\alpha : \boldsymbol{\kappa}) \tag{16.2-2}$$

in which $\tilde{G}_{st}^\alpha$ and $\mathbf{M}_t^\alpha$ are quantities given in Table 16.1-2 and $\mathscr{F}_t^{(h)\alpha}$ is a "generalized hydrodynamic force" associated with the tth degree of freedom of the macromolecular model. Equation 16.2-2 is valid for any model, with or without constraints, and with or without hydrodynamic interaction. This equation can be regarded as a "turned-wrong-side-out" version of the general Stokes-law expression in Eq. 16.3-3. As discussed in §18.2 it is convenient to introduce the generalized hydrodynamic forces $\mathscr{F}_s^{(h)\alpha}$ in the solution of the Stokes-law equations, since the number of these generalized forces is the same as the

[1] Equation 16.2-1 is the generalization of the continuity equation in Eq. 13.2-12 for elastic dumbbells and Eq. 14.2-7 for rigid dumbbells. Equation 16.2-2 is the generalization of the components of

$$\llbracket \dot{\boldsymbol{Q}} \rrbracket = -\frac{1}{\zeta}(\boldsymbol{F}_2^{(h)} - \boldsymbol{F}_1^{(h)}) + [\boldsymbol{\kappa}\cdot\boldsymbol{Q}] \tag{16.2-2a}$$

which is obtained from the two equations in Eq. 13.2-2 for elastic dumbbells without hydrodynamic interaction. The analogous equation for rigid dumbbells is

$$\llbracket \dot{\boldsymbol{u}} \rrbracket = \left(-\frac{1}{\zeta L}(\boldsymbol{F}_1^{(h)} - \boldsymbol{F}_{-1}^{(h)}) + [\boldsymbol{\kappa}\cdot\boldsymbol{u}]\right)\cdot(\boldsymbol{\delta} - \boldsymbol{uu}) \tag{16.2-2b}$$

which is obtained by projecting out the θ and ϕ components from the difference of the two Stokes-law equations given in Eq. 14.2-4. By starting with Eq. 14.6-10 the hydrodynamic-interaction analog of Eq. 16.2-2b is obtained.

number of generalized velocities $[\![\dot{Q}_s]\!]$, whereas the number of effective total forces $\boldsymbol{F}_v^{(h)}$ is larger.

Next the generalized hydrodynamic force $\mathscr{F}_t^{(h)\alpha}$ can be eliminated by using a *force-balance equation* (or equation of motion), which is (see Eq. 17.5-15)

$$\mathscr{F}_t^{(h)\alpha} + \mathscr{F}_t^{(\phi)\alpha} + \mathscr{F}_t^{(b)\alpha} + \mathscr{F}_t^{(e)\alpha} = 0 \tag{16.2-3}$$

in which

$$\mathscr{F}_t^{(\phi)\alpha} = -\frac{\partial}{\partial Q_t^\alpha}\phi^\alpha \tag{16.2-4}$$

is the generalized spring force associated with the intramolecular potential ϕ^α, and $\mathscr{F}_t^{(b)\alpha}$ and $\mathscr{F}_t^{(e)\alpha}$ are the generalized Brownian and external forces respectively; when equilibration in momentum space is assumed the generalized Brownian force is

$$\mathscr{F}_t^{(b)\alpha} = -kT\frac{\partial}{\partial Q_t^\alpha}\ln\left(\frac{\psi_\alpha}{\sqrt{g_\alpha}}\right) \tag{16.2-5}$$

When $\mathscr{F}_t^{(h)\alpha}$ from the above equation is inserted into Eq. 16.2-2, and $[\![\dot{Q}_s]\!]^\alpha$ from that equation is substituted into Eq. 16.2-1, we get

$$\frac{\partial}{\partial t}\psi_\alpha = -\sum_s\sum_t \frac{\partial}{\partial Q_s^\alpha}\left\{\tilde{G}_{st}^\alpha\left[(\mathbf{M}_t^\alpha : \boldsymbol{\kappa})\psi_\alpha - kT\sqrt{g_\alpha}\frac{\partial}{\partial Q_t^\alpha}\left(\frac{\psi_\alpha}{\sqrt{g_\alpha}}\right) - \left(\frac{\partial\phi^\alpha}{\partial Q_t^\alpha}\right)\psi_\alpha + \mathscr{F}_t^{(e)\alpha}\psi_\alpha\right]\right\}$$

Hydrodynamic | Brownian | Intramolecular | External

(16.2-6)

This is the *diffusion equation* for the configurational distribution function ψ_α for solute species α in a multicomponent solution. It includes the effects of hydrodynamic interaction (complete or equilibrium averaged), external forces that do not depend on the center-of-mass location, and beads with differing masses and friction coefficients; it contains Eqs. 13.2-13, 14.6-13, and 15.1-7 as special cases. Let us now list the assumptions inherent in Eq. 16.2-6: (i) dilute solution, (ii) equilibration in momentum space, (iii) homogeneous macroscopic flow field, (iv) mass-times-acceleration terms omitted in the equation of motion for the beads (i.e., no inertial effects), and (v) structureless beads.

If the effective friction tensors, $\zeta_{v\mu}$, are diagonal and constant, as in the approximation of equilibrium-averaged hydrodynamic interaction, or if hydrodynamic interaction is neglected, then (see Table 16.1-2, Eq. F)

$$\mathbf{M}_s + \mathbf{M}_s^\dagger = \frac{\partial}{\partial Q_s}\mathbf{K} \tag{16.2-7}$$

where $\mathbf{K}$ is the *structure tensor*

$$\mathbf{K} = \sum_v\sum_\mu \tilde{\zeta}_{v\mu}\boldsymbol{R}_\mu\boldsymbol{R}_v \tag{16.2-8}$$

Thus for potential flows, that is flows described by a symmetric $\boldsymbol{\kappa}$,

$$(\boldsymbol{\kappa}:\mathbf{M}_s) = \frac{1}{2}\left(\boldsymbol{\kappa}:\frac{\partial}{\partial Q_s}\mathbf{K}\right) = \frac{1}{2}\frac{\partial}{\partial Q_s}(\boldsymbol{\kappa}:\mathbf{K}) \tag{16.2-9}$$

From this it follows that for *steady state, homogeneous, potential flows, and equilibrium-averaged (or no) hydrodynamic interaction* the solution to Eq. 16.2-6 is

$$\boxed{\psi_\alpha = \frac{1}{J_\alpha}\sqrt{g_\alpha}\exp[\tfrac{1}{2}(\boldsymbol{\kappa}:\mathbf{K}^\alpha) - \phi^\alpha - \phi^{(e)\alpha}]/kT} \tag{16.2-10}$$

where J_α is the normalization constant; it is assumed here that the generalized external force $\mathscr{F}_t^{(e)\alpha}$ is derivable from a potential: $\mathscr{F}_t^{(e)\alpha} = -\partial\phi^{(e)\alpha}/\partial Q_t^\alpha$. Equation 16.2-10 may be verified by introducing this ψ_α into Eq. 16.2-5; then the generalized force-balance equation gives

$$\mathscr{F}_s^{(h)\alpha} = (\mathbf{M}_s^\alpha:\boldsymbol{\kappa}) \tag{16.2-11}$$

and hence, from Eq. 16.2-2, $[\![\dot{Q}_s]\!] = 0$.

EXAMPLE 16.2-1 The Diffusion Equation for the Orientational Distribution Function for the Multibead-Rod Model

Develop the explicit form of the diffusion equation, Eq. 16.2-6, for the multibead-rod model described in §14.1, including complete hydrodynamic interaction using the Rotne–Prager–Yamakawa interaction tensors.

SOLUTION For the multibead-rod model the Rotne–Prager–Yamakawa hydrodynamic interaction tensors[2] may be written in the form

$$\boldsymbol{\Omega}_{\nu\mu} = \Omega_{\nu\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + \Omega_{\nu\mu}^{(2)}\boldsymbol{uu} \tag{16.2-12}$$

$$\Omega_{\nu\mu}^{(1)} = \frac{(1-\delta_{\nu\mu})}{4\pi a\eta_s|\nu-\mu|}\left[1 + \frac{2\xi^2}{3(\nu-\mu)^2}\right] \tag{16.2-13}$$

$$\Omega_{\nu\mu}^{(2)} = \frac{(1-\delta_{\nu\mu})}{2\pi a\eta_s|\nu-\mu|}\left[1 - \frac{2\xi^2}{3(\nu-\mu)^2}\right] \tag{16.2-14}$$

where ξ is the ratio of the diameter of the spheres to the distance between the spheres, a; the parameter ξ goes from 0 (mass points) to 1 (osculating spheres). If $\xi = 0$ the Oseen–Burgers tensors are obtained.

From Table 16.1-2, Eq. A, one finds that the dimensionless diffusion tensors are

$$\boldsymbol{\Upsilon}_{\nu\mu} = \delta_{\nu\mu}\boldsymbol{\delta} + \zeta\Omega_{\nu\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + \zeta\Omega_{\nu\mu}^{(2)}\boldsymbol{uu} \tag{16.2-15}$$

where ζ is the friction coefficient of a bead. Since the dimensionless mobility tensors $\mathbf{B}_{\nu\mu}$ are functions of the unit vector $\boldsymbol{u}$ only, they must be linear combinations of the unit tensor $\boldsymbol{\delta}$ and the dyad $\boldsymbol{uu}$. Thus we write these tensors in the form

$$\mathbf{B}_{\nu\mu} = B_{\nu\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + B_{\nu\mu}^{(2)}\boldsymbol{uu} \tag{16.2-16}$$

[2] The expressions given here for $\boldsymbol{\Omega}_{\nu\mu}$ simplify to the tensor $\boldsymbol{\Omega}$ in Eq. 14.6-2 by setting $\nu = -1$ and $\mu = +1$, and replacing a by L

One then finds from the definition of these tensors that

$$\sum_{\eta} B_{\nu\eta}^{(k)}[\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}^{(k)}] = \delta_{\nu\mu} \qquad (k = 1, 2) \tag{16.2-17}$$

These equations may be solved for the coefficients $B_{\nu\mu}^{(k)}$. It turns out, however, that we need evaluate only certain sums of the coefficients (see Eq. 14.6-18), and hence we define

$$B_{\mu}^{(k)} = \tfrac{1}{2}\sum_{\nu} \nu B_{\nu\mu}^{(k)} \qquad (k = 1, 2) \tag{16.2-18}$$

and similarly

$$\mathbf{B}_{\mu} = \tfrac{1}{2}\sum_{\nu} \nu \mathbf{B}_{\nu\mu} = B_{\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + B_{\mu}^{(2)}\boldsymbol{uu} \tag{16.2-19}$$

The $B_{\mu}^{(k)}$ are then determined by the equations

$$\sum_{\eta} B_{\eta}^{(k)}[\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}^{(k)}] = \tfrac{1}{2}\mu \tag{16.2-20}$$

Explicit solutions of these equations have been developed by Bird and Curtiss[3] for $N \leq 5$, with $\xi \neq 0$, and for $N = 6$ and 7 with $\xi = 0$. In particular one finds that for $N = 2$

$$B_1^{(1)} = \tfrac{1}{2}[1 - h(1 + \tfrac{1}{6}\xi^2)]^{-1} \tag{16.2-21}$$

$$B_1^{(2)} = \tfrac{1}{2}[1 - 2h(1 - \tfrac{1}{6}\xi^2)]^{-1} \tag{16.2-22}$$

with $h = \zeta/8\pi\eta_s a$, and for $N = 3$.

$$B_2^{(1)} = [1 - \tfrac{1}{2}h(1 + \tfrac{1}{24}\xi^2)]^{-1} \tag{16.2-23}$$

$$B_2^{(2)} = [1 - h(1 - \tfrac{1}{24}\xi^2)]^{-1} \tag{16.2-24}$$

It may be shown from the form of the equations that in general

$$B_{-\nu}^{(k)} = -B_{\nu}^{(k)} \qquad (k = 1, 2) \tag{16.2-25}$$

and therefore $B_0^{(k)} = 0$.

It follows directly from Eq. B of Table 16.1-2 that the effective friction tensors are

$$\boldsymbol{\zeta}_{\nu\mu} = \zeta\mathbf{B}_{\nu\mu} \tag{16.2-26}$$

and from Eq. 16.2-17 that $B_{\nu\mu}^{(k)} = B_{\mu\nu}^{(k)}$; and thus from Eq. 16.2-16 it is seen that $\mathbf{B}_{\nu\mu} = \mathbf{B}_{\mu\nu}$. It then follows from Eq. D of Table 16.1-2, the antisymmetry of the $B_{\mu}^{(k)}$, Eq. 16.2-25, and Eq. 16.2-19 that

$$\tfrac{1}{2}\sum_{\nu} \nu\boldsymbol{\lambda}_{\nu} = \zeta\left\{\mathbf{Z}^{-1} \cdot \sum_{\mu} \mathbf{B}_{\mu}\right\} = \mathbf{0} \tag{16.2-27}$$

[3] R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **14**, 85–101 (1984). The coefficients defined here are related to the ϕ_{ν} of this paper and §14.6 as follows: $B_{\nu}^{(1)} = \phi_{\nu}(h, \xi^2, N)$ and $B_{\nu}^{(2)} = \phi_{\nu}(2h, -\xi^2, N)$.

Next, making use of the last result, one finds from Eq. E that a weighted sum of the modified effective friction tensors is

$$\begin{aligned}\zeta &= \tfrac{1}{4}\sum_{\nu}\sum_{\mu}\nu\mu\tilde{\zeta}_{\nu\mu} \\ &= \tfrac{1}{2}\zeta\sum_{\mu}\mu\mathbf{B}_{\mu} \\ &= \tfrac{1}{4}\zeta\sum_{\nu}\sum_{\mu}\nu\mu\mathbf{B}_{\nu\mu}\end{aligned} \tag{16.2-28}$$

This sum is defined as the effective friction tensor of the molecule, in which the effect of each of the beads is weighted by its distance from the center of mass; the tensor is anisotropic with one part proportional to $\boldsymbol{uu}$ and another part proportional to $(\boldsymbol{\delta} - \boldsymbol{uu})$. Explicit expressions for these tensors for small values of N have also been developed by Bird and Curtiss.[3]

One next finds from Eqs. 16.1-19, 16.1-20, and 16.2-28, and from Table 16.1-2, Eq. F, that the coupling tensors are

$$\mathbf{M}_s = a^2\{\boldsymbol{uc}_s\cdot\zeta\} \tag{16.2-29}$$

and from Eq. G that the elements of the modified metric matrix are

$$\tilde{g}_{st} = a^2\{\boldsymbol{c}_s\cdot\zeta\cdot\boldsymbol{c}_t\} \tag{16.2-30}$$

From these expressions it may be shown that

$$\mathbf{M}_s = a^2\zeta B^{(1)}\boldsymbol{uc}_s \tag{16.2-31}$$

$$\tilde{g}_{st} = a^2\zeta B^{(1)}(\boldsymbol{c}_s\cdot\boldsymbol{c}_t) = a^2\zeta B^{(1)}\begin{pmatrix}1 & 0\\ 0 & \sin^2\theta\end{pmatrix} \tag{16.2-32}$$

with

$$B^{(1)} = \tfrac{1}{2}\sum_{\nu}\nu B_{\nu}^{(1)} \tag{16.2-33}$$

The modified contravariant metric matrix is then

$$\tilde{G}_{st} = \frac{1}{a^2\zeta B^{(1)}}\begin{pmatrix}1 & 0\\ 0 & 1/\sin^2\theta\end{pmatrix} \tag{16.2-34}$$

The diffusion equation for the configurational distribution function is given in general by Eq. 16.2-6. Making use of Eqs. 16.2-31 and 34 we find

$$\begin{aligned}\frac{\partial}{\partial t}\psi = &-\frac{\partial}{\partial\theta}(\boldsymbol{uc}_1:\boldsymbol{\kappa})\psi - \frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi}(\boldsymbol{uc}_2:\boldsymbol{\kappa})\psi \\ &+\frac{1}{6\lambda_N^{(1)}}\left\{\frac{\partial}{\partial\theta}\sin\theta\left[\frac{\partial}{\partial\theta}\left(\frac{\psi}{\sin\theta}\right)\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi\right\} \\ &+\frac{1}{6kT\lambda_N^{(1)}}\left\{\frac{\partial}{\partial\theta}\left(\psi\frac{\partial}{\partial\theta}\phi^{(e)}\right) + \frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi}\left(\psi\frac{\partial\phi^{(e)}}{\partial\phi}\right)\right\}\end{aligned} \tag{16.2-35}$$

where

$$\lambda_N^{(1)} = \frac{a^2\zeta}{6kT} B^{(1)} \tag{16.2-36}$$

is the time constant for a rod with N beads. Using the notation of §14.1, we may write this equation in the more concise form

$$\frac{\partial}{\partial t}\left(\frac{\psi}{\sin\theta}\right) = \frac{1}{6\lambda_N^{(1)}}\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}}\left(\frac{\psi}{\sin\theta}\right)\right) - \left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\left[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu} - \frac{1}{6kT\lambda_N^{(1)}}\left(\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right)\right]\left(\frac{\psi}{\sin\theta}\right)\right) \tag{16.2-37}$$

This is the diffusion equation for the multibead rigid rod model, with complete hydrodynamic interaction. It is identical in form to that for the rigid dumbbell with no hydrodynamic interaction, Eq. 14.2-8, and differs only in the definition of the time constant $\lambda_N^{(1)}$.

It follows from Eq. 16.2-20 that in the "free-draining" approximation (hydrodynamic interaction neglected):

$$B_v^{(k)} = \tfrac{1}{2}v \qquad k = 1, 2 \tag{16.2-38}$$

and then from Eq. 16.2-18 that

$$B^{(k)} = \tfrac{1}{4}\sum_v v^2 \qquad k = 1, 2 \tag{16.2-39}$$

The sum here, however, is to be taken over the values associated with the beads as indicated in Eq. 16.1-19. Thus,

$$B^{(k)} = \tfrac{1}{12}N(N^2 - 1) \qquad k = 1,2 \tag{16.2-40}$$

and for the rigid dumbbell ($N = 2$), $B^{(k)} = \frac{1}{2}$. The expression for the time constant, Eq. 16.2-36, then reduces to that of the rigid dumbbell (with $a = L$) without hydrodynamic interaction, $\lambda = \zeta L^2/12kT$.

§16.3 EXPRESSIONS FOR THE STRESS TENSOR

In Chapter 13 it is shown how an expression for the stress tensor can be obtained for a dilute polymer solution, in which the polymer molecules are modeled as elastic dumbbells. The derivation given there is quite simple, and the four major contributions—solvent, spring force, external force, and bead momentum transport—are accounted for by elementary physical arguments. These elementary arguments are, however, difficult to apply for models with constraints, for concentrated systems, and for models with complicating factors such as hydrodynamic interaction, anisotropic friction factors, or reptational Brownian motion.

Therefore in Chapters 17 and 18 a general expression for the stress tensor is derived by starting from the Liouville equation in the complete phase space of the polymeric fluid (polymer solution or undiluted polymer). The macroscopic equation of motion is then derived, and in the process formal expressions are obtained for the various contributions to the stress tensor. After that, special restricted expressions can be obtained by introducing approximations appropriate for various kinds of modeling. In this section we summarize

some of the key results for dilute solutions of a mixture of solute species $\alpha = 1, 2, 3, \ldots$; these various species may also be regarded as the molecules of differing lengths present in a polydisperse solution.

The starting point for this discussion is Eq. 18.1-10, which is valid for mixtures, for models with constraints, for beads with internal structure, for systems with hydrodynamic interaction, and for friction coefficients and Brownian motion that may be anisotropic. The only assumptions that are inherent in Eq. 18.1-10 are those of two-body forces and short-range interactions, assumptions that we believe to be not very restrictive in the understanding of the macroscopic properties of polymeric liquids.

Equation 18.1-10 involves a sum over the species index α, which includes all the chemical species in the polymeric liquid. In the present discussion we separate off the contribution of the solvent molecules and consider only the polymer contribution to the stress tensor $\boldsymbol{\pi}_p$; the sums on α then imply summations over the polymer solute species only. Equation 18.1-10 contains a term $\boldsymbol{\pi}_k$, the contribution of the Brownian motion of the centers of mass of the molecules, for which a formal expression is given by Eq. 17.6-6. If equilibration in momentum space is assumed (this corresponds to the assumption of a Maxwellian velocity distribution in §13.3) then the integrals in $\boldsymbol{\pi}_k$ can be evaluated, and this integration leads to an isotropic contribution to the stress tensor, $(\sum_\alpha n_\alpha)kT\boldsymbol{\delta}$. The polymer contribution to the stress tensor is then (with $\bar{N} = 1$ in Eq. 18.1-10 for dilute solutions)

$$\boxed{\boldsymbol{\pi}_p = -\sum_\alpha n_\alpha \sum_\nu \langle \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} \rangle + \sum_\alpha n_\alpha kT\boldsymbol{\delta}} \tag{16.3-1}$$

The brackets indicate the phase-space average, which in this case reduces to the simpler configuration-space average

$$\langle \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} \rangle = \int \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} \psi_\alpha(Q^\alpha, t)\, dQ^\alpha \tag{16.3-2}$$

The quantity $\boldsymbol{F}_\nu^{(h)\alpha}$ is the hydrodynamic force on bead ν of a molecule of species α arising from interactions with the solvent molecules. The hydrodynamic force is given by a generalized Stokes' law expression that accounts for model constraints and hydrodynamic interaction (see Eq. 18.2-23)

$$\boldsymbol{F}_\nu^{(h)\alpha} = -\sum_\mu \tilde{\boldsymbol{\zeta}}_{\nu\mu}^\alpha \cdot \left\{ \frac{1}{\sqrt{m_\mu^\alpha}} \left(\sum_s [\![\dot{Q}_s]\!]^\alpha \boldsymbol{b}_{\mu s}^\alpha \right) - [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu^\alpha] \right\} \tag{16.3-3}$$

We point out in passing that Eq. 16.3-3 is a set of $3N_\alpha$ equations (for each α), and that from this set of equations the set of $d_\alpha \leq 3(N_\alpha - 1)$ equations (for each α) for the $[\![\dot{Q}_s]\!]^\alpha$ ($s = 1, 2, 3, \ldots, d_\alpha$) can be obtained as shown in Eq. 16.2-2. This "turning-wrong-side-out" of the Stokes' law expressions to get the expressions for the $[\![\dot{Q}_s]\!]^\alpha$ is facilitated by the use of the quantities displayed in Table 16.1-2, and the details of this inversion are the subject of §18.2. Finally we note that Eq. 16.3-3 includes as special cases Eq. 13.2-2 (for elastic dumbbells), and Eqs. 14.6-9 and 14.6-10 (for rigid dumbbells with hydrodynamic interaction).

Equation 16.3-1 is a generalization of the *Kramers–Kirkwood expression for the stress tensor*. The only assumptions inherent in this generalization are (i) dilute solutions, (ii) pairwise additivity of forces, (iii) the short-range force assumption, and (iv) equilibration in momentum space. We now show how three other forms for $\boldsymbol{\pi}_p$ can be obtained from Eq.

16.3-1. The first of these is as general as Eq. 16.3-1, but the other two result from introducing two different sets of restrictions.

First we use the expression for the average, $[\![\dot{Q}_s]\!]^\alpha$, given by Eq. 16.2-2 in the expression for the hydrodynamic force, $\boldsymbol{F}_\nu^{(h)\alpha}$, in Eq. 16.3-3. Then it follows from the definition of the coupling tensor $\mathbf{M}_s^\alpha$ (see Eq. F of Table 16.1-2) and the symmetry of the $\tilde{\zeta}_{\nu\mu}^\alpha$, Eq. 18.2-21, that

$$\sum_\nu \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} = \sum_{st} \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha (\mathscr{F}_t^{(h)\alpha} - \mathbf{M}_t^\alpha : \boldsymbol{\kappa}) + \sum_{\nu\mu} \{\boldsymbol{R}_\nu^\alpha \boldsymbol{R}_\mu^\alpha \cdot \boldsymbol{\kappa}^\dagger \cdot \zeta_{\mu\nu}^\alpha\} \tag{16.3-4}$$

One may then use this result in the expression for the stress tensor, Eq. 16.3-1, along with the force balance on the generalized forces and the approximation of equilibration in momentum space to show that

$$\begin{aligned}
\boldsymbol{\pi}_p = & \sum_\alpha n_\alpha kT \sum_{st} \left\langle \frac{1}{\sqrt{g^\alpha}} \frac{\partial}{\partial Q_t^\alpha} (\sqrt{g^\alpha}\, \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha) \right\rangle \\
& + \sum_\alpha n_\alpha \sum_{st} \langle \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha (\mathscr{F}_t^{(\phi)\alpha} + \mathscr{F}_t^{(e)\alpha}) \rangle \\
& + \sum_\alpha n_\alpha \sum_{st} \langle \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha \mathbf{M}_t^{\alpha\dagger} \rangle : \boldsymbol{\kappa}^\dagger \\
& - \sum_\alpha n_\alpha \sum_{\nu\mu} \langle \boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\mu^\alpha \rangle : \boldsymbol{\kappa}^\dagger \\
& + \sum_\alpha n_\alpha kT \boldsymbol{\delta}
\end{aligned} \tag{16.3-5}$$

This expression can be put into an alternative form by making use of the modified reciprocal base vectors

$$\boldsymbol{a}_{\nu s}^\alpha = \sum_t \sum_\mu \frac{1}{\sqrt{m_\nu^\alpha m_\mu^\alpha}} \tilde{G}_{st}^\alpha [\boldsymbol{b}_{\mu t}^\alpha \cdot \tilde{\zeta}_{\mu\nu}^\alpha] \tag{16.3-6}$$

These vectors satisfy the relations

$$\sum_\nu \sqrt{m_\nu^\alpha}\, \boldsymbol{a}_{\nu s}^\alpha = \mathbf{0} \tag{16.3-7}$$

$$\sum_\nu (\boldsymbol{a}_{\nu s}^\alpha \cdot \boldsymbol{b}_{\nu t}^\alpha) = \delta_{st} \tag{16.3-8}$$

as may be seen by using the definitions in Table 16.1-2. Then

$$\sum_t \tilde{G}_{st}^\alpha \mathbf{M}_t^\alpha = \sum_\nu \sqrt{m_\nu^\alpha}\, \boldsymbol{R}_\nu^\alpha \boldsymbol{a}_{\nu s} \tag{16.3-9}$$

$$\sum_s \sum_t \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha \mathbf{M}_t^\alpha = \sum_{t\nu\mu\eta} \sqrt{\frac{m_\nu^\alpha}{m_\mu^\alpha}}\, \boldsymbol{R}_\nu^\alpha \boldsymbol{a}_{\nu t}^\alpha \tilde{\zeta}_{\eta\mu}^\alpha \cdot \boldsymbol{b}_{\mu t}^\alpha \boldsymbol{R}_\eta^\alpha \tag{16.3-10}$$

The expression for the stress tensor may then be written

$$\boldsymbol{\pi}_p = \sum_\alpha n_\alpha kT \sum_{sv} \left\langle \frac{1}{\sqrt{g^\alpha}} \frac{\partial}{\partial Q_s^\alpha} (\sqrt{g^\alpha m_v^\alpha}\, \boldsymbol{R}_v^\alpha \boldsymbol{a}_{vs}^\alpha) \right\rangle$$
$$+ \sum_\alpha n_\alpha \sum_{sv} \langle \sqrt{m_v^\alpha}\, \boldsymbol{R}_v^\alpha a_{vs}^\alpha (\mathscr{F}_s^{(\phi)\alpha} + \mathscr{F}_s^{(e)\alpha}) \rangle$$
$$+ \sum_\alpha n_\alpha \sum_{v\mu\eta} \sqrt{\frac{m_v^\alpha}{m_\eta^\alpha}} \left\langle \boldsymbol{R}_v^\alpha \left[\left(\sum_s a_{vs}^\alpha \boldsymbol{b}_{\eta s}^\alpha \right) - \delta_{v\eta} \boldsymbol{\delta} \right] \cdot \tilde{\zeta}_{\eta\mu}^\alpha \boldsymbol{R}_\mu^\alpha \right\rangle : \boldsymbol{\kappa}^\dagger$$
$$+ \sum_\alpha n_\alpha kT \boldsymbol{\delta} \tag{16.3-11}$$

This relation is a generalization of the *modified Kramers expression for the stress tensor* given in Eq. B of Table 14.3-1. Equations 16.3-1 and 16.3-11 are completely equivalent in that they contain the same physical assumptions.

Next we obtain two simplified expressions for $\boldsymbol{\pi}_p$: one for models with no constraints, by simplifying Eq. 16.3-11, and another for models with equilibrium-averaged or no hydrodynamic interaction, by simplifying Eq. 16.3-1.

a. Models with No Constraints

If the molecular model involves no constraints one may use Eq. 12D.3-5 along with Eqs. 16.3-6 and 7 to show that $a_{vs}^\alpha = \sum_t G_{st}^\alpha \boldsymbol{b}_{vt}^\alpha$. With this relation one may show that the third and fourth terms on the right of Eq. 16.3-11 cancel and that the first two terms may be rearranged to give as the expression for the stress tensor

$$\boldsymbol{\pi}_p = \sum_\alpha n_\alpha \sum_v \langle \boldsymbol{R}_v^\alpha (\boldsymbol{F}_v^{(b)\alpha} + \boldsymbol{F}_v^{(\phi)\alpha} + \boldsymbol{F}_v^{(e)\alpha}) \rangle + \sum_\alpha n_\alpha kT \boldsymbol{\delta} \tag{16.3-12}$$

In this expression

$$\boldsymbol{F}_v^{(b)\alpha} = -kT \frac{\partial}{\partial \boldsymbol{r}_v^\alpha} \ln \left(\frac{\Psi_\alpha}{\sqrt{g^\alpha}} \right) \tag{16.3-13}$$

$$\boldsymbol{F}_v^{(\phi)\alpha} = -\frac{\partial}{\partial \boldsymbol{r}_v^\alpha} \phi^\alpha \tag{16.3-14}$$

$$\boldsymbol{F}_v^{(e)\alpha} = -\frac{\partial}{\partial \boldsymbol{r}_v^\alpha} \phi^{(e)\alpha} \tag{16.3-15}$$

are the Brownian, intramolecular, and external forces on a bead. The integral involving the Brownian force may then be evaluated to give an isotropic contribution and one finds that

$$\boldsymbol{\pi}_p = \sum_\alpha n_\alpha \sum_v \langle \boldsymbol{R}_v^\alpha (\boldsymbol{F}_v^{(\phi)\alpha} + \boldsymbol{F}_v^{(e)\alpha}) \rangle + \sum_\alpha N_\alpha n_\alpha kT \boldsymbol{\delta} \tag{16.3-16}$$

This relation is a generalization of the *modified Kramers expression for the stress tensor* given in Table 15.2-1.

b. Models with Equilibrium-Averaged Hydrodynamic Interaction or No Hydrodynamic Interaction

To develop another expression for the stress tensor we return to Eqs. 16.3-1 and 3. By combining these relations, we find that the symmetric part of the stress tensor is

$$\boldsymbol{\pi}_p^{(s)} = -\tfrac{1}{2}\sum_\alpha n_\alpha \sum_{\nu\mu} \{\langle \boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\mu^\alpha\rangle : \boldsymbol{\kappa}^\dagger + \boldsymbol{\kappa} : \langle \boldsymbol{R}_\mu^\alpha \tilde{\zeta}_{\mu\nu}^\alpha \boldsymbol{R}_\nu^\alpha\rangle\}$$
$$+ \tfrac{1}{2}\sum_\alpha n_\alpha \sum_{\nu\mu s} \frac{1}{\sqrt{m_\mu^\alpha}} \langle [\![\dot{Q}_s^\alpha]\!] \{\boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \cdot \boldsymbol{b}_{\mu s}^\alpha + \boldsymbol{b}_{\mu s}^\alpha \cdot \tilde{\zeta}_{\mu\nu}^\alpha \boldsymbol{R}_\nu^\alpha\}\rangle$$
$$+ \sum_\alpha n_\alpha kT\boldsymbol{\delta} \tag{16.3-17}$$

It also follows from the equation of continuity, Eq. 16.2-1, that

$$\frac{\partial}{\partial t}\sum_{\nu\mu} \langle \boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\mu^\alpha\rangle = \sum_{\nu\mu s} \left\langle [\![\dot{Q}_s]\!]^\alpha \frac{\partial}{\partial Q_s^\alpha} (\boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\mu^\alpha) \right\rangle \tag{16.3-18}$$

If the $\tilde{\zeta}_{\nu\mu}^\alpha$ are diagonal, $\tilde{\zeta}_{\nu\mu}^\alpha = \zeta_{\nu\mu}^\alpha \boldsymbol{\delta}$, with constant $\zeta_{\nu\mu}^\alpha$, these two equations may be combined to give

$$\boldsymbol{\pi}_p^{(s)} = \tfrac{1}{2}\sum_\alpha n_\alpha \left\{ \frac{\partial}{\partial t} \langle \mathbf{K}^\alpha\rangle - \boldsymbol{\kappa}\cdot\langle \mathbf{K}^\alpha\rangle - \langle \mathbf{K}^\alpha\rangle \cdot \boldsymbol{\kappa}^\dagger \right\} + \sum_\alpha n_\alpha kT\boldsymbol{\delta} \tag{16.3-19}$$

in which $\mathbf{K}^\alpha = \sum_{\nu\mu} \zeta_{\nu\mu}^\alpha \boldsymbol{R}_\nu^\alpha \boldsymbol{R}_\mu^\alpha$ are the tensors defined in Eq. 16.2-8. This expression then applies in the approximation of equilibrium-averaged hydrodynamic interaction or if hydrodynamic interaction is neglected. Hence, we find that in these cases

$$\boxed{\boldsymbol{\pi}_p^{(s)} = \tfrac{1}{2}\sum_\alpha n_\alpha \langle \mathbf{K}^\alpha\rangle_{(1)} + \sum_\alpha n_\alpha kT\boldsymbol{\delta}} \tag{16.3-20}$$

in which the operation of convected differentiation is introduced (see Eq. D.2-4). It may be shown that in the absence of external forces the stress tensor is symmetric, so that Eq. 16.3-20 is a generalization of the *Giesekus expression for the stress tensor*, special examples of which have been encountered in Eq. D of Tables 13.3-1, 14.3-1, and 15.2-1. One important consequence of Eq. 16.3-20 is that *for any bead-rod-spring model with equilibrium-averaged (or no) hydrodynamic interaction, Ψ_2 is identically zero* in a steady shear flow with $v_x = \dot{\gamma}y$, $v_y = 0$, $v_z = 0$, since in such a flow the yy- and zz-components of $\langle \mathbf{K}^\alpha\rangle_{(1)}$ are always zero.

EXAMPLE 16.3-1 The Stress Tensor for the Multibead-Rod Model

Develop an explicit expression for the stress tensor for the multibead-rod model described in §14.1 and further discussed in Examples 16.1-1 and 16.2-1.

SOLUTION We use the coordinates and notation developed in Example 16.2-1 and the general expression for the stress tensor, Eq. 16.3-1. Since there is no intramolecular potential ($\phi = 0$), one finds from Eqs. 16.2-2 to 5 that

$$[\![\dot{Q}_s]\!] = -\sum_t \tilde{G}_{st}\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] \tag{16.3-21}$$

When this expression is used in Eq. 16.3-3 one finds that

$$\sum_\nu \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(h)} = \sum_\nu \sum_\mu \boldsymbol{R}_\nu \left\{\boldsymbol{\xi}_{\nu\mu}\cdot\left(\frac{1}{\sqrt{m_\mu}}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{b}_{\mu s} \times\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] + [\boldsymbol{\kappa}\cdot\boldsymbol{R}_\mu]\right)\right\} \tag{16.3-22}$$

Then using the results of the previous examples (Eqs. 16.1-20, 16.2-19, 16.2-26, 16.2-28), one finds that

$$\begin{aligned}\sum_\nu \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(h)} &= a^2\left\{\boldsymbol{u}\boldsymbol{\zeta}\cdot\left(\sum_s\sum_t \tilde{G}_{st}\boldsymbol{c}_s\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] + [\boldsymbol{\kappa}\cdot\boldsymbol{u}]\right)\right\} \\ &= a^2\zeta B^{(1)}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{u}\boldsymbol{c}_s\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] \\ &\quad + a^2\zeta B^{(1)}\{\boldsymbol{u}\boldsymbol{u}\cdot\boldsymbol{\kappa}^\dagger\} + a^2\zeta(B^{(2)} - B^{(1)})\{\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}:\boldsymbol{\kappa}\}\end{aligned} \tag{16.3-23}$$

where $B^{(1)}$ is the quantity defined in Eq. 16.2-33 and

$$B^{(2)} = \tfrac{1}{2}\sum_\nu \nu B_\nu^{(2)} \tag{16.3-24}$$

On the other hand, it follows from Eqs. 16.2-31 and 34 that

$$\begin{aligned}a^2\zeta B^{(1)}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{u}\boldsymbol{c}_s(\mathbf{M}_t:\boldsymbol{\kappa}) &= a^2\zeta B^{(1)}\left\{\boldsymbol{u}\left[\boldsymbol{c}_1\boldsymbol{c}_1 + \frac{\boldsymbol{c}_2\boldsymbol{c}_2}{\sin^2\theta}\right]\boldsymbol{u}:\boldsymbol{\kappa}^\dagger\right\} \\ &= a^2\zeta B^{(1)}\{\boldsymbol{u}[\boldsymbol{\delta} - \boldsymbol{u}\boldsymbol{u}]\boldsymbol{u}:\boldsymbol{\kappa}^\dagger\}\end{aligned} \tag{16.3-25}$$

Thus, Eq. 16.3-23 can be simplified appreciably

$$\begin{aligned}\sum_\nu \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(h)} &= a^2\zeta\left\{B^{(2)}\{\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}:\boldsymbol{\kappa}\} + B^{(1)}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{u}\boldsymbol{c}_s\left(kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - \mathscr{F}_t^{(e)}\right)\right\} \\ &= a^2\zeta B^{(2)}\{\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}:\boldsymbol{\kappa}\} + kT\boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\left[\ln\left(\frac{\psi}{\sqrt{g}}\right) + \frac{1}{kT}\phi^{(e)}\right]\end{aligned} \tag{16.3-26}$$

The last result may be used in Eq. 16.3-1 to obtain an expression for the polymer contribution to the stress tensor of a dilute solution of multibead rigid rods, with complete hydrodynamic interaction. For a system involving a single solute the expression becomes

$$\begin{aligned}\boldsymbol{\pi}_p = &-na^2\zeta B^{(2)}\langle\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\rangle:\boldsymbol{\kappa} \\ &-nkT\int\boldsymbol{u}\left(\frac{\partial}{\partial\boldsymbol{u}}\frac{\psi}{\sin\theta}\right)d\boldsymbol{u} + nkT\boldsymbol{\delta} - n\left\langle\boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\phi^{(e)}\right\rangle\end{aligned} \tag{16.3-27}$$

where the angular brackets indicate an average weighted with the orientational distribution function, ψ. Then using Eq. E.7-3 one finds that

$$\boldsymbol{\pi}_p = -3nkT\langle \boldsymbol{uu} \rangle - 6nkT\lambda_N^{(2)}\langle \boldsymbol{uuuu} \rangle : \boldsymbol{\kappa} - n\left\langle \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)} \right\rangle + 2nkT\boldsymbol{\delta} \tag{16.3-28}$$

where

$$\lambda_N^{(2)} = \frac{a^2\zeta}{6kT}B^{(2)} \tag{16.3-29}$$

is another time constant associated with this model (cf. Eq. 16.2-36 for the definition of $\lambda_N^{(1)}$).

The last expression for the stress tensor is identical in form to that for the rigid dumbbell without hydrodynamic interaction (see Eq. 14.3-3) and differs only in the definition of the time constant, $\lambda_N^{(2)}$. It is noted that with hydrodynamic interaction, two time constants arise: $\lambda_N^{(1)}$ in the diffusion equation, and $\lambda_N^{(2)}$ in the expression for the stress tensor. As discussed in Example 16.2-1, in the "free-draining approximation", $B^{(1)} = B^{(2)}$ and thus the two time constants are identical. For the rigid dumbbell ($N = 2$) without hydrodynamic interaction, $B^{(2)} = \frac{1}{2}$ and $\lambda_N^{(2)}$ in Eq. 16.3-28 reduces to the λ for the rigid dumbbell defined just after Eq. 14.2-6.

§16.4 SECOND-ORDER FLUID CONSTANTS FOR ARBITRARY BEAD-ROD-SPRING MODELS WITH EQUILIBRIUM-AVERAGED HYDRODYNAMIC INTERACTION[1]

In §15.3 we found that for the Rouse bead-spring chain model with no hydrodynamic interaction, we could get the complete constitutive equation without having to solve the diffusion equation for the configurational distribution function. In §15.4 we found the analogous result for equilibrium-averaged hydrodynamic interaction. In Chapter 14 we found that for rigid dumbbells we could, after considerable effort, obtain the first few terms in a memory-integral expansion for arbitrary time-dependent flows.

If, however, we restrict our attention to the first- and second-order fluid constants in the retarded-motion expansion, we discover that formal expressions can be obtained for bead-rod-spring models of arbitrary complexity. We show in this section how to obtain these general expressions.

We start by writing down two expressions that we wish to equate—the first is the retarded motion expansion from continuum mechanics (cf. Eqs. 6.2-1 and D.4-3) and the second is the molecular theory expression (cf. Eq. 16.3-20):

$$\text{Continuum theory:} \quad \boldsymbol{\tau} = -[b_1\boldsymbol{\gamma}_{(1)} + b_2\boldsymbol{\gamma}_{(2)} + b_{11}\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(1)}\} + \cdots] \tag{16.4-1}$$

$$\text{Molecular theory:} \quad \boldsymbol{\tau} = -\eta_s\boldsymbol{\gamma}_{(1)} + \tfrac{1}{2}n\langle \mathbf{K} \rangle_{(1)} \tag{16.4-2}$$

Equation 16.3-20 has been written here for a single polymer solute species. Keep in mind that Eq. 16.4-2 is valid for models with equilibrium-averaged hydrodynamic interaction (or no hydrodynamic interaction) and no external forces. We now want to obtain formal expressions for the constants b_1, b_2, and b_{11} in terms of the constants that describe the

[1] This section is an extension of Section XVI of C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (I. Prigogine and S. A. Rice, eds.) (1976).

mechanical model. The constants b_1 and b_2 are obtainable from linear viscoelastic measurements or from steady-state shear flow experiments

$$\text{Steady-state shear flow:} \quad b_1 = \lim_{\dot\gamma \to 0} \eta \qquad b_2 = -\tfrac{1}{2} \lim_{\dot\gamma \to 0} \Psi_1 \tag{16.4-3}$$

$$\text{Small-amplitude oscillatory motion:} \quad b_1 = \lim_{\omega \to 0} \eta' \qquad b_2 = -\lim_{\omega \to 0} \frac{\eta''}{\omega} \tag{16.4-4}$$

Furthermore, a dimensionless ratio formed from b_1 and b_2 is related to the "steady-state compliance" J_e^0 used by polymer chemists (cf. Eq. 3.4-15) thus

$$-\frac{nkTb_2}{(b_1 - \eta_s)^2} = \frac{J_e^0 \tilde{N} kT}{cM[\eta]_0^2} \tag{16.4-5}$$

which is known experimentally to be in the range of 0.2 to 0.4 for many macromolecular solutions.

First we note that b_{11} is equal to $\Psi_{2,0}$, the second normal-stress coefficient at zero shear rate. But we know that Eq. 16.4-2 gives $\Psi_2 = 0$ for all shear rates, and therefore b_{11} must be zero (see comments after Eq. 16.3-20).

Next we show that b_1 and b_2 may be obtained by considering steady-state, homogeneous, potential flows only. For this special flow category, with $\boldsymbol{v} = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}]$ and $\boldsymbol{\kappa} = \boldsymbol{\kappa}^\dagger$, we have from Eqs. 16.4-1 and 16.4-2

$$\text{Continuum theory:} \quad \boldsymbol{\tau} = -2b_1\boldsymbol{\kappa} + 4b_2\{\boldsymbol{\kappa} \cdot \boldsymbol{\kappa}\} + \cdots \tag{16.4-6}$$

$$\text{Molecular theory:} \quad \boldsymbol{\tau} = -2\eta_s\boldsymbol{\kappa} - \tfrac{1}{2}n\{\boldsymbol{\kappa} \cdot \langle \mathbf{K} \rangle + \langle \mathbf{K} \rangle \cdot \boldsymbol{\kappa}\} \tag{16.4-7}$$

We now have to evaluate $\langle \mathbf{K} \rangle$ by using the expression for ψ in Eq. 16.2-10; in the latter we expand that portion of the exponential involving κ in a Taylor series and retain two terms only

$$\langle \mathbf{K} \rangle \doteq \frac{\int \mathbf{K} \sqrt{g}\, e^{-\phi/kT}[1 + (1/2kT)(\boldsymbol{\kappa}:\mathbf{K})]\, dQ}{\int \sqrt{g}\, e^{-\phi/kT}[1 + (1/2kT)(\boldsymbol{\kappa}:\mathbf{K})]\, dQ} = \frac{\mathbf{I}_{n1} + \mathbf{I}_{n2}}{I_{d1} + I_{d2}} \tag{16.4-8}$$

The scalar I_{d1} is just the normalizing constant for $\psi_{eq}(Q)$:

$$I_{d1} = \int \sqrt{g}\, e^{-\phi/kT}\, dQ \tag{16.4-9}$$

as may be seen from Eq. 12.3-4. To get I_{d2} we consider the integrations over the Euler angles separately and then make use of Eq. E.11-5

$$\begin{aligned} I_{d2} &= \frac{1}{2kT}\boldsymbol{\kappa}:\int\left[\iiint \mathbf{K}\sin\beta\, d\alpha\, d\beta\, d\gamma\right]\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \frac{1}{2kT}\boldsymbol{\kappa}:\int[8\pi^2(\tfrac{1}{3})(\mathbf{K}:\boldsymbol{\delta})\boldsymbol{\delta}]\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= 0 \end{aligned} \tag{16.4-10}$$

since $(\boldsymbol{\kappa}:\boldsymbol{\delta}) = \operatorname{tr}\boldsymbol{\kappa} = 0$ for an incompressible fluid. Here we have used Eq. L of Table 16.1-1 and used the abbreviation $\Gamma = \det(\Gamma_{uv})$; in addition the abbreviation $dQ' = dQ_4 dQ_5 dQ_6 \ldots$ has been used. In a similar way the tensor $\mathbf{I}_{n1}$ is evaluated

$$\begin{aligned} \mathbf{I}_{n1} &= \int \mathbf{K}\sqrt{g}\, e^{-\phi/kT}\, dQ \\ &= \int\left\{\iiint \mathbf{K}\sin\beta\, d\alpha\, d\beta\, d\gamma\right\}\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \int\{8\pi^2(\tfrac{1}{3})(\operatorname{tr}\mathbf{K})\boldsymbol{\delta}\}\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \tfrac{1}{3}\boldsymbol{\delta}\int(\operatorname{tr}\mathbf{K})\sqrt{g}\, e^{-\phi/kT}\, dQ \end{aligned} \tag{16.4-11}$$

To evaluate the tensor $\mathbf{I}_{n2}$ we make use of §E.9, in which the fourth-order isotropic tensors are discussed

$$\begin{aligned} \mathbf{I}_{n2} &= \frac{1}{2kT}\boldsymbol{\kappa}:\int \mathbf{KK}\sqrt{g}\, e^{-\phi/kT}\, dQ \\ &= \frac{1}{2kT}\sum_{J=0}^{2}(\boldsymbol{\kappa}:\mathbf{I}_J)\int(8\pi^2\,\mathbf{KK}\vdots\mathbf{I}_J)\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \frac{1}{2kT}(\boldsymbol{\kappa}:\mathbf{I}_2)\int(\mathbf{KK}\vdots\mathbf{I}_2)\sqrt{g}\, e^{-\phi/kT}\, dQ \\ &= \frac{1}{2kT}\left(\frac{1}{\sqrt{5}}\boldsymbol{\kappa}\right)\int\frac{1}{\sqrt{5}}((\operatorname{tr}\mathbf{K}^2)-\tfrac{1}{3}(\operatorname{tr}\mathbf{K})^2)\sqrt{g}\, e^{-\phi/kT}\, dQ \end{aligned} \tag{16.4-12}$$

When the last four results are combined and use is made of the definition of $\langle\ \rangle_{eq}$ in Eq. 12.4-6, we get (through terms linear in velocity gradients)

$$\langle\mathbf{K}\rangle = \tfrac{1}{3}\langle\operatorname{tr}\mathbf{K}\rangle_{eq}\boldsymbol{\delta} + \frac{1}{10kT}\langle(\operatorname{tr}\mathbf{K}^2)-\tfrac{1}{3}(\operatorname{tr}\mathbf{K})^2\rangle_{eq}\boldsymbol{\kappa} \tag{16.4-13}$$

When this expression for $\langle\mathbf{K}\rangle$ is substituted into Eq. 16.4-7 and the coefficients of $\boldsymbol{\kappa}$ and $\{\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}\}$ compared with those of Eq. 16.4-6 we get for the *second-order-fluid constants* for

arbitrary bead-rod-spring models with or without equilibrium-averaged hydrodynamic interaction

$$b_1 = \eta_s + \frac{n}{6}\langle \text{tr } \mathbf{K} \rangle_{\text{eq}} \tag{16.4-14}$$

$$b_2 = -\frac{n}{40kT}\langle (\text{tr } \mathbf{K}^2) - \tfrac{1}{3}(\text{tr } \mathbf{K})^2 \rangle_{\text{eq}} \tag{16.4-15}$$

The tensor $\mathbf{K}$ is defined in Eq. 16.2-8 and $\langle B \rangle_{\text{eq}}$ is defined by Eq. 12.4-6

$$\langle B \rangle_{\text{eq}} = \frac{\int B\sqrt{g}\, e^{-\phi/kT}\, dQ}{\int \sqrt{g}\, e^{-\phi/kT}\, dQ} = \frac{\int B\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ'}{\int \sqrt{\Gamma}\, e^{-\phi/kT}\, dQ'} \tag{16.4-16}$$

the first form implying integrations over all generalized coordinates Q_s ($s = 1, 2, 3, \ldots, d$), and the second implying that Q_1, Q_2, Q_3 have been taken to be the Euler angles α, β, γ, and that the integrations are to be performed over $Q_4, Q_5, Q_6, \ldots, Q_d$. In obtaining the second form we make use of the invariance of the expressions to be averaged in Eqs. 16.4-14 and 16.4-15 to a pure rotation of the molecular model. For rigid models the only generalized coordinates are the Euler angles, and hence the averaging indicated by $\langle \ldots \rangle$ does not need to be performed.

It is therefore possible to get the second-order-fluid constants b_1, b_2, b_{11} for dilute polymer solutions using any bead-rod-spring models with equilibrium-averaged hydrodynamic interaction (or no hydrodynamic interaction). To get these results it is necessary to know only the *equilibrium* configuration-space distribution function, the latter being obtainable from Eq. 12.3-4. It can be shown that b_2 is negative (or zero) for all molecular models of the type used here (see Problem 16B.1).

In Table 16.4-1 we give some examples of b_1 and b_2 values for a variety of models without hydrodynamic interaction in order to illustrate the connection between structure and rheological properties. A few comments about this table are appropriate:

1. In general b_2 is much more sensitive to structure than b_1; usually the normal stresses are higher for the more flexible structures.
2. Note that a rigid square, a rigid rhombus, a freely jointed rhombus, and an elastic rhombus (all with side length L) have the same viscosity, whereas they have different normal stresses.
3. A rod with three beads and length $2L$ has $b_1 - \eta_s = \frac{1}{3}n\zeta L^2$ whereas the freely jointed system with the same overall length has $b_1 - \eta_s = \frac{2}{9}n\zeta L^2$; this shows the influence of flexibility on viscosity.
4. Note that the rigid tridumbbell has a zero first normal stress coefficient if all three dumbbell lengths are the same; this is characteristic of spherically symmetric systems.
5. The three-bead-two-rod model with a bending potential is interesting because it shows that the viscosity and normal stress coefficient both decrease as one goes from a stiff three-bead rod to a "bendable" rod. A similar decrease occurs

TABLE 16.4-1

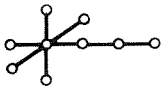
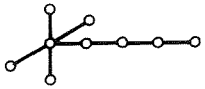
Values of b_1 and b_2 for Several Models with No Hydrodynamic Interaction[a, b]

Model	Meaning of L	$\frac{b_1 - \eta_s}{n\zeta L^2}$	$-\frac{b_2 kT}{n\zeta^2 L^4}$	$-\frac{nkTb_2}{(b_1 - \eta_s)^2}$
Rigid dumbbell[c] with two beads connected by a rod.	Length of rod	$\frac{1}{12}$	$\frac{1}{240}$	0.60
Lopsided rigid dumbbell[d] with two dissimilar beads connected by a rod; $(1/\zeta) = (1/\zeta_1) + (1/\zeta_2)$.	Length of rod	$\frac{1}{12}$	$\frac{1}{240}$	0.60
Hookean dumbbell[c] with two beads connected by a linear spring with spring constant H.	$\sqrt{kT/H}$	$\frac{1}{4}$	$\frac{1}{16}$	1
Kramers freely jointed bead-rod chain[e, f, g] (3, 4, and 5 beads)	Length of each rod	$\frac{2}{9}$ $\frac{5}{12}$ $\frac{2}{3}$	0.02069 0.06554 0.16224	0.419 $N = 3$ 0.378 $N = 4$ 0.365 $N = 5$
Freely jointed bead-spring chain with Fraenkel springs in the limit that the springs are infinitely stiff[f, g] (3, 4, and 5 beads)	Length of infinitely stiff springs	$\frac{2}{9}$ $\frac{5}{12}$ $\frac{2}{3}$	0.02099 0.06667 0.16489	0.425 $N = 3$ 0.384 $N = 4$ 0.371 $N = 5$
Three-bead, two-rod model with bending potential $\phi = \frac{1}{2}K(\chi - \pi)^2$ where χ is the included angle[f, l]	Length of each rod	$\frac{1}{3}\left(1 - \frac{kT}{3K} + \cdots\right)$	$\frac{1}{15}\left(1 - \frac{7}{6}\frac{kT}{K} + \cdots\right)$	$0.60\left(1 - \frac{kT}{2K} + \cdots\right)$
Rouse model of N beads joined linearly by $N - 1$ linear springs each with spring constant H.	$\sqrt{kT/H}$	$\frac{(N^2 - 1)}{12}$	$\frac{(N^2 - 1)(2N^2 + 7)}{720}$	$\frac{(2N^2 + 7)}{5(N^2 - 1)} = 0.4\left(1 + \frac{9}{2N^2} + \cdots\right)$

Bead-spring ring[n] of N beads joined by N linear springs with spring constant H	$\sqrt{kT/H}$	$\frac{(N^2-1)}{24}$	$\frac{(N^2-1)(N^2+11)}{2880}$	$\frac{(N^2+11)}{5(N^2-1)} = 0.2\left(1+\frac{12}{N^2}+\cdots\right)$
Freely jointed bead-spring chain with infinitely stiffened Fraenkel springs[f] of length L_0	L_0	$\frac{(N^2-1)}{36}$	$\frac{(N^2-1)(10N^3-12N^2+35N-12)}{32400N}$	$0.4\left(1-\frac{6}{5N}+\cdots\right)$
Kirkwood–Riseman freely rotating bead-rod chain[h] with $\xi_1 = \xi_2 = \cdots = \arccos\frac{1}{3} = 70.53^\circ$ in Fig. 11.2-1 (3, 4. . . . , 8 beads)	Length of each rod	0.2593 0.5389 0.9272 1.427 2.039 2.764	0.0255 0.1015 0.2963 0.7047 1.453 2.697	0.380 $N=3$ 0.349 $N=4$ 0.345 $N=5$ 0.346 $N=6$ 0.349 $N=7$ 0.353 $N=8$
Two beads joined by a string[i]	Length of string	$\frac{3}{5}$	$\frac{9}{35}$	0.71
Rigid plane polygon[m] of N beads connected by N rods of length b.	Radius of circumscribed circle $L = \frac{b/2}{\sin(\pi/N)}$	$\frac{N}{6}$	$\frac{N^2}{240}$	0.15
Four beads joined with rods to form a rigid plane rhombus[j] with included angle 2σ (cf. Fig. 16.4-2).	Side of rhombus	$\frac{1}{3}$	$\frac{1}{15}(1-\frac{3}{4}\sin^2 2\sigma)$	$0.60(1-\frac{3}{4}\sin^2 2\sigma)$
Four beads joined with rods to form a freely jointed plane rhombus.[j]	Side of rhombus	$\frac{1}{3}$	$\frac{1}{30}$	0.30
Four beads joined with rods to form a freely jointed rhombus[j]; one opposite pair of beads is joined by a Fraenkel spring with spring constant H and equilibrium position $L/\sqrt{2}$.	Side of rhombus	$\frac{1}{3}$	$\frac{1}{60}[1+(24I_5+60\sqrt{2}I_4+96I_3+24\sqrt{2}I_2)(2I_1+\sqrt{2}I_0)^{-1}]$ where $I_n = \int_{-1/\sqrt{2}}^{1-1/\sqrt{2}} u^n e^{-a^2u^2}\,du$ and $a^2 = 2HL^2/kT$	$0.30\left[1-\frac{2\sqrt{2}}{105}a^2+\cdots\right]$

(continued)

TABLE 16.4-1 (*Continued*)

Rigid tridumbbell ("Doppelkreuzhantel")[k], formed by joining three identical rigid dumbbells at their midpoints in a mutually orthogonal configuration.	Length of one dumbbell rod	$\frac{1}{4}$	0	0
	Length of rod between beads	$\frac{7}{3}$	$\frac{16}{15}$	0.20
	Length of rod between beads	$\frac{73}{27}$	$\frac{2116}{1215}$	0.24
	Length of rod between beads	$\frac{103}{27}$	$\frac{5776}{1215}$	0.34

[a] This table is an extension of Table V of C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31-117 (I. Prigogine and S. A. Rice, eds.) (1976).
[b] See §6.2 for a discussion of the retarded motion expansion.
[c] R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1-90 (1971).
[d] S. I. Abdel-Khalik and R. B. Bird, *Appl. Sci. Res.*, **30**, 268-270 (1975).
[e] R. S. Rivlin, *Trans. Faraday Soc.*, **45**, 737-748 (1949).
[f] O. Hassager, *J. Chem. Phys.*, **60**, 2111 2124 (1974); see also §16.5.
[g] C. F. Curtiss and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **2**, 392 396 (1977).
[h] X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303-321 (1986).
[i] H. R. Warner, Jr., *Ind. Eng. Chem. Fundamentals*, **11**, 379-387 (1972).
[j] C. F. Curtiss, R. B. Bird and O. Hassager, *loc. cit.*, Table V.
[k] H. Giesekus, *Rheol. Acta*, **2**, 101-112 (1962).
[l] D. B. Roitman and B. H. Zimm, *J. Chem. Phys.*, **81**, 6333-6347 (1984).
[m] E. Paul and R. M. Mazo, *J. Chem. Phys.*, **51**, 1102-1107 (1969); errata in this paper are discussed in C. Y. Mou and R. M. Mazo, *J. Chem. Phys.*, **67**, 5972-5973 (1977).
[n] J. M. Wiest, S. R. Burdette, T. W. Liu, and R. B. Bird, *J. Non-Newtonian Fluid Mech.* (1987).

in going from the Kirkwood–Riseman chain with fixed angles to the Kramers freely jointed chain.

6. The last three models show how the viscosity and normal stress coefficients increase as the structures become more and more lopsided.
7. Values of the dimensionless group $-nkTb_2/(b_1 - \eta_s)^2$ for the models listed vary from 0 to 1. Note that this group does not contain the model parameters ζ and L.
8. It is interesting to compare the results for the Kramers freely jointed bead-rod chain and the freely jointed bead-rod chain obtained by freezing out Fraenkel springs (see Example 12.5-2): the b_1 values are identical, and the b_2 values differ by less than 2% for $N = 3$, 4, and 5.

To illustrate the use of Eqs. 16.4-14 and 16.4-15 we give three examples—the first two for rigid models including equilibrium averaged hydrodynamic interaction, and the third for a flexible model with an internal potential.

EXAMPLE 16.4-1 Second-Order Fluid Constants for the Multibead-Rod Model with Equilibrium Averaged Hydrodynamic Interaction

Obtain the second-order-fluid constants, b_1 and b_2, for the multibead-rod model described in §14.1 and further discussed in Examples 16.1-1, 16.2-1, and 16.3-1. Include the effects of hydrodynamic interaction in the equilibrium-averaged approximation.

SOLUTION The dimensionless diffusion tensors for this model are given by Eq. 16.2-15. Upon equilibrium averaging this expression, that is, averaging over all orientations of the rod with an isotropic distribution, one finds that the $H_{\nu\mu}$ of Eq. I of Table 16.1-2 are

$$H_{\nu\mu} = \delta_{\nu\mu} + \zeta\Omega_{\nu\mu} \tag{16.4-17}$$

where from Eqs. 16.2-13 and 14,

$$\Omega_{\nu\mu} = \tfrac{2}{3}\,\Omega^{(1)}_{\nu\mu} + \tfrac{1}{3}\,\Omega^{(2)}_{\nu\mu} = \frac{(1 - \delta_{\nu\mu})}{3\pi a\eta_s|\nu - \mu|} \tag{16.4-18}$$

It is interesting to note that since the parameter ξ is lost in the equilibrium averaging, in this approximation the Rotne–Prager–Yamakawa interaction tensors and the Oseen–Burgers tensors lead to the same result.

The dimensionless mobility coefficients $B_{\nu\mu}$ are (see Eq. J of Table 16.1-2) now determined by the equations

$$\sum_{\eta} B_{\nu\eta}\,(\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}) = \delta_{\nu\mu} \tag{16.4-19}$$

which are similar to Eqs. 16.2-17 but with the two sets of matrices, $\Omega^{(1)}_{\nu\mu}$ and $\Omega^{(2)}_{\nu\mu}$ replaced by the average, $\Omega_{\nu\mu}$. As in the treatment of complete hydrodynamic interaction, we next define the sums

$$B_\eta = \tfrac{1}{2}\sum_{\nu} \nu B_{\nu\eta} \tag{16.4-20}$$

which are determined by the equations

$$\sum_{\eta} B_\eta\,(\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}) = \tfrac{1}{2}\mu \tag{16.4-21}$$

From these equations it may be shown that

$$B_{-\eta} = -B_{\eta} \tag{16.4-22}$$

It is also interesting to note that these equations are similar to the equations for the $B_{\eta}^{(1)}$ and $B_{\eta}^{(2)}$ in Eqs. 16.2-20. The solutions, B_{η}, may be obtained from those of the previous equations by setting $\xi = 0$ and from $B_{\eta}^{(1)}$ by replacing h by $\frac{4}{3}h$ or from $B_{\eta}^{(2)}$ by replacing h by $\frac{2}{3}h$.

From the definition of the tensor, $\mathbf{K}$ (see Eq. 16.2-8), the expression for the $\boldsymbol{R}_{\nu}$ (see Fig. 14.1-2), and the antisymmetry of the B_{η} one finds that

$$\mathbf{K} = a^2\zeta B\boldsymbol{uu} \tag{16.4-23}$$

where

$$B = \tfrac{1}{2}\sum_{\eta} \eta B_{\eta} = \tfrac{1}{4}\sum_{\nu\mu} \nu\mu B_{\nu\mu} \tag{16.4-24}$$

One then finds from Eqs. 16.4-14 and 15 that

$$b_1 = \eta_s + \tfrac{1}{6}na^2\zeta B \tag{16.4-25}$$

$$b_2 = -\frac{n\zeta^2a^4}{60kT}B^2 \tag{16.4-26}$$

One may compare the present results with those obtained without equilibrium averaging, which may be shown from Eqs. 14.6-23 and 24 to be

$$b_1 = \eta_s + \tfrac{1}{30}n\zeta a^2(3B^{(1)} + 2B^{(2)}) \tag{16.4-27}$$

$$b_2 = -\frac{n\zeta^2a^4}{60kT}(B^{(1)})^2 \tag{16.4-28}$$

That is, in the approximation of equilibrium averaging the two constants $B^{(1)}$ and $B^{(2)}$ are replaced by a single average constant, B, or equivalently the two time constants of Eqs. 14.6-23 and 14.6-24 are replaced by a single average time constant. In particular one finds that for the rigid dumbbell ($N = 2$), with equilibrium averaging

$$b_1 = \eta_s + \tfrac{1}{12}n\zeta a^2[1 - \tfrac{4}{3}h]^{-1} \tag{16.4-29}$$

$$b_2 = -\frac{n\zeta^2a^4}{240kT}[1 - \tfrac{4}{3}h]^{-2} \tag{16.4-30}$$

as compared to the analogous results with complete hydrodynamic interaction, obtained from Eqs. 14.6-23 and 24

$$b_1 = \eta_s + \frac{\tfrac{1}{12}n\zeta a^2[1 - \tfrac{8}{5}h(1 - \tfrac{1}{12}\xi^2)]}{[1 - h(1 + \tfrac{1}{6}\xi^2)][1 - 2h(1 - \tfrac{1}{6}\xi^2)]} \tag{16.4-31}$$

$$b_2 = -\frac{n\zeta^2a^4}{240kT}[1 - h(1 + \tfrac{1}{6}\xi^2)]^{-2} \tag{16.4-32}$$

For rigid dumbbells we have summarized the results in Table 16.4-2.

TABLE 16.4-2

Effect of Hydrodynamic Interaction on the Second-Order-Fluid Constants for Rigid Dumbbells (all entries for $h = \frac{3}{8}$, its maximum value)

Type of hydrodynamic interaction	$\frac{b_1 - \eta_s(\text{H.I.})}{b_1 - \eta_s(\text{no H.I.})}$	$\frac{b_2(\text{H.I.})}{b_2(\text{no H.I.})}$
Equilibrium averaged hydrodynamic interaction	2	4
Complete hydrodynamic interaction according to Oseen–Burgers	$\frac{64}{25} = 2.56$	$\frac{64}{25} = 2.56$
Complete hydrodynamic interaction according to Rotne–Prager–Yamakawa (with $\xi = 1$)	$\frac{32}{15} = 2.13$	$\frac{256}{81} = 3.16$

EXAMPLE 16.4-2 Second-Order Fluid Constants for the Rigid Tridumbbell with Equilibrium-Averaged Hydrodynamic Interaction

Obtain b_1 and b_2 for the rigid tridumbbell, made up of dumbbells with lengths L_1, L_2, and L_3. Use a set of embedded vectors as shown in Fig. 16.4-1, and number the beads as indicated; all m_ν and ζ_ν are taken to be equal. Include hydrodynamic interaction in the equilibrium averaged approximation.

SOLUTION The position vectors of the six beads are

$$\boldsymbol{R}_\nu = \tfrac{1}{2} L_\nu \check{\boldsymbol{\delta}}_\nu \tag{16.4-33}$$

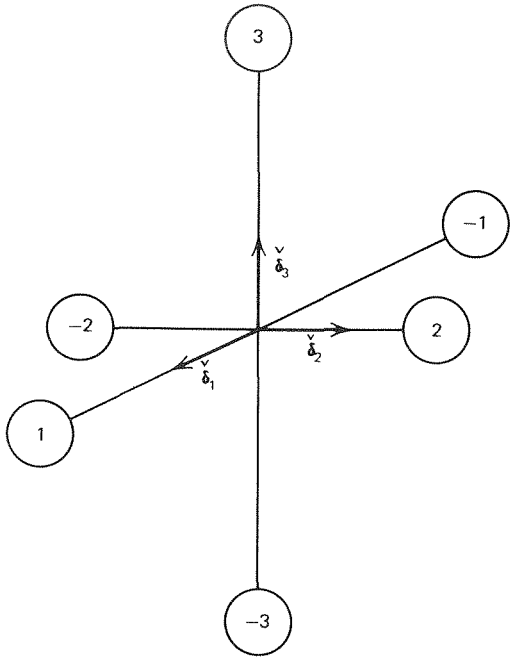


FIGURE 16.4-1. The rigid tridumbbell showing the embedded unit vectors $\check{\boldsymbol{\delta}}_n$.

where for convenience we let $L_{-\nu} = -L_\nu$ and $\check{\boldsymbol{\delta}}_{-\nu} = \check{\boldsymbol{\delta}}_\nu$. The vector between a pair of beads is then

$$\boldsymbol{R}_{\nu\mu} = \boldsymbol{R}_\mu - \boldsymbol{R}_\nu = \tfrac{1}{2}(L_\mu \check{\boldsymbol{\delta}}_\mu - L_\nu \check{\boldsymbol{\delta}}_\nu) \tag{16.4-34}$$

and the magnitude of this vector is

$$R_{\nu\mu} = \tfrac{1}{4}[L_\nu^2 + L_\mu^2 - 2L_\nu L_\mu(\delta_{\nu\mu} + \delta_{\nu,-\mu})] \tag{16.4-35}$$

a constant. The equilibrium average of the Rotne-Prager-Yamakawa interaction tensor (Eq. 14.6-2) is then the same as that of the Oseen-Burgers interaction tensor (Eqs. 13.6-5 and 15.4-3):

$$\Omega_{\nu\mu} = \frac{(1 - \delta_{\nu\mu})}{6\pi\eta_s R_{\nu\mu}} \tag{16.4-36}$$

The dimensionless mobility coefficients, $B_{\nu\eta}$, are determined by

$$\sum_\eta B_{\nu\eta}(\delta_{\eta\mu} + \Omega_{\eta\mu}) = \delta_{\nu\mu} \tag{16.4-37}$$

Next it is convenient to define a set of vectors

$$\boldsymbol{B}_\eta = \tfrac{1}{2}\sum_\nu L_\nu B_{\nu\eta}\check{\boldsymbol{\delta}}_\nu \tag{16.4-38}$$

From Eqs. 16.4-37, it follows that these vectors are determined by the equations

$$\sum_\eta \boldsymbol{B}_\eta(\delta_{\eta\mu} + \Omega_{\eta\mu}) = \tfrac{1}{2}L_\mu\check{\boldsymbol{\delta}}_\mu \tag{16.4-39}$$

From Eqs. 16.4-35 and 16.4-36 it follows that $\Omega_{-\nu,-\mu} = \Omega_{\nu\mu}$ and thus one finds from the last equation that

$$\boldsymbol{B}_{-\eta} = -\boldsymbol{B}_\eta \tag{16.4-40}$$

With this antisymmetry we find that for $\mu > 0$

$$\sum_{\eta>0} \boldsymbol{B}_\eta(\delta_{\eta\mu} + \tilde{\Omega}_{\eta\mu}) = \tfrac{1}{2}L_\mu\check{\boldsymbol{\delta}}_\mu \tag{16.4-41}$$

where for $\eta > 0$ and $\mu > 0$

$$\begin{aligned}\tilde{\Omega}_{\eta\mu} &= \Omega_{\eta\mu} - \Omega_{-\eta\mu} \\ &= -\frac{1}{6\pi\eta_s L_\eta}\delta_{\eta\mu}\end{aligned} \tag{16.4-42}$$

is diagonal. One then finds from Eqs. 16.4-41 and 42, that for $\mu > 0$

$$\boldsymbol{B}_\mu = \tfrac{1}{2}L_\mu(1 - \tfrac{4}{3}h_\mu)^{-1}\check{\boldsymbol{\delta}}_\mu \tag{16.4-43}$$

$$h_\mu = \frac{1}{8\pi\eta_s L_\mu} \tag{16.4-44}$$

From Eq. M of Table 16.1-2, Eq. 16.4-38, and the antisymmetry of the $\boldsymbol{B}_\eta$, Eq. 16.4-40, one finds that

$$\begin{aligned}\sum_\nu l_\nu L_\nu \check{\boldsymbol{\delta}}_\nu &= \frac{\sum_{\nu\mu} B_{\nu\mu} L_\nu \check{\boldsymbol{\delta}}_\nu}{\sum_{\nu\mu} B_{\nu\mu}} \\ &= 2\frac{\sum_\mu \boldsymbol{B}_\mu}{\sum_{\nu\mu} B_{\nu\mu}} \\ &= \mathbf{0}\end{aligned} \tag{16.4-45}$$

One may now show from Eqs. 16.2-8, 16.4-33, and N of Table 16.1-2

$$\begin{aligned}\mathbf{K} &= \tfrac{1}{4}\zeta \sum_\nu \sum_\mu L_\nu L_\mu B_{\nu\mu} \check{\boldsymbol{\delta}}_\nu \check{\boldsymbol{\delta}}_\mu \\ &= \tfrac{1}{2}\zeta \sum_\nu L_\nu \boldsymbol{B}_\nu \check{\boldsymbol{\delta}}_\nu \\ &= \tfrac{1}{2}\zeta \sum_{\nu>0} L_\nu^2 (1 - \tfrac{4}{3}h_\nu)^{-1} \check{\boldsymbol{\delta}}_\nu \check{\boldsymbol{\delta}}_\nu\end{aligned} \tag{16.4-46}$$

From this it follows that

$$b_1 = \eta_s + \frac{n\zeta}{12} \sum_{\nu=1}^{3} L_\nu^2 (1 - \tfrac{4}{3}h_\nu)^{-1} \tag{16.4-47}$$

$$b_2 = -\frac{n\zeta^2}{160kT} \left\{ \sum_{\nu=1}^{3} L_\nu^4 (1 - \tfrac{4}{3}h_\nu)^{-2} - \tfrac{1}{3}\left[\sum_{\nu=1}^{3} L_\nu^2 (1 - \tfrac{4}{3}h_\nu)^{-1} \right]^2 \right\} \tag{16.4-48}$$

In the limit that two of the L_ν become zero this result reduces to that for the rigid dumbbell with equilibrium averaged hydrodynamic interaction given at the end of the last example.

EXAMPLE 16.4-3 Second-Order Fluid Constants for the Elastic Rhombus

Use the results given in Problem 16C.4 to obtain the coefficients b_1 and b_2 for the elastic rhombus model, shown in Fig. 16.4-2. Neglect hydrodynamic interaction.

SOLUTION The position vectors for the beads are given in Eq. 16C.4-1. From these we can compute the elements of the (K_{mn})-matrix:

$$K_{11} = 2\zeta L^2 \cos^2\sigma, \qquad K_{22} = 2\zeta L^2 \sin^2\sigma \tag{16.4-49}$$

Then from the elements of the (Γ_{uv})-matrix we can obtain the determinant:

$$\Gamma = 8m^2 L^8 \sin^2 2\sigma \tag{16.4-50}$$

The potential energy of the system is

$$\phi = \tfrac{1}{2}H(2L\cos\sigma - \sqrt{2}L)^2 \tag{16.4-51}$$

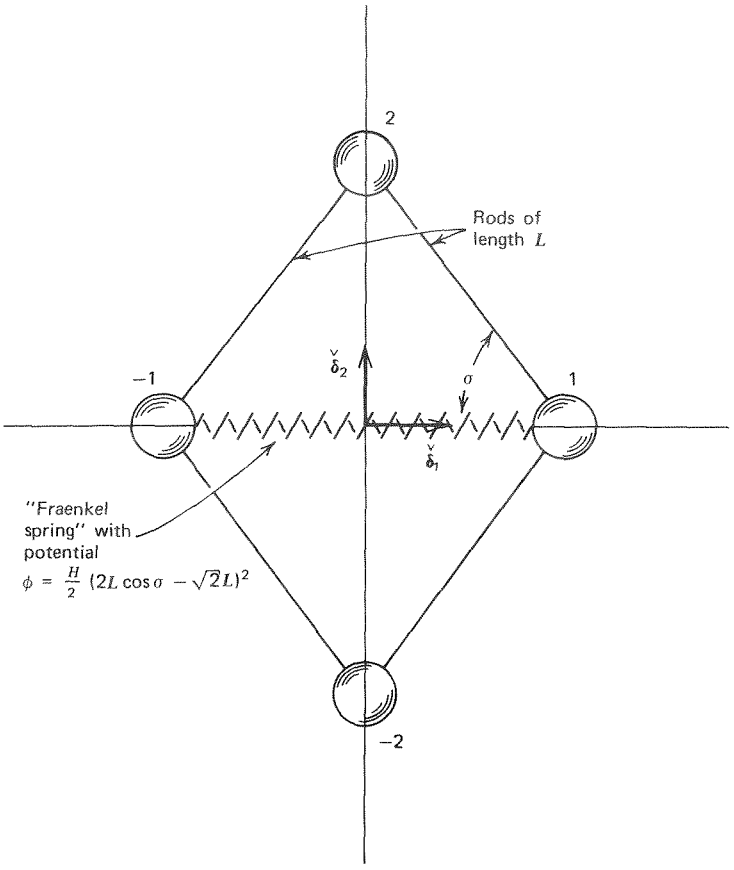


FIGURE 16.4-2. Elastic rhombus model with four identical beads.

Then b_1 is found using the second form of Eq. 16.4-16 for the $\langle\ \rangle_{eq}$ averaging

$$b_1 - \eta_s = \frac{n\zeta}{6}\langle 2L^2\rangle_{eq} = \frac{n\zeta L^2}{3} \tag{16.4-52}$$

which is the same as b_1 for the "limp" (i.e., flexible but with no spring) rhombus or the rigid rhombus. Finally b_2 is calculated thus

$$\begin{aligned} b_2 &= -\frac{n\zeta^2 L^4}{15kT}\frac{\int_0^{\pi/2}(\sin 2\sigma)[\exp - H(2L\cos\sigma - \sqrt{2}L)^2/2kT](1 - \frac{3}{4}\sin^2 2\sigma)d\sigma}{\int_0^{\pi/2}(\sin 2\sigma)[\exp - H(2L\cos\sigma - \sqrt{2}L)^2/2kT]d\sigma} \\ &= -\frac{n\zeta^2 L^4}{30kT}\left(1 - \frac{4\sqrt{2}}{105}\frac{HL^2}{kT} + \cdots\right) \end{aligned} \tag{16.4-53}$$

The factor in front is just b_2 for a limp rhombus, and the quantity in brackets is the "correction factor" for a weak Hookean spring.

§16.5 STEADY FLOWS OF FREE-DRAINING KRAMERS BEAD-ROD CHAINS

In this section we consider the Kramers freely jointed, linear, bead-rod chain model, which is appropriate for linear, flexible polymers. Some of the properties of this model have been discussed in §§11.3, 12.1, and 12.3. To discuss this model further we use a double-index notation to indicate the generalized coordinates, which are taken to be the polar angles $\theta_k = Q_{k1}$ and $\phi_k = Q_{k2}$ specifying the direction of the unit vector, $\boldsymbol{u}_k$, from bead k to bead $k+1$. That is, the first index indicates the number of the rod and the second index specifies the polar angle. Then the vector representing the kth rod is

$$\begin{aligned} a\boldsymbol{u}_k &= \boldsymbol{R}_{k+1} - \boldsymbol{R}_k \\ &= \sum_v \bar{B}_{kv}\boldsymbol{R}_v \end{aligned} \tag{16.5-1}$$

where a is the length of a rod, and the $\bar{B}_{kv}$ are the coefficients defined by Eq. 11.6-5. This relation may be inverted to give (cf. Eq. 12.1-13):

$$\boldsymbol{R}_v = a\sum_k B_{vk}\boldsymbol{u}_k \tag{16.5-2}$$

where the B_{vk} are the coefficients defined by Eq. 11.6-6. In addition, we note that

$$\sum_v \boldsymbol{R}_v\boldsymbol{R}_v = a^2\sum_{ij} C_{ij}\boldsymbol{u}_i\boldsymbol{u}_j \tag{16.5-3}$$

where the C_{ij} are the elements of the Kramers matrix defined by Eq. 11.6-7. This quantity appears in the tensor $\mathbf{K}$ of Eq. 16.2-8; when there is no hydrodynamic interaction $\mathbf{K} = \zeta\sum_v \boldsymbol{R}_v\boldsymbol{R}_v$.

It is shown in §12.1 that for the Kramers chain the base vectors are

$$\boldsymbol{b}_{v,kp} = a\sqrt{m}B_{vk}\boldsymbol{c}_{kp} \tag{16.5-4}$$

where the $\boldsymbol{c}_{kp}$ are the vectors defined in Table E.5-1. From these expressions one finds that the elements of the metric matrix are

$$g_{ip,jq} = ma^2C_{ij}(\boldsymbol{c}_{ip}\cdot\boldsymbol{c}_{jq}) \tag{16.5-5}$$

To discuss the inverse metric matrix we first define the elements of a modified Rouse matrix

$$\hat{A}_{ij} = (\boldsymbol{u}_i\cdot\boldsymbol{u}_j)A_{ij} \tag{16.5-6}$$

where the A_{ij} are the elements of the Rouse matrix defined by Eq. 11.6-8. The elements of the matrix inverse to the modified Rouse matrix are designated by $\hat{C}_{ij}$, so that

$$\sum_j \hat{A}_{ij}\hat{C}_{jk} = \delta_{ik} \tag{16.5-7}$$

It may be shown[1] that the elements of the inverse metric matrix are

$$G_{ip,jq} = \frac{1}{ma^2} \sum_{kl} A_{ik} A_{jl} (\mathbf{K}_{kl} : \boldsymbol{d}_{jq} \boldsymbol{d}_{ip}) \tag{16.5-8}$$

where the $\boldsymbol{d}_{jq}$ are vectors which are also defined in Table E.5-1 and the $\mathbf{K}_{kl}$ are the *Kramers tensors*

$$\mathbf{K}_{ij} = C_{ij}\boldsymbol{\delta} - \hat{C}_{ij}\boldsymbol{u}_i\boldsymbol{u}_j \tag{16.5-9}$$

These expressions are used in the discussion of undiluted polymers in Chapter 19. Up to this point we have been concerned solely with geometric quantities related to the chain model. Keep in mind that the metric matrices occur in the diffusion equation, Eq. 16.2-6, and in the stress-tensor expression of Eq. 16.3-5.

The equilibrium configurational distribution function, ψ_{eq}, of a Kramers chain is discussed in §12.3 and given by Eq. 12.3-5 in terms of the determinant, g, of the metric matrix. A recursive expression for this determinant is given by Eqs. 12.1-18 and 19 and explicit expressions for $N = 3$ are developed in Examples 12.1-1 and 16.1-2. Using these expressions for the equilibrium configurational distribution function and the methods developed in the previous section, one may calculate the second-order fluid constants. The results for $N = 3$ with the constraints (the bead-rod model) are

$$b_1 = \eta_s + \frac{2}{9} n\zeta a^2 \tag{16.5-10}$$

$$b_2 = -\frac{1}{1080}\left(\frac{80\pi + 3\sqrt{3}}{2\pi + 3\sqrt{3}}\right)\frac{n\zeta^2 a^4}{kT} \tag{16.5-11}$$

These values for b_1 and b_2 as well as those for $N = 4$ and 5 are given[2] in Table 16.4-1. In the same table we also list the corresponding results for a bead-spring chain with Fraenkel springs that have been taken to be infinitely stiff. Such chains have the random-walk distribution at equilibrium (Eq. 12.5-14), and for this distribution b_1 and b_2 can be obtained[3] for any N:

$$b_1 = \eta_s + \tfrac{1}{36}(N^2 - 1)n\zeta a^2 \tag{16.5-12}$$

$$b_2 = -\frac{(N^2 - 1)(10N^3 - 12N^2 + 35N - 12)}{32400N}\frac{n\zeta^2 a^4}{kT} \tag{16.5-13}$$

These last two formulas (also listed in Table 16.4-1) can be derived from Eqs. 16.4-14 and 15 by using θ_i and ϕ_i ($i = 1, 2, \ldots, N - 1$) as the generalized coordinates. Of course $b_{11} = 0$ for this model since hydrodynamic interaction is neglected.

It turns out that Eq. 16.5-12 for b_1 is also valid for the Kramers chain,[2] but, as can be seen in Table 16.4-1, Eq. 16.5-13 for b_2 gives results different from those of the Kramers chain. For $N = 3$, 4, and 5 the difference is less than 2%.

[1] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016–2025 (1981).

[2] C. F. Curtiss and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **2**, 392–396 (1977).

[3] R. S. Rivlin, *Trans. Faraday Soc.*, **45**, 739–748 (1949); O. Hassager, *J. Chem. Phys.*, **60**, 2111–2124 (1974). Rivlin did not obtain the b_1 and b_2 of the retarded-motion expansion, which was not known in 1949, but instead got the coefficients in the Reiner–Rivlin equation for potential flows.

EXAMPLE 16.5-1 Elongational Viscosity for the Kramers Bead-Rod Chain[4]

Consider a dilute suspension of Kramers chains in a steady elongational flow field. Develop expressions for the steady-state elongational viscosity asymptotically valid in the limits of large and small elongation rates.

SOLUTION (a) General Expression for the Elongational Viscosity

Since we are dealing with a steady potential flow, the distribution function is given formally by Eq. 16.2-10. Hence we may follow the general procedure used in Example 13.5-1 for a FENE dumbbell. First we write the $\boldsymbol{\kappa}$ tensor for steady elongational flow in the form

$$\boldsymbol{\kappa} = (3\boldsymbol{\delta}_3\boldsymbol{\delta}_3 - \boldsymbol{\delta})\frac{\dot{\varepsilon}}{2} \tag{16.5-14}$$

Here $\boldsymbol{\delta}$ is the second-order unit tensor and $\boldsymbol{\delta}_3$ is the space-fixed unit vector along the axis of elongation. According to the Giesekus expression, Eq. 16.3-20, we may write the stress tensor as follows:

$$\begin{aligned}\boldsymbol{\tau} &= -\eta_s\dot{\boldsymbol{\gamma}} - n\zeta\left\{\boldsymbol{\kappa}\cdot\sum_v \langle \boldsymbol{R}_v\boldsymbol{R}_v\rangle\right\} \\ &= -\eta_s\dot{\boldsymbol{\gamma}} - n\zeta a^2\left\{\boldsymbol{\kappa}\cdot\sum_i\sum_j C_{ij}\langle \boldsymbol{u}_i\boldsymbol{u}_j\rangle\right\}\end{aligned} \tag{16.5-15}$$

Here we have also used Eq. 16.5-3. We now find for the elongational viscosity defined by Eq. D.5-14:

$$\begin{aligned}\bar{\eta} &= \frac{\tau_{22} - \tau_{33}}{\dot{\varepsilon}} \\ &= \frac{((\boldsymbol{\delta}_2\boldsymbol{\delta}_2 - \boldsymbol{\delta}_3\boldsymbol{\delta}_3):\boldsymbol{\tau})}{\dot{\varepsilon}}\end{aligned} \tag{16.5-16}$$

We substitute Eqs. 16.5-14 and 15 into Eq. 16.5-16. After using the expression for $\boldsymbol{u}_i$ in Table E.5-2 we find

$$\bar{\eta} = 3\eta_s + n\zeta a^2\left\langle\sum_i\sum_j C_{ij}(C_iC_j + \tfrac{1}{2}S_iS_js_is_j)\right\rangle \tag{16.5-17}$$

We here use the notation that $C_k = \cos\theta_k$, $S_k = \sin\theta_k$, $c_k = \cos\phi_k$, and $s_k = \sin\phi_k$. We may also show that

$$\left(\boldsymbol{\kappa}:\sum_v \boldsymbol{R}_v\boldsymbol{R}_v\right) = a^2\sum_i\sum_j C_{ij}[C_iC_j - \tfrac{1}{2}S_iS_j(s_is_j + c_ic_j)]\dot{\varepsilon}/2 \tag{16.5-18}$$

Hence it follows from Eq. 16.2-10 and Eqs. 16.5-17 and 18 that

$$\bar{\eta} = 3\eta_s + n\zeta a^2 I_2/I_1 \tag{16.5-19}$$

[4] O. Hassager, *J. Chem. Phys.*, **60**, 2111–2124 (1974).

where

$$I_1 = \tfrac{1}{2}\int_0^{2\pi}\cdots\int_0^{\pi}\exp\left\{X\sum_i\sum_j C_{ij}[C_iC_j - 1 - \tfrac{1}{2}S_iS_j(s_is_j + c_ic_j)]\right\}h_N\prod_k S_k\,d\theta_k\,d\phi_k \tag{16.5-20}$$

$$I_2 = \tfrac{1}{2}\int_0^{2\pi}\cdots\int_0^{\pi}\sum_k\sum_l C_{kl}(C_kC_l + \tfrac{1}{2}S_kS_ls_ks_l)\exp\left\{X\sum_i\sum_j C_{ij}[C_iC_j - 1 - \tfrac{1}{2}S_iS_j(s_is_j + c_ic_j)]\right\}h_N\prod_k S_k\,d\theta_k\,d\phi_k \tag{16.5-21}$$

Here $X = \zeta a^2\dot{\varepsilon}/2kT$ is a dimensionless elongation rate, and we have multiplied both numerator and denominator by $\frac{1}{2}\exp(-X\sum_i\sum_j C_{ij})$ for later convenience.

The elongational viscosity for the particular freely jointed chain with $N = 3$ as computed from Eqs. 16.5-19 to 16.5-21 is shown in Fig. 16.5-1. For large values of N, however, a numerical evaluation of the integrals in Eqs. 16.5-20 and 21 is not feasible, and we therefore turn to a discussion of asymptotic expansions.

(b) Asymptotic Expansion for High Elongation Rates

We notice that the exponents in Eqs. 16.5-20 and 21 are negative everywhere except at the points $\theta_i = 0$ $(i = 1, 2, \ldots, (N-1))$ and $\theta_i = \pi$ $(i = 1, 2, \ldots, (N-1))$ where they are zero. As X becomes large, practically all the contribution to the integrals will occur in a small region around these points, and we may consequently restrict the ranges of integration to these regions. After expanding the θ_i part of the integrands in powers of θ_i retaining terms through second order in θ_i we find for I_2

$$I_2 = \int_0^{2\pi}\cdots\int_0^{\varepsilon}\sum_k\sum_l C_{kl}(1 - \tfrac{1}{2}\theta_k^2 - \tfrac{1}{2}\theta_l^2 + \tfrac{1}{2}\theta_k\theta_ls_ks_l)\exp\left\{X\sum_i\sum_j C_{ij}[1 - \tfrac{1}{2}\theta_i^2 - \tfrac{1}{2}\theta_j^2 - \tfrac{1}{2}\theta_i\theta_j(s_is_j + c_ic_j)]\right\}\prod_h \theta_h\,d\theta_h\,d\phi_h \tag{16.5-22}$$

where ε is a small number chosen so that the integrand is negligible for $\theta_i > \varepsilon$. The expression for I_1 is the same as the expression for I_2 except that the integrand consists of the exponential function alone. We have here used the expansion $h_N = 1 + O(\theta_i^4)$ for the correlation function (see Eqs. 12.1-18, 19). We now introduce a Cartesian coordinate system that locally maps the (θ_i, ϕ_i) system

$$\begin{cases} x_i = \theta_i c_i, \\ y_i = \theta_i s_i, \end{cases} \qquad i = 1, 2, \ldots, (N-1) \tag{16.5-23}$$

We emphasize that this coordinate transformation is a local transformation for the region of interest, and that there does not exist a global Cartesian coordinate system for the entire configuration space. The Jacobian of the transformation in Eq. 16.5-23 is

$$\det\left\{\frac{\partial(\theta_i, \phi_i)}{\partial(x_i, y_i)}\right\} = \prod_k S_k^{-1} \tag{16.5-24}$$

We may now rewrite the integrals I_2 and I_1 as follows:

$$I_2 \sim \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\sum_k\sum_l [C_{kl} - \tfrac{1}{2}D_{kl}(x_kx_l + y_ky_l) + \tfrac{1}{2}C_{kl}(x_kx_l) + 2y_ky_l]\exp\left[-\frac{X}{2}\sum_i\sum_j D_{ij}(x_ix_j + y_iy_j)\right]\prod_h dx_h\,dy_h \qquad (X \to \infty) \tag{16.5-25}$$

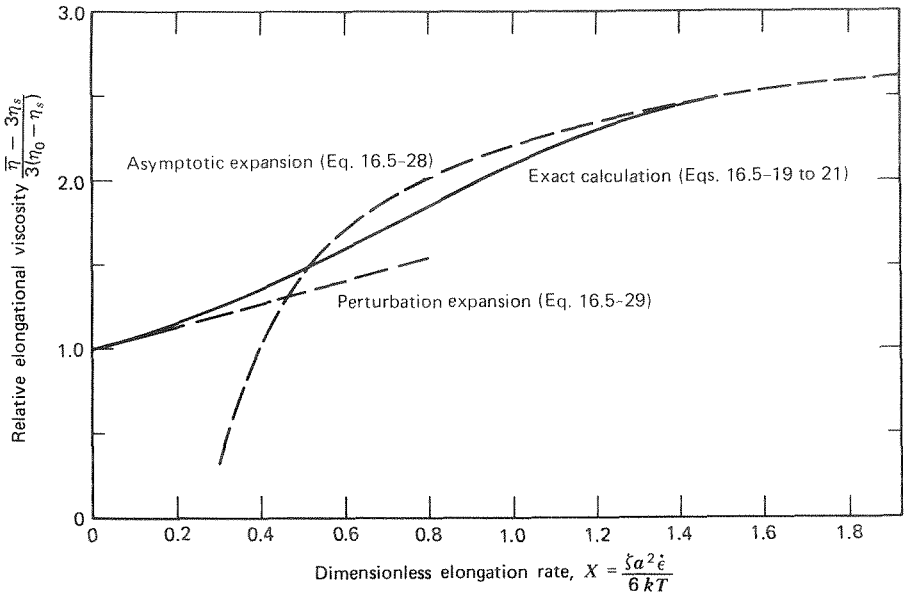


FIGURE 16.5-1. Elongational viscosity of the freely jointed bead-rod model with $N = 3$. The figure compares the asymptotic expansion Eq. 16.5-28 for large elongation rates and the perturbation expansion Eq. 16.5-29 for small elongation rates with the exact calculation from Eqs. 16.5-19 to 16.5-21. Reproduced from O. Hassager, *J. Chem. Phys.*, **60**, 2111–2124 (1974).

Again the expression for I_1 is the same as the expression for I_2 except that the integrand consists of the exponential function alone. We have also introduced the matrix with elements D_{ij} defined by

$$D_{ii} = C_{ii} + 2\sum_k C_{ik} = (N+1)C_{ii} \tag{16.5-26}$$

$$D_{ij} = C_{ij} \qquad i \neq j \tag{16.5-27}$$

It may be shown that the quadratic form $\sum_i \sum_j D_{ij} x_i x_j$ is non-negative for all values of x_i and zero only at the origin. Hence for large values of X the integrands in I_1 and I_2 will be practically zero outside the region of interest around the origin, and the ranges of integration have conveniently been extended to infinity with negligible error. The integrals I_1 and I_2 are now in standard forms and may be performed analytically. After some manipulation we may write the elongational viscosity for the freely jointed chain at large elongational rates in the form

$$\frac{\bar{\eta} - 3\eta_s}{3(\eta_0 - \eta_s)} \sim N - \frac{24[N - 1 - \frac{3}{2}\sum_i \sum_j C_{ij} D_{ji}^{-1}]kT}{(N^2 - 1)\zeta a^2 \dot{\varepsilon}} + \cdots \qquad (\dot{\varepsilon} \to \infty)$$

$$\sim N\left(1 - \frac{24kT}{N^2 \zeta a^2 \dot{\varepsilon}} + \cdots\right) \qquad (N \gg 1) \qquad (\dot{\varepsilon} \to \infty) \tag{16.5-28}$$

where $\eta_0 - \eta_s = (1/36)n\zeta a^2(N^2 - 1)$ is the polymer contribution to the zero-shear-rate viscosity. In the second line we have specialized the expression to chains with a large number of links.[5]

[5] The quantity $\sum_i \sum_j C_{ij} D_{ji}^{-1}$ is tabulated by O. Hassager, *J. Chem. Phys.*, **60**, p. 2121 (1974).

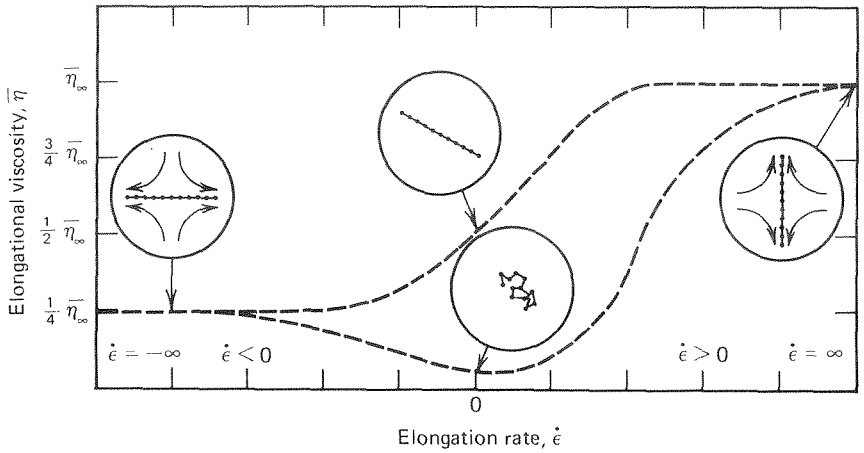


FIGURE 16.5-2. Qualitative plot of elongational viscosity versus elongation rate, illustrating the different behavior of flexible and rigid macromolecules. At large rates of deformation both kinds of molecules are in a linear configuration, and the curves have common asymptotes. At small rates of deformation the flexible molecules coil up, whereas the rigid ones do not. Reproduced from O. Hassager, *J. Chem. Phys.*, **60**, 2111–2124 (1974).

(c) Expansion for Low Elongation Rates

The expansion for low elongation rates may be obtained directly from the second-order-fluid model with the approximate constants given in Eqs. 16.5-12 and 16.5-13. We find then

$$\frac{\bar{\eta} - 3\eta_s}{3(\eta_0 - \eta_s)} \sim 1 + \left(\frac{10N^3 - 12N^2 + 35N - 12}{900N}\right)\frac{\zeta a^2 \dot{\varepsilon}}{kT} + \cdots \qquad (\dot{\varepsilon} \to 0)$$

$$\sim 1 + \frac{N^2 \zeta a^2 \dot{\varepsilon}}{90kT} + \cdots \qquad (N \gg 1) \qquad (\dot{\varepsilon} \to 0) \qquad (16.5\text{-}29)$$

Here again in the second line we have specialized the expression for chains with a large number of links. An appreciation of the extent to which the analytical expansions for small and large elongation rates portray the exact behavior of $\bar{\eta}$ may be obtained for $N = 3$ from a comparison with the exact numerical evaluation of the integrals as shown in Fig. 16.5-1.

It is interesting to note that the elongational viscosity increases by a factor of N from zero elongation rate to large elongation rates. For flexible macromolecules this may be a very large number. The result in Eq. 16.5-28 compares favorably with one set of experimental data.[6]

In conclusion it is fitting to point out the difference in behavior between the freely jointed bead-rod chain (with N beads and $N - 1$ rods of length a) and the multibead rod (with N beads and interbead distance a). In Fig. 16.5-2 we see a qualitative comparison of the elongational viscosity curves as a function of elongation rate and the corresponding molecular-model behavior (cf. Table 14.4-2 for $\bar{\eta}$ vs. $\dot{\varepsilon}$ for rigid dumbbells).

§16.6 STEADY FLOWS FOR FREE-DRAINING KIRKWOOD–RISEMAN BEAD-ROD CHAINS

The Kirkwood–Riseman freely rotating chain model differs from the Kramers chain discussed in the previous section in that the angles between successive rods are fixed. In this discussion we take all of these angles to be the same and equal to ξ as shown in Fig. 11.2-1.

[6] S. T. J. Peng and R. F. Landel, *Rheology*, Vol. 2, Plenum Press, New York (1980), pp. 385–391; the fluids used in their experiments were not dilute and some entanglement effects must have been present. See also fn. 15 of §13.5.

To describe this system we first consider an "embedded" coordinate system in which the z-axis with associated unit vector $\check{\boldsymbol{\delta}}_3$ is in the direction of the unit vector $\boldsymbol{u}_1$. The unit vector $\check{\boldsymbol{\delta}}_1$ is then normal to $\check{\boldsymbol{\delta}}_3$ and in the plane containing the first and second links with $(\check{\boldsymbol{\delta}}_1 \cdot \boldsymbol{u}_2)$ being positive. A third unit vector is chosen so that the vectors $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$ form a right-handed set. The Euler angles describing the orientation of this embedded $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$-frame are taken as the first three generalized coordinates, $Q_1 = \alpha$, $Q_2 = \beta$, and $Q_3 = \gamma$; these are the angles labelled ξ_{01}, ξ_1, and ξ_{12} in Fig. 11.6-1. The coordinates ξ_1 and ξ_{01} are also the same as the polar angles θ_1 and ϕ_1, respectively, of the unit vector $\boldsymbol{u}_1$. The remaining $N - 3$ generalized coordinates, $Q_4, Q_5, Q_6, \ldots, Q_N$ are the angles between the planes containing successive pairs of links, the angles $\xi_{23}, \xi_{34}, \ldots, \xi_{N-2,N-1}$ of Fig. 11.6-1; each of these angles goes from 0 to 2π.

The (Ω_{mn})-matrix, defined by Eq. 16.1-1, is an orthogonal matrix, which describes the relation between the space-fixed and body-fixed axes. The matrix elements can be written as the scalar products of the unit vectors associated with the two coordinate systems:

$$\Omega_{mn} = (\check{\boldsymbol{\delta}}_m \cdot \boldsymbol{\delta}_n) \tag{16.6-1}$$

We may also define a tensor $\boldsymbol{\Omega}$, which has components Ω_{mn} in the space-fixed frame:

$$\begin{aligned} \boldsymbol{\Omega} &= \sum_m \sum_n \boldsymbol{\delta}_m \boldsymbol{\delta}_n \Omega_{mn} \\ &= \sum_n \boldsymbol{\delta}_n \check{\boldsymbol{\delta}}_n \end{aligned} \tag{16.6-2}$$

The tensor $\boldsymbol{\Omega}$ converts the space-fixed unit vectors to the body-fixed unit vectors according to $[\boldsymbol{\delta}_n \cdot \boldsymbol{\Omega}] = \check{\boldsymbol{\delta}}_n$.

It is now convenient to introduce a set of orthogonal matrices with elements $\Omega^{(k)}_{mn}$, which are scalar products of unit vectors associated with neighboring links in the chain

$$\Omega^{(k)}_{mn} = (\boldsymbol{\delta}^{(k)}_m \cdot \boldsymbol{\delta}^{(k-1)}_n) \tag{16.6-3}$$

The orthonormal triad of unit vectors $\boldsymbol{\delta}^{(k)}_1$, $\boldsymbol{\delta}^{(k)}_2$, $\boldsymbol{\delta}^{(k)}_3$ is identical to the triad of unit vectors $\boldsymbol{s}_k$, $\boldsymbol{t}_k$, $\boldsymbol{u}_k$ introduced in §11.6; the unit vectors $\boldsymbol{\delta}^{(0)}_n$ are identical to the space-fixed unit vectors $\boldsymbol{\delta}_n$. The $\Omega^{(k)}_{mn}$, with $k > 1$, are given by the matrix of Eq. 16.1-2, but with α, β, γ replaced by $\xi_{k-1,k}$, ξ, 0 respectively; and $\Omega^{(1)}_{mn}$ is given by the same matrix with α, β, γ replaced by ξ_{01}, ξ_1, 0. Next we define a set of tensors $\boldsymbol{\Omega}^{(k)}$, which have components $\Omega^{(k)}_{mn}$ with respect to axes corresponding to the unit vectors $\boldsymbol{\delta}^{(k)}_m$, so that

$$\begin{aligned} \boldsymbol{\Omega}^{(k)} &= \sum_m \sum_n \boldsymbol{\delta}^{(k)}_m \boldsymbol{\delta}^{(k)}_n \Omega^{(k)}_{mn} \\ &= \sum_n \boldsymbol{\delta}^{(k-1)}_n \boldsymbol{\delta}^{(k)}_n \end{aligned} \tag{16.6-4}$$

Note further that $[\boldsymbol{\delta}^{(k-1)}_n \cdot \boldsymbol{\Omega}^{(k)}] = \boldsymbol{\delta}^{(k)}_n$. The parallelism between this paragraph and the foregoing one should be evident.

The vector from the center of mass of the chain to bead v is given by an expression identical to that for the Kramers chain (see Eq. 16.5-2):

$$\boldsymbol{R}_v = a \sum_k B_{vk} \boldsymbol{u}_k \tag{16.6-5}$$

(where $\boldsymbol{u}_k$ is identical to $\boldsymbol{\delta}_3^{(k)}$). As pointed out just after Eq. 16.6-4, $\boldsymbol{u}_k = [\boldsymbol{u}_{k-1} \cdot \boldsymbol{\Omega}^{(k)}]$; when this relation is applied recursively we get

$$\boldsymbol{u}_k = [\boldsymbol{\delta}_3 \cdot \boldsymbol{\Omega}^{(1)} \cdot \boldsymbol{\Omega}^{(2)} \cdot \cdots \cdot \boldsymbol{\Omega}^{(k-1)} \cdot \boldsymbol{\Omega}^{(k)}] \tag{16.6-6}$$

Then using the relation following Eq. 16.6-2, we get

$$\boldsymbol{u}_k = [\check{\boldsymbol{\delta}}_3 \cdot \boldsymbol{\Omega}^{-1} \cdot \boldsymbol{\Omega}^{(1)} \cdot \boldsymbol{\Omega}^{(2)} \cdot \cdots \cdot \boldsymbol{\Omega}^{(k-1)} \cdot \boldsymbol{\Omega}^{(k)})] \tag{16.6-7}$$

Next we define a tensor $\tilde{\boldsymbol{\Omega}}^{(2)}$ closely related to $\boldsymbol{\Omega}^{(2)}$

$$\tilde{\boldsymbol{\Omega}}^{(2)} = \{\boldsymbol{\Omega}^{-1} \cdot \boldsymbol{\Omega}^{(1)} \cdot \boldsymbol{\Omega}^{(2)}\} = \sum_m \check{\boldsymbol{\delta}}_m \boldsymbol{\delta}_m^{(2)} \tag{16.6-8}$$

The components of this tensor in the coordinate system with unit vectors $\boldsymbol{\delta}_n^{(2)}$ are $\tilde{\Omega}_{mn}^{(2)} = (\boldsymbol{\delta}_m^{(2)} \cdot \check{\boldsymbol{\delta}}_n)$, whereas the components of $\boldsymbol{\Omega}^{(2)}$ in the same frame are $\Omega_{mn}^{(2)} = (\boldsymbol{\delta}_m^{(2)} \cdot \boldsymbol{\delta}_n^{(1)})$. Hence the $\Omega_{mn}^{(2)}$ are given by Eq. 16.1-2 with α, β, γ replaced by 0, ξ, 0.

As defined in Eq. 16.1-3, the R_{vn} are the components of $\boldsymbol{R}_v$ in the body-fixed frame. Hence from Eqs. 16.6-5 through 8 we get

$$\begin{aligned} R_{vn} = {} & aB_{v1}\delta_{n3} + aB_{v2}(\check{\boldsymbol{\delta}}_n \check{\boldsymbol{\delta}}_3 : \tilde{\boldsymbol{\Omega}}^{(2)}) \\ & + a\sum_{k=3}^{N-1} B_{vk}(\check{\boldsymbol{\delta}}_n \check{\boldsymbol{\delta}}_3 : \{\tilde{\boldsymbol{\Omega}}^{(2)} \cdot \boldsymbol{\Omega}^{(3)} \cdots \boldsymbol{\Omega}^{(k-1)} \cdot \boldsymbol{\Omega}^{(k)}\}) \end{aligned} \tag{16.6-9}$$

When this expression is written more explicitly using Eqs. 16.6-3, 4, and 8 one finds that

$$R_{vn} = a[B_{v1}\delta_{n3} + B_{v2}\tilde{\Omega}_{3n}^{(2)} + B_{v3}\sum_m \Omega_{3m}^{(3)}\tilde{\Omega}_{mn}^{(2)} + B_{v4}\sum_{mp} \Omega_{3p}^{(4)}\Omega_{pm}^{(3)}\tilde{\Omega}_{mn}^{(2)} + \cdots] \tag{16.6-10}$$

From Eq. 16.1-2 it may be shown that derivative of Ω_{mn} with respect to the first Euler angle is

$$\frac{\partial}{\partial \alpha}\Omega_{mn} = \sum_p \Omega_{mp}\varepsilon_{pn3} \tag{16.6-11}$$

Because the $\Omega_{mn}^{(k)}$ are given by the same matrix as Ω_{mn} in Eq. 16.1-2, but with α, β, γ replaced by $\xi_{k-1,k}$, ξ, 0 (or Q_{k+1}, ξ, 0), it follows at once that ($k \geq 3$)

$$\frac{\partial}{\partial Q_{k+1}}\Omega_{mn}^{(k)} = \sum_p \Omega_{mp}^{(k)}\varepsilon_{pn3} \tag{16.6-12}$$

We have now accumulated enough information to get expressions for the b^{vun} of Eq. 16.1-9 for the Kirkwood–Riseman chain.

From the definition of the b^{vun} we find for $u \geq 4$

$$\begin{aligned} b^{vun} = a\sqrt{m}\Bigg[& B_{v,u-1}\sum_{m,\ldots,r,s}\left(\frac{\partial}{\partial Q_u}\Omega_{3s}^{(u-1)}\right)\Omega_{sr}^{(u-2)}\cdots\tilde{\Omega}_{mn}^{(2)} \\ & + B_{vu}\sum_{m,\ldots,p,r,s}\Omega_{3s}^{(u)}\left(\frac{\partial}{\partial Q_u}\Omega_{sr}^{(u-1)}\right)\Omega_{rp}^{(u-2)}\cdots\tilde{\Omega}_{mn}^{(2)} + \cdots\Bigg] \end{aligned} \tag{16.6-13}$$

Then using the definition for $\tilde{\Omega}^{(2)}_{mn}$ and $\Omega^{(k)}_{mn}$ above we find that, for $u \geq 4$

$$b^{vun} = \sqrt{m}(\boldsymbol{R}_{vu} \cdot \boldsymbol{\Lambda}^{(u)} \cdot \check{\boldsymbol{\delta}}_n) \tag{16.6-14}$$

where

$$\boldsymbol{\Lambda}^{(u)} = \boldsymbol{\delta}_1^{(u-2)}\boldsymbol{\delta}_2^{(u-2)} - \boldsymbol{\delta}_2^{(u-2)}\boldsymbol{\delta}_1^{(u-2)} \tag{16.6-15}$$

$$\boldsymbol{R}_{vu} = a \sum_{v=u-1}^{N-1} B_{vv}\boldsymbol{u}_v \tag{16.6-16}$$

The expression for the b^{vun} for $u \geq 4$ may also be written as

$$b^{vun} = \sqrt{m}([\boldsymbol{v}_u \times \boldsymbol{R}_{vu}] \cdot \check{\boldsymbol{\delta}}_n) \tag{16.6-17}$$

in which $\boldsymbol{v}_u = \boldsymbol{u}_{u-2}$. Equation 16.6-17 can be made valid for $u \leq 3$ by extending the definition of $\boldsymbol{R}_{vu}$

$$\boldsymbol{R}_{vu} = a \sum_{v=1}^{N-1} B_{vv}\boldsymbol{u}_v = \boldsymbol{R}_v \tag{16.6-18}$$

and letting $\boldsymbol{v}_u = -\check{\boldsymbol{\delta}}_u$.

Using Eq. 16.6-17 in the definition of the elements of the generalized moment of inertia matrix, one finds that the elements are

$$\begin{aligned}\Gamma_{uv} &= m \sum_{v} ([\boldsymbol{v}_u \times \boldsymbol{R}_{vu}] \cdot [\boldsymbol{v}_v \times \boldsymbol{R}_{vv}]) \\ &= m \sum_{v} [(\boldsymbol{v}_u \cdot \boldsymbol{v}_v)(\boldsymbol{R}_{vu} \cdot \boldsymbol{R}_{vv}) - (\boldsymbol{v}_v \cdot \boldsymbol{R}_{vu})(\boldsymbol{v}_u \cdot \boldsymbol{R}_{vv})]\end{aligned} \tag{16.6-19}$$

Thus one sees that in determining the elements of the generalized moment of inertia matrix, in which at least one index is associated with a generalized coordinate rather than an Euler angle, the vector $\boldsymbol{R}_{vu}$ replaces the vector $\boldsymbol{R}_v$ and the unit vector $\boldsymbol{v}_u$ replaces the unit vector $\check{\boldsymbol{\delta}}_u$ of the body-fixed axes. From the last result it may be shown that the elements of the generalized moment of inertia matrix are for $s, u \leq 3$

$$\Gamma_{su} = ma^2 \sum_{v=1}^{N-1} \sum_{w=1}^{N-1} C_{vw}[\delta_{su}(\boldsymbol{u}_v \cdot \boldsymbol{u}_w) - (\check{\boldsymbol{\delta}}_u \cdot \boldsymbol{u}_v)(\check{\boldsymbol{\delta}}_s \cdot \boldsymbol{u}_w)] \tag{16.6-20}$$

and for $s \leq 3$, $u \geq 4$

$$\Gamma_{su} = -ma^2 \sum_{v=1}^{N-1} \sum_{w=u-1}^{N-1} C_{vw}[(\check{\boldsymbol{\delta}}_s \cdot \boldsymbol{v}_u)(\boldsymbol{u}_v \cdot \boldsymbol{u}_w) - (\boldsymbol{v}_u \cdot \boldsymbol{u}_v)(\check{\boldsymbol{\delta}}_s \cdot \boldsymbol{u}_w)] \tag{16.6-21}$$

and for $s, u \geq 4$

$$\Gamma_{su} = ma^2 \sum_{v=s-1}^{N-1} \sum_{w=u-1}^{N-1} C_{vw}[(\boldsymbol{v}_s \cdot \boldsymbol{v}_u)(\boldsymbol{u}_v \cdot \boldsymbol{u}_w) - (\boldsymbol{v}_u \cdot \boldsymbol{u}_v)(\boldsymbol{v}_s \cdot \boldsymbol{u}_w)] \tag{16.6-22}$$

The elements of the metric matrix, g_{su}, are given in terms of these elements by Eq. 16.1-10.

a. Equilibrium

The equilibrium configurational distribution function is given by Eq. 12.3-4, a consequence of the canonical distribution in phase space. For the freely rotating chain model the intramolecular potential is zero, so that

$$\psi_{eq} = \frac{\sqrt{g}}{\int \sqrt{g}\, dQ} = \frac{\sqrt{\Gamma} \sin \beta}{8\pi^2 \int \sqrt{\Gamma}\, dQ'} \tag{16.6-23}$$

Here $\int \ldots dQ$ indicates integration over all the generalized coordinates (Q_1 to Q_N), and $\int \ldots dQ'$ is the integration over Q_4 to Q_N (i.e., ξ_{23} to $\xi_{N-2,N-1}$); the quantity Γ is the determinant of the generalized moment-of-intertia tensor (see Eq. J of Table 16.1-1).

It is interesting to compare the above expression for ψ_{eq} with that which one obtains by considering a "modified random walk" distribution. In this modified random walk one considers a sequence of N vectors, each of length a. The angle between successive vectors is fixed at ξ, but the point on the circle determined by this fixed angle is taken to be random. Using this modified random walk, Eyring[1] obtained an equilibrium distribution function which in the present notation is

$$\psi_{eq} = \frac{\sin \beta}{8\pi^2 \int_0^{2\pi} \cdots \int_0^{2\pi} d\xi_{23} \cdots d\xi_{N-2,N-1}} = \frac{\sin \beta}{2(2\pi)^{N-1}} \quad \text{(modified random walk)} \tag{16.6-24}$$

This differs from the expression in Eq. 16.6-23 by a factor of $\sqrt{\Gamma}$ (and the concomitant change in the normalization constant). For $N = 3$, that is, three beads and two rods, there are no generalized coordinates other than the Euler angles, and Γ is a constant. Thus for this case the two distributions are identical; but for larger values of N they differ.

For $N = 4$, the four bead-three rod chain, Fan and Liu[2] have developed an explicit expression for Γ and investigated the difference between the distribution functions in Eqs. 16.6-23 and 16.6-24. For $\xi = \arccos(\frac{1}{3})$, the two functions, each divided by $(\sin \beta)/8\pi^2$, are shown in Fig. 16.6-1 as functions of $Q_4 = \xi_{23}$, the angle between the planes containing the first two and the last two rods. The modified random walk value is $1/2\pi$; the distribution function obtained from Eq. 16.6-2 is symmetric about $\xi_{23} = \pi$ with maxima at 0.525π and 1.475π, and local minima at 0 and π. The maxima are 14.5% higher than the random walk value, and the minima are 9.4 and 21.1% lower.

For $N = 5$ ψ_{eq} is a function of two angles, ξ_{23} and ξ_{34}. For the special case of $\xi = \arccos(\frac{1}{3})$ a plot of $8\pi^2\psi_{eq}/\sin \beta$ is given in Fig. 16.6-2. It is clear that there are appreciable deviations from the random walk value.

The equilibrium average of the square of the end-to-end distance of Rouse chains is evaluated in Example 11.4-1. Fan and Liu[2] have evaluated this quantity for freely rotating chains consisting of 8 or fewer beads. Their results are compared with the random walk

[1] H. Eyring, *Phys. Rev.*, **39**, 746–748 (1932); the random-walk distribution has been used for getting the mean square end-to-end distances and other properties by L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd ed., Oxford University Press, New York (1958), p. 46; M. Volkenstein, *Configurational Statistics of Polymer Chains*, Interscience, New York (1963); P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969), pp. 16–18, 326–333; H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), pp. 35–37. None of these references concern themselves with Eq. 16.6-23, which comes from applying equilibrium statistical mechanics to the Kirkwood–Riseman chain model.

[2] X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303–321 (1986).

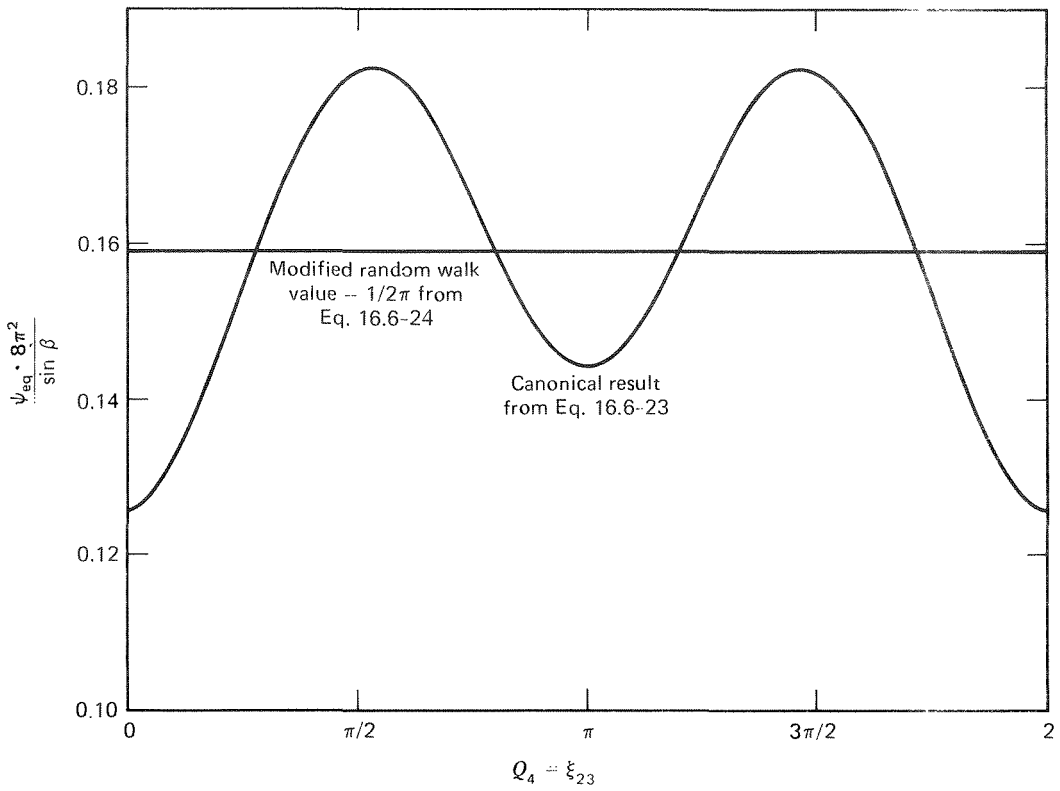


FIGURE 16.6-1. Equilibrium configurational distribution function for the Kirkwood-Riseman chain with four beads and three rods. Reproduced from X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303-321 (1986).

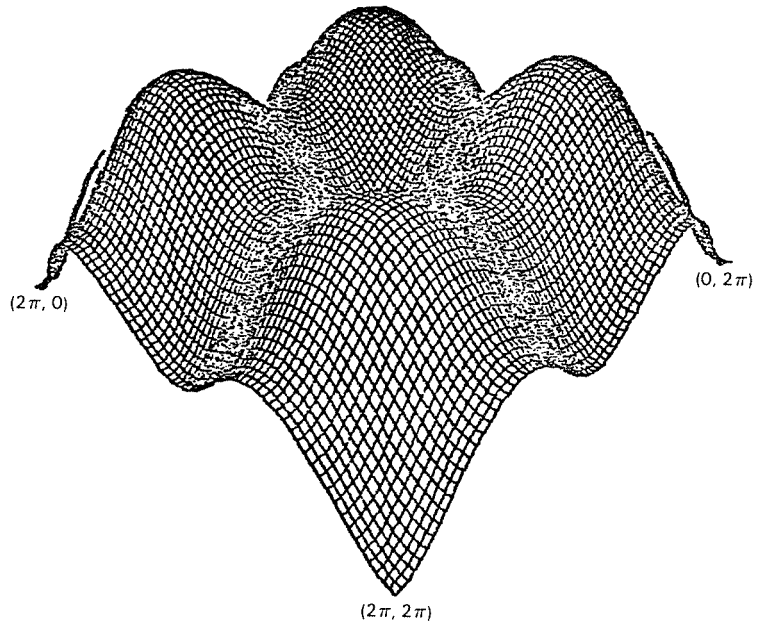


FIGURE 16.6-2. Equilibrium configurational distribution function for the Kirkwood-Riseman chain with five beads and four rods. Reproduced from X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303-321 (1986).

TABLE 16.6-1[a]

Quantities Computed For the Free-Draining Kirkwood–Riseman Chain
[with $\xi = \arccos \frac{1}{3}$]

Quantity	Number of Beads, N	Canonical[b]	Random Walk[c]	Ratio
Mean square	3	2.667	2.667	1.000
end-to-end	4	4.601	4.556	0.9901
distance	5	6.621	6.519	0.9846
$\langle r^2 \rangle_{eq}/a^2$	6	8.671	8.506	0.9811
	7	10.727	10.502	0.9790
	8	12.783	12.501	0.9779
Zero-shear-rate	3	0.25926	0.25926	1.0000
viscosity	4	0.53894	0.53704	0.9965
$(\eta_0 - \eta_s)/n\zeta a^2$	5	0.92720	0.92099	0.9933
	6	1.4268	1.4132	0.9905
	7	2.0390	2.0149	0.9882
	8	2.7643	2.7266	0.9863
Zero-shear-rate	3	0.02551	0.02551	1.0000
first-normal-stress	4	0.10150	0.10062	0.9913
coefficient	5	0.29630	0.29284	0.9883
$\Psi_{1,0} kT/2n\zeta^2 a^4$	6	0.70472	0.69496	0.9862
	7	1.4525	1.4299	0.9844
	8	2.6967	2.6506	0.9829

[a] X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303–321 (1986).
[b] From Eq. 16.6-23.
[c] From Eq. 16.6-24.

values in Table 16.6-1. It is interesting to note that the deviation of the ratio of these two numbers from unity increases monotonically with N for $N \leq 8$; the behavior for larger values of N is not known.

b. Second-Order Fluid Constants

It was pointed out in the previous section that one may use the methods developed in §16.4 to evaluate the second order fluid constants b_1 and b_2, once one knows the equilibrium configurational distribution function. Fan and Liu[2] have evaluated b_1 and b_2 for freely rotating chains with 3 and 4 beads analytically and for $N \leq 8$ numerically. For $N = 3$ they find that

$$\frac{(b_1 - \eta_s)}{n\zeta a^2} = \frac{1}{9}(2 + \cos \xi) \tag{16.6-25}$$

$$\frac{-b_2 kT}{n\zeta^2 a^4} = \frac{1}{540}(7 + 16 \cos \xi + 13 \cos^2 \xi) \tag{16.6-26}$$

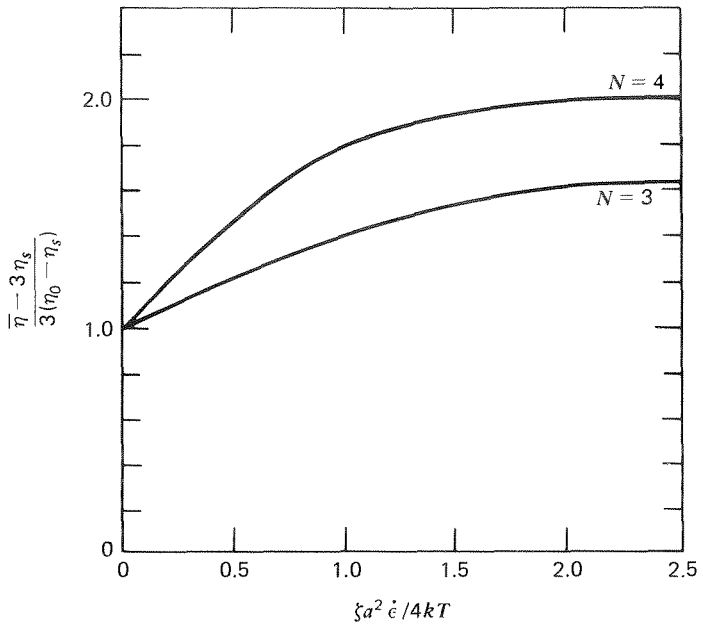


FIGURE 16.6-3. Elongational viscosity for Kirkwood–Riseman chains with three and four beads.

The values which they obtained for chains with $N \leq 8$ and with $\xi = \arccos(\frac{1}{3})$ are compared with the values obtained using the random walk distribution in Table 16.6-1. Again, it is interesting to note that the deviation of the ratio of these values from unity grows with increasing N.

c. Elongational Viscosity

Fan and Liu[2] have also computed the steady state elongational viscosity for freely rotating chains of three and four beads. The values which they obtained are illustrated in Fig. 16.6-3 as plots of the reduced elongational viscosity $(\bar{\eta} - 3\eta_s)/3(\eta_0 - \eta_s)$ as functions of a dimensionless elongation rate $\dot{\epsilon}\zeta a^2/4kT$. For both $N = 3$ and $N = 4$ the reduced elongational viscosity increases monotonically with elongation rate, apparently approaching a limit as $\dot{\epsilon} \to \infty$. Comparison of the curves in Fig. 16.6-3 with the Kramers chain results in Fig. 16.5-1 and in Eq. 16.5-28 suggests that incorporation of "chain stiffness" into the chain model (by fixing the angles between pairs of adjacent rods) lowers the limiting value of $\bar{\eta}$ as $\dot{\epsilon} \to \infty$. Unfortunately there are no experimental data on $\bar{\eta}$ for dilute solutions of polymer chains of varying backbone stiffness.

§16.7 UNSTEADY FLOWS FOR FREE-DRAINING BEAD-ROD MODELS

In this section we present a general framework[1] for obtaining the relaxation modulus of linear viscoelasticity for bead-rod models with identical beads and no internal potentials. The method summarized in Eqs. 16.7-12 to 16.7-15 is in principle applicable to

[1] O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974).

flexible bead-rod models of arbitrary complexity although it is practical only for models with a small number of degrees of freedom.

Let us introduce a homogeneous periodic potential flow of the form

$$\boldsymbol{\kappa} = \boldsymbol{\kappa}_0 \, \mathscr{R}e\{e^{i\omega t}\} \tag{16.7-1}$$

in which $\boldsymbol{\kappa}_0 = \boldsymbol{\kappa}_0^\dagger$ and $(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2} \ll kT/\zeta L^2$ where L designates any fixed length characteristic of the model. Under the linear conditions considered here, the distribution function ψ will be of the form

$$\psi = \frac{1}{J} g^{1/2}[1 + \mathscr{R}e\{\phi_1 e^{i\omega t}\} + \cdots] \tag{16.7-2}$$

Here J is a normalization constant, and ϕ_1, which is a function of the generalized coordinates and linear in $(\zeta L^2/kT)(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2}$, may be complex, thus allowing for a phase lag. When this expression is introduced in the general diffusion equation for ψ (Eq. 16.2-6), it follows that for potential flow ϕ_1 must be a solution of

$$\left(\frac{kT}{\zeta L^2}\right)\nabla^2\phi_1 - i\omega\phi_1 = (1/2L^2)\nabla^2\left(\boldsymbol{\kappa}_0 : \sum_v \boldsymbol{R}_v\boldsymbol{R}_v\right) \tag{16.7-3}$$

In Eq. 16.7-3 we use the notation ∇^2 for the Laplacian operator in the configuration space defined by

$$\nabla^2\Lambda = mL^2 g^{-1/2} \sum_t \sum_u \frac{\partial}{\partial Q_t}\left(g^{1/2} G_{tu} \frac{\partial}{\partial Q_u}\Lambda\right) \tag{16.7-4}$$

In order to solve Eq. 16.7-3 we consider first the "Helmholtz equation" in the configuration space

$$\nabla^2 f + \nu f = 0 \tag{16.7-5}$$

This equation has nontrivial solutions for a set of real, non-negative eigenvalues $\nu = \nu_p$. The corresponding eigenfunctions $f = f_p$ are orthogonal with respect to the weighting function $g^{1/2}$ and may be normalized such that

$$\int \bar{f}_p f_q g^{1/2}\, dQ = \delta_{pq} \tag{16.7-6}$$

where the bar on f_p indicates a complex conjugate. We now expand ϕ_1 and $(\boldsymbol{\kappa}_0 : \Sigma_v \boldsymbol{R}_v\boldsymbol{R}_v)$ as follows:

$$\phi_1 = \sum_{p=0}^{\infty} A_p f_p \tag{16.7-7}$$

$$\left(\boldsymbol{\kappa}_0 : \sum_v \boldsymbol{R}_v\boldsymbol{R}_v\right) = (\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2} L^2 \sum_{p=0}^{\infty} \alpha_p f_p \tag{16.7-8}$$

where the A_p and the α_p are independent of the generalized coordinates. Using the orthogonality of the eigenfunctions we may solve the latter equation formally for α_p to get

$$\alpha_p = (\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{-1/2} L^{-2} \left(\boldsymbol{\kappa}_0 : \int \sum_\nu R_\nu R_\nu \bar{f}_p g^{1/2}\, dQ \right) \tag{16.7-9}$$

When Eqs. 16.7-7 and 8 are introduced in the linearized diffusion equation Eq. 16.7-3, we may solve the resulting equation for the expansion coefficients A_p. The final result is that the distribution function *in the linear range* considered may be formally written

$$\psi = \frac{1}{J_{eq}} g^{1/2} \left[1 + \frac{\zeta}{2} (\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2} L^2 \, \mathscr{R}e \left\{ \sum_{p=0}^{\infty} \frac{\alpha_p \nu_p f_p e^{i\omega t}}{\nu_p kT + i\omega\zeta L^2} \right\} + \cdots \right] \tag{16.7-10}$$

where

$$J_{eq} = \int g^{1/2}\, dQ \tag{16.7-11}$$

The distribution function in Eq. 16.7-10 must now be introduced in the expression for the stress tensor Eq. 16.3-11 to obtain the rheological response of the suspension to the imposed velocity gradient. After a lengthy development the result may be recast in terms of the relaxation modulus $G(s)$ of linear viscoelasticity (or the G_I of the memory-integral expansion in Eq. 9.6-12) as follows:

$$G(s) = 2\eta_s \delta(s) + n\zeta L^2 a \delta(s) + nkT \sum_{p=0}^{\infty} b_p e^{-s/\lambda_p} \tag{16.7-12}$$

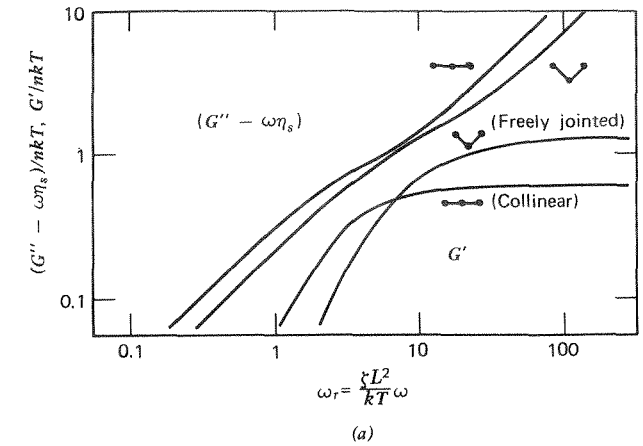
$$a = \frac{1}{J_{eq}} \left[\left(\frac{1}{3L^2} \sum_\nu \int (R_\nu \cdot R_\nu) g^{1/2}\, dQ \right) - \frac{1}{4} \sum_{p=0}^{\infty} |\alpha_p|^2 \nu_p \right] \tag{16.7-13}$$

$$b_p = \frac{1}{8J_{eq}} |\alpha_p|^2 \nu_p^2 \tag{16.7-14}$$

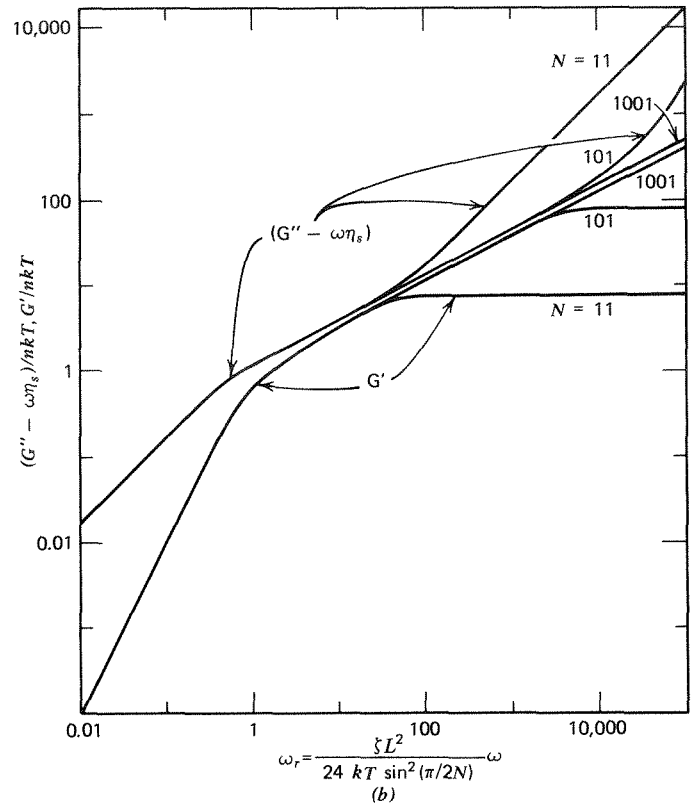
$$\lambda_p = \frac{\zeta L^2}{\nu_p kT} \tag{16.7-15}$$

Thus we see that the relaxation modulus of linear viscoelasticity for arbitrary bead-rod models with no internal potentials may be determined by the following sequence of steps:

- **i.** The metric tensor components g_{tu} and G_{tu} and the determinant g of §16.1 must be calculated in terms of a set of generalized coordinates and a model-fixed reference length L.
- **ii.** The Helmholtz equation given in Eqs. 16.7-4 and 5 must be formulated and solved for the eigenvalues ν_p and eigenfunctions f_p.
- **iii.** The expansion coefficients α_p must be determined from the eigenfunctions f_p by use of Eq. 16.7-8 or 16.7-9 with any arbitrary symmetrical $\boldsymbol{\kappa}_0$. Then the relaxation modulus $G(s)$ is given by Eqs. 16.7-12 to 16.7-15.



(a)



(b)

FIGURE 16.7-1. The dynamic moduli G' and G'' for various chainlike bead-rod models of N identical beads with friction coefficients ζ joined by rigid rods of length a: (*a*) Results of O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974) for $N = 3$ comparing the freely jointed three-bead model with the three-bead model in which the rods are required to be collinear. (*b*) Results of M. Fixman and J. Kovac, *J. Chem. Phys.*, **61**, 4950–4954 (1974) for freely jointed chains with large values of N.

The fluid response in any arbitrary linear viscoelastic experiment may in principle be calculated from the relaxation modulus $G(s)$ as illustrated in Chapter 5. In Fig. 16.7-1a we show the dynamic moduli G' and G'' for a free-draining chainlike bead-rod model with $N = 3$ as calculated by the above procedure. Furthermore Fixman and Kovac[2] have recalculated the dynamic moduli for a chainlike model with three beads by using a method in which the constant bond lengths are incorporated by the use of infinitely stiff springs. The dynamic moduli as calculated by these two methods agree within about 1 % over the entire frequency range; these results therefore provide additional evidence in favor of the suggestion in §16.5 that the practical difference between the two different methods of treating constraints is small, at least in the linear range.

The method of Fixman and Kovac is efficient for models with a large number of degrees of freedom. Thus in Fig. 16.7-1b we show the Fixman–Kovac[2] results for the dynamic moduli of free-draining chainlike bead-rod models for various large values of N. We see that the results are in good qualitative agreement with the data in Fig. 13.5-3. In particular we see that $G''(\omega) - \omega\eta_s$ increases linearly with ω at high frequencies or equivalently that the dynamic viscosity $\eta'(\omega) - \eta_s$ approaches a limiting value larger than zero at high frequencies. This important qualitative feature is not predicted by the Rouse–Zimm molecular theories discussed in Chapter 15. As is shown in Problem 16C.5 the nonzero plateau value of $\eta'(\omega) - \eta_s$ at high frequencies is related to the constraints or "stiff" potentials that keep bond lengths and bond angles nearly constant. There may, however, be other factors such as excluded volume effects that could be responsible for the observed nonzero limiting value of the polymer contribution to the dynamic viscosity.

We conclude this section with an example that illustrates the use of the method given here for obtaining the relaxation modulus for bead-rod models.

EXAMPLE 16.7-1 Calculation of the Relaxation Modulus for Arbitrary Rigid Axisymmetrical Bead-Rod Models

Consider a rigid collection of identical beads (each with mass m) with two principal moments of inertia equal. It is desired to find the relaxation modulus of linear viscoelasticity for this model in terms of the principal moments of inertia, $I_1 (= I_2)$ and I_3.

SOLUTION We use the method outlined in the text above.

i. First, we install a triad of unit vectors $\check{\boldsymbol{\delta}}_m$ fixed in the model such that $\check{\boldsymbol{\delta}}_3$ is along the axis of symmetry of the moment of inertia ellipsoid. As generalized coordinates for the model we use the three Euler angles specifying the orientation of the model-fixed unit vectors $\check{\boldsymbol{\delta}}_m$ with respect to a set of space-fixed unit vectors $\boldsymbol{\delta}_m$. The position vector $\boldsymbol{R}_v$ of the vth bead with respect to the center of mass may then be expressed by

$$\boldsymbol{R}_v = \sum_m \check{\boldsymbol{\delta}}_m R_{vm} \tag{16.7-16}$$

The principal moments of inertia, I_1 and I_3, are then

$$I_1 = m \sum_v (R_{v2}^2 + R_{v3}^2) \tag{16.7-17}$$

$$I_3 = 2m \sum_v R_{v1}^2 \tag{16.7-18}$$

[2] M. Fixman and J. Kovac, *J. Chem. Phys.*, **61**, 4950–4954 (1974).

We may now specify the various configurational quantities for the model using the framework given in Table 16.1-1. In particular we need the results that

$$g = I_1^2 I_3 S^2 \tag{16.7-19}$$

and

$$(G_{uv}) = \begin{pmatrix} I_1^{-1}S^{-2} & 0 & -I_1^{-1}S^{-2}C \\ 0 & I_1^{-1} & 0 \\ -I_1^{-1}S^{-2}C & 0 & I_1^{-1}S^{-2}C^2 + I_3^{-1} \end{pmatrix} \tag{16.7-20}$$

where $S = \sin\beta$ and $C = \cos\beta$. Furthermore from Eqs. 16.7-11 and 16.7-19 we find that

$$J_{eq} = 8\pi^2 I_1 I_3^{1/2} \tag{16.7-21}$$

ii. Second, we need to formulate the Helmholtz equation for the configuration space distribution function from the determinant g and the components of the contravariant metric matrix G_{uv}. From Eqs. 16.7-4, 5, 19, and 20 we find after some reduction

$$\frac{mL^2}{I_1}\left\{\frac{\partial^2 f}{\partial\beta^2} + \frac{C}{S}\frac{\partial f}{\partial\beta} + \frac{1}{S^2}\frac{\partial^2 f}{\partial\alpha^2} + \left[\left(\frac{C}{S}\right)^2 + \frac{I_1}{I_3}\right]\frac{\partial^2 f}{\partial\gamma^2} - 2\frac{C}{S^2}\frac{\partial^2 f}{\partial\alpha\partial\gamma}\right\} + \nu f = 0 \tag{16.7-22}$$

Equation 16.7-22 is identical to the quantum mechanical Schrödinger equation for the rotational wave function of a "symmetric top" molecule. The solutions of the equation which are everywhere finite[3] and also periodic in α and γ may be written in the form

$$f_{JKM} = \sqrt{\frac{2J+1}{8\pi^2 I_1 I_3^{1/2}}}\, D^J(\alpha, \beta, \gamma)_{KM} \tag{16.7-23}$$

The eigenvalues corresponding to these eigenfunctions are

$$\nu_{JKM} = \frac{mL^2}{I_1} J(J+1) + mL^2\left(\frac{1}{I_3} - \frac{1}{I_1}\right)K^2 \tag{16.7-24}$$

The indices J, K, and M may assume the following values:

$$\begin{aligned} J &= 0, 1, 2, 3, \ldots \\ K &= 0, \pm 1, \pm 2, \ldots, \pm J \\ M &= 0, \pm 1, \pm 2, \ldots, \pm J \end{aligned}$$

The functions $D^J(\alpha, \beta, \gamma)_{KM}$ are known as the representation coefficients of the three-dimensional rotation group, and are generalizations of the spherical harmonics to three angles. These functions are discussed in Appendix E, and the orthogonality relations they satisfy are given in Eq. E.12-4. From Eqs. E.12-4, 16.7-11, and 16.7-19 the normalization constant given in Eq. 16.7-23 can be derived.

[3] The solution given by O. Hassager, *J. Chem Phys.*, **60**, 4001–4008 (1974), was given in terms of the Jacobi polynomials.

iii. Third, we must consider the expansion coefficients α_{JKM} (called α_p in Eq. 16.7-9). For this purpose we consider the integral appearing on the right side of Eq. 16.7-9. It follows from Eq. 16.7-16 that this integral is

$$\sum_{\nu} \iiint \boldsymbol{R}_\nu \boldsymbol{R}_\nu f_{JKM} \sqrt{g}\, dQ_1\, dQ_2\, dQ_3 = \sqrt{\frac{(2J+1)}{8\pi^2}} I_1 I_3^{1/2} \sum_{\nu mn} R_{\nu m} R_{\nu n} \times \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \check{\boldsymbol{\delta}}_m \check{\boldsymbol{\delta}}_n D^J(\alpha, \beta, \gamma)_{KM} \sin\beta\, d\alpha\, d\beta\, d\gamma \quad (16.7\text{-}25)$$

The unit vectors $\check{\boldsymbol{\delta}}_m$, embedded in the rigid bead-rod structure, are functions of the Euler angles. These unit vectors are related to the space-fixed unit vectors according to Eq. 16.1-1. Hence the last expression becomes

$$\sqrt{\frac{(2J+1)}{8\pi^2}} I_1 I_3^{1/2} \sum_{\nu mnpq} R_{\nu m} R_{\nu n} \boldsymbol{\delta}_p \boldsymbol{\delta}_q \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \Omega_{mp} \Omega_{nq} D^J(\alpha, \beta, \gamma)_{KM} \sin\beta\, d\alpha\, d\beta\, d\gamma \quad (16.7\text{-}26)$$

The rotation matrix elements Ω_{mn} are, however, closely related to the functions $D^J(\alpha, \beta, \gamma)_{KM}$ with $J = 1$ (they are both irreducible representations of degree 1). Using this relation, which is given by Eqs. E.12-5 and E.12-6, the integral in Eq. 16.7-26 then becomes

$$\sum_{K'K''M'M''} \bar{T}_{K'm} T_{M'p} \bar{T}_{K''n} T_{M''q} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} D^1_{K'M'} D^1_{K''M''} D^J_{KM} \sin\beta\, d\alpha\, d\beta\, d\gamma = 8\pi^2 \sum_{K'K''M'M''} \bar{T}_{K'm} T_{M'p} \bar{T}_{K''n} T_{M''q} \begin{pmatrix} 1 & 1 & J \\ K' & K'' & K \end{pmatrix} \begin{pmatrix} 1 & 1 & J \\ M' & M'' & M \end{pmatrix} \quad (16.7\text{-}27)$$

Here we have written the integrals in terms of quantities known as "3j-symbols" (see Eq. E.12-12). When this result is substituted into Eq. 16.7-25, we find that

$$\sum_{\nu} \iiint \boldsymbol{R}_\nu \boldsymbol{R}_\nu f_{JKM} \sqrt{g}\, dQ_1\, dQ_2\, dQ_3 = \sqrt{\frac{8\pi^2}{2J+1}} I_1 I_3^{1/2} \sum_{\nu mn} R_{\nu m} R_{\nu n} \Theta_{JK,mn} \bar{\Theta}_{JM} \quad (16.7\text{-}28)$$

in which the $\boldsymbol{\Theta}_{JM}$ are the tensors defined by Eq. E.12-12 and the $\Theta_{JK,mn}$ are the elements of these tensors defined by Eq. E.12-13. This result is then substituted into Eq. 16.7-9 to obtain an expression for the expansion coefficients α_{JKM}

$$\alpha_{JKM} = \sqrt{\frac{8\pi^2}{2J+1}} I_1 I_3^{1/2} \frac{(\boldsymbol{\kappa}_0 : \bar{\boldsymbol{\Theta}}_{JM})}{\sqrt{(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)}} \frac{1}{L^2} \sum_{\nu mn} R_{\nu m} R_{\nu n} \Theta_{JK,mn} \quad (16.7\text{-}29)$$

The tensors $\boldsymbol{\Theta}_{JM}$ are nonzero only for $J = 0, 1, 2$; they are displayed in Table E.12-1. Because $\boldsymbol{\Theta}_{00}$ is a multiple of the unit tensor and because $\boldsymbol{\kappa}_0$ is traceless, we conclude that α_{000} is zero. The three tensors with $J = 1$ are antisymmetric, and since $\boldsymbol{\kappa}_0$ is symmetric, it is evident that the α_{1KM} are also zero. We thus know that the α_{JKM} are nonzero only for $J = 2$. Note that the $\boldsymbol{\Theta}_{2M}$ are all traceless and symmetric. From the explicit expressions for the $\boldsymbol{\Theta}_{2M}$ and Eqs. 16.7-17 and 16.7-18, we find that the sum in Eq. 16.7-29 is zero unless $K = 0$. Thus the only nonzero α_{JKM} are

$$\alpha_{20M} = \sqrt{8\pi^2 \cdot \tfrac{2}{15} \cdot I_1 I_3^{1/2}} \left(\frac{I_1 - I_3}{mL^2} \right) \frac{(\boldsymbol{\kappa}_0 : \bar{\boldsymbol{\Theta}}_{2M})}{\sqrt{(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)}} \quad (16.7\text{-}30)$$

The corresponding eigenvalues are independent of M and are given by Eq. 16.7-24 as

$$\nu_{20M} = \frac{6mL^2}{I_1} \tag{16.7-31}$$

An arbitrary traceless symmetric tensor involves five independent coefficients and may therefore by written as a linear combination of the five independent tensors $\mathbf{\Theta}_{2K}$. This enables us to write $\boldsymbol{\kappa}_0$ as

$$\boldsymbol{\kappa}_0 = \sum_K a_K \mathbf{\Theta}_{2K} \tag{16.7-32}$$

where the a_K are the independent constants. It may be shown then, using Eq. E.12-14 that

$$(\boldsymbol{\kappa}_0 : \bar{\mathbf{\Theta}}_{2M}) = a_M \tag{16.7-33}$$

$$(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0) = \sum_K |a_K|^2 = 2\kappa_0^2 \tag{16.7-34}$$

in which the scalar κ_0 is the magnitude of the tensor $\boldsymbol{\kappa}_0$. One then finds from Eq. 16.7-30 that

$$\alpha_{20M} = \sqrt{\frac{I_1 I_3^{1/2}}{30}} \frac{4\pi(I_1 - I_3)}{mL^2} \frac{a_M}{\kappa_0} \tag{16.7-35}$$

and therefore

$$\sum_M |\alpha_{20M}|^2 = \frac{16\pi^2}{15}(I_1 - I_3)^2 \frac{I_1 I_3^{1/2}}{m^2 L^4} \tag{16.7-36}$$

This expression is clearly independent of the detailed form of $\boldsymbol{\kappa}_0$, and the eigenvalues given by Eq. 16.7-31 are independent of M. From these results it follows that the relaxation modulus given by Eq. 16.7-12 is independent of the flow field as, of course, the continuum theory requires.

With the results in Eqs. 16.7-16, 17, 18, 21, 31, and 36 we find from Eqs. 16.7-12 to 15 that the relaxation modulus for the general rigid collection of identical beads in which two of the principal moments of inertia are equal is:

$$G(s) = 2\eta_s \delta(s) + n\zeta L^2 a \delta(s) + nkTbe^{-s/\lambda} \tag{16.7-37}$$

in which

$$a = \frac{2I_1 + I_3}{6mL^2} - \frac{(I_1 - I_3)^2}{5mL^2 I_1}, \quad b = \frac{3(I_1 - I_3)^2}{5I_1^2}, \quad \lambda = \frac{\zeta L^2}{\nu kT} = \frac{\zeta I_1}{6mkT} \tag{16.7-38}$$

The principal moments of inertia, I_1 and I_3, must be determined for individual models from Eqs. 16.7-17 and 16.7-18. Values of a, b, and ν for several models are given in Table 16.7-1.

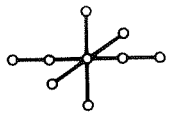
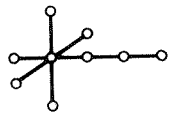
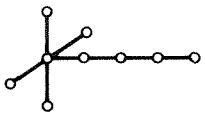
The relaxation modulus in Eq. 16.7-37 may be used to calculate the dynamic moduli of linear viscoelasticity defined in the text that follows Eq. D.5-5:

$$\frac{2G'(\omega)}{ankTv} = \frac{2b}{av} \frac{(\lambda\omega)^2}{1 + (\lambda\omega)^2} \tag{16.7-39}$$

$$\frac{2[G''(\omega) - \omega\eta_s]}{ankTv} = \lambda\omega\left[1 + \frac{2b}{av} \frac{1}{1 + (\lambda\omega)^2}\right] \tag{16.7-40}$$

TABLE 16.7-1

Values of a, b, and ν of Eq. 16.7-38 and of Fig. 16.7-2 for Several Axisymmetrical Models[a]

Model	Meaning of L	a	b	ν	$\frac{2b}{a\nu}$
Rigid dumbbell with two beads connected by a rod[b]	Length of rod	$\frac{1}{15}$	$\frac{3}{5}$	12	1.5000
Rigid plane polygon[c] of N beads connected by N rods of length b	Radius of circumscribed circle $L = \frac{b/2}{\sin(\pi/N)}$	$\frac{7}{30}N$	$\frac{3}{5}$	$12/N$	0.4286
Rigid tridumbbell (Doppelkreuzhantel[d]), formed by joining three identical rigid dumbbells at their midpoint in a mutually orthogonal configuration	Length of one dumbbell rod	$\frac{1}{2}$	0	6	0.0000
	Length of rod[e] between beads	$\frac{18}{5}$ 3.6000	$\frac{4}{15}$ 0.2666	$\frac{1}{2}$ 0.5000	0.2962
	Length of rod[e] between beads	4253/1080 3.9380	1587/5120 0.3100	27/64 0.4219	0.3732
	Length of rod[e] between beads	31082/6345 4.8987	4332/11045 0.3920	27/94 0.2872	0.5573

[a] Table from O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974).
[b] R. B. Bird, H. R. Warner, Jr. and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971).
[c] E. Paul and R. M. Mazo, *J. Chem. Phys.*, **51**, 1102–1107 (1969); for errata see C. Y. Mou and R. M. Mazo, *J. Chem. Phys.*, **67**, 5972–5973 (1977).
[d] H. Giesekus, *Rheol. Acta*, **2**, 101–112 (1962).
[e] C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (I. Prigogine and S. A. Rice, eds.) (1976).

These dimensionless moduli are shown in Fig. 16.7-2 for various values of $2b/a\nu$. The ordering parameter $2b/a\nu$ provides a measure of the extent to which the model deviates from a spherically symmetrical structure. The minimum value of $2b/a\nu$ is 0, which is obtained for spherically symmetrical structures such as the symmetric rigid tridumbbell, and the maximum value is $\frac{3}{2}$, which is obtained for long slender bodies such as the rigid dumbbell model or the multibead-rod model.

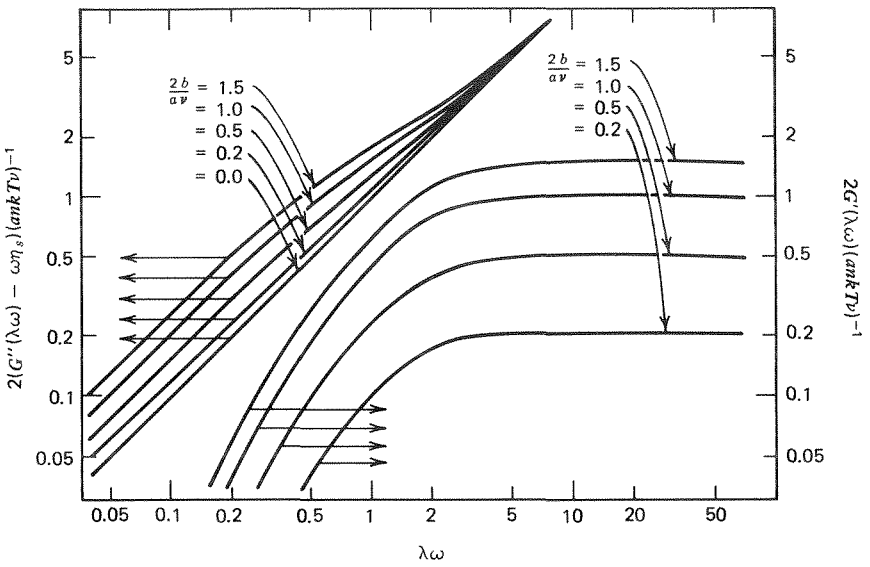


FIGURE 16.7-2. The dimensionless dynamic moduli of Eqs. 16.7-39 and 16.7-40 for axisymmetrical rigid models for various values of the ordering parameter $2b/av$. The parameters a, b, and v are determined from the principal moments of inertia of the molecule by Eq. 16.7-38. Values for sample models are given in Table 16.7-1. Reproduced from O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974).

PROBLEMS

16B.1 Proof that b_2 in the Second Order Fluid is Negative

Show that Eq. 16.4-15 can be rewritten as

$$b_2 = -\frac{n}{40kT}\left\langle \sum_p \sum_q \left(K_{pq} - \frac{1}{3}\delta_{pq} \sum_r K_{rr} \right)^2 \right\rangle_{eq} \tag{16B.1-1}$$

and that therefore b_2 is negative (or zero) for dilute solutions of polymers modeled by arbitrary bead-rod-spring models with equilibrium-averaged hydrodynamic interaction.

16B.2 Second Normal-Stress Coefficient

Verify the statement after Eq. 16.3-20 that Eq. 16.3-20 predicts that the second normal-stress coefficient is zero in steady shear flow. How is this result used in §16.4? Is the nonzero Ψ_2 in Eq. 14.6-25 in conflict with the above cited statement?

16B.3 Configurational Distribution Function for Steady, Homogeneous, Potential Flow

Show how to go from the general expression in Eq. 16.2-10 to expressions given earlier in Eqs. 13.2-14 and 14.2-9.

16C.1 Effect of Ring Closure on Second-Order-Fluid Constants

Obtain the entries in Table 16.4-1 for the ringlike model made up of N beads joined by N linear springs, each with spring constant H. How do η_0 and $\Psi_{1,0}$ change when N-bead linear chains undergo ring closure to form N-bead rings?

16C.2 Diffusion Equation for the Configurational Distribution Function for Rouse Chains

Show how to obtain Eq. 15.1-7, the diffusion equation for chainlike bead-spring models, by simplification of the general equation in Eq. 16.2-6. Use the generalized coordinates suggested in Example 12.1-2. Show that for the chain with equal masses and friction coefficients we get

$$\frac{\partial \psi}{\partial t} + \sum_n \sum_i \sum_p \sum_j \frac{\partial}{\partial Q_{in}} \left\{ \frac{1}{\zeta} A_{ij} \delta_{np} \left[\psi \zeta \sum_v (\boldsymbol{\kappa} : \boldsymbol{R}_v B_{vj} \boldsymbol{\delta}_p) - kT \frac{\partial \psi}{\partial Q_{jp}} - \psi \frac{\partial}{\partial Q_{jp}} \phi \right] \right\} = 0 \qquad \text{(16C.2-1)}$$

Consider now the hydrodynamic term. When Eq. 12.1-20 is used, this term becomes

$$\sum_n \sum_i \sum_p \sum_j \sum_v \sum_k \frac{\partial}{\partial Q_{in}} [A_{ij} \delta_{np} \psi (\boldsymbol{\kappa} : B_{vk} \boldsymbol{Q}_k B_{vj} \boldsymbol{\delta}_p)] \qquad \text{(16C.2-2)}$$

The sums on v and j can be performed (in that order) using Eq. 11.6-7 and the fact that the Kramers and Rouse matrices are the inverse of one another. Then the sums on k and p may be carried out using the definition of the Kronecker delta. This leads finally to

$$\sum_n \sum_i \frac{\partial}{\partial Q_{in}} (\psi \boldsymbol{\kappa} : \boldsymbol{Q}_i \boldsymbol{\delta}_n) = \sum_n \sum_i \frac{\partial}{\partial Q_{in}} (\psi [\boldsymbol{\kappa} \cdot \boldsymbol{Q}_i]_n) = \sum_i \left(\frac{\partial}{\partial \boldsymbol{Q}_i} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{Q}_i] \psi \right) \qquad \text{(16C.2-3)}$$

which is just the hydrodynamic term in Eq. 15.1-7. The other terms may be transformed in a similar way.

16C.3 Stress Tensor for the Rouse Model from General Formula

Show how to get Eqs. A and D of Table 15.2-1 from general results in §16.3. To do this assume a monodisperse solution, and use the free-draining bead-spring chain.

16C.4 Calculation of Configurational Quantities for the Elastic Rhombus Model[1]

This model is shown in Fig. 16.4-2; it consists of four identical beads arranged in planar fashion joined by four rods of length L arranged to form a rhombus. The joints at the beads are universal joints and two opposing beads are connected by a Fraenkel spring (Table 11.5-1) whose equilibrium length is $L\sqrt{2}$. Hence, if the rhombus is not acted on by any forces, it assumes the shape of a square. Forces acting on the model will then deform it into a rhombus in which the spring is either compressed or extended.

[1] C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (1976). A sign error in Eq. 17.7 of this reference is corrected in Eq. 16C.5-2.