CHAPTER 17

PHASE-SPACE THEORY OF POLYMERIC LIQUIDS[1]

In this chapter we derive from first principles the equation of continuity for the configuration-space distribution function, the equations of internal motion for the constituent molecules, and the expression for the stress tensor. The derivations are sufficiently general that the results are applicable to both polymer solutions and undiluted polymers; the fluids may be mixtures of different polymers, or they may be polydisperse polymers. In the first four sections the only assumptions that are made are the assumption of some kind of mechanical model for the molecules and the assumption of pairwise additivity of forces between "beads." In the final two sections a few additional minor assumptions are made: the variation of the distribution functions over molecular-scale distances is neglected, and the acceleration terms in the equation of motion are omitted. It is felt that these assumptions have little effect on the molecular descriptions of rheological phenomena.

In §17.1 we start with a discussion of the classical mechanics of a polymeric fluid, whose constituent molecules are modeled as bead-spring-rod systems; here we allow the "beads" to be of finite size and arbitrary shape. In §17.2 statistical ideas are introduced and the equations of continuity and motion of classical hydrodynamics are obtained from the "general equation of change." This general equation of change is used at several points in this chapter; its importance in the development of the theory cannot be overemphasized (see Fig. 17.0-1). Then in §17.3 various contracted distribution functions are defined, and notations for average values are introduced; it is here that the configurational distribution functions for single molecules and for pairs of molecules are defined. In §17.4 the various contributions to the stress tensor are obtained as integrals involving the distribution functions; the pictorial presentation in Fig. 17.4-1 should be examined before embarking on this section. The stress tensor expressions obtained in this section are further simplified in §17.6, by making use of the equations of motion for the internal degrees of freedom developed in §17.5.

The chapter is so designed that it can be read superficially by those who just wish to have some idea as to the origins of the key starting equations of Chapters 13 through 16. On the other hand, a careful study of this and the following two chapters can provide a good understanding of the fundamental principles of polymer kinetic theory. Many of the topics in these three chapters have not yet been fully explored or exploited.

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[1] This chapter is based on C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (1976); C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191–204 (1983). The approach used here was inspired by the pioneering work on statistical mechanical theory and transport phenomena by J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 817–829 (1950).

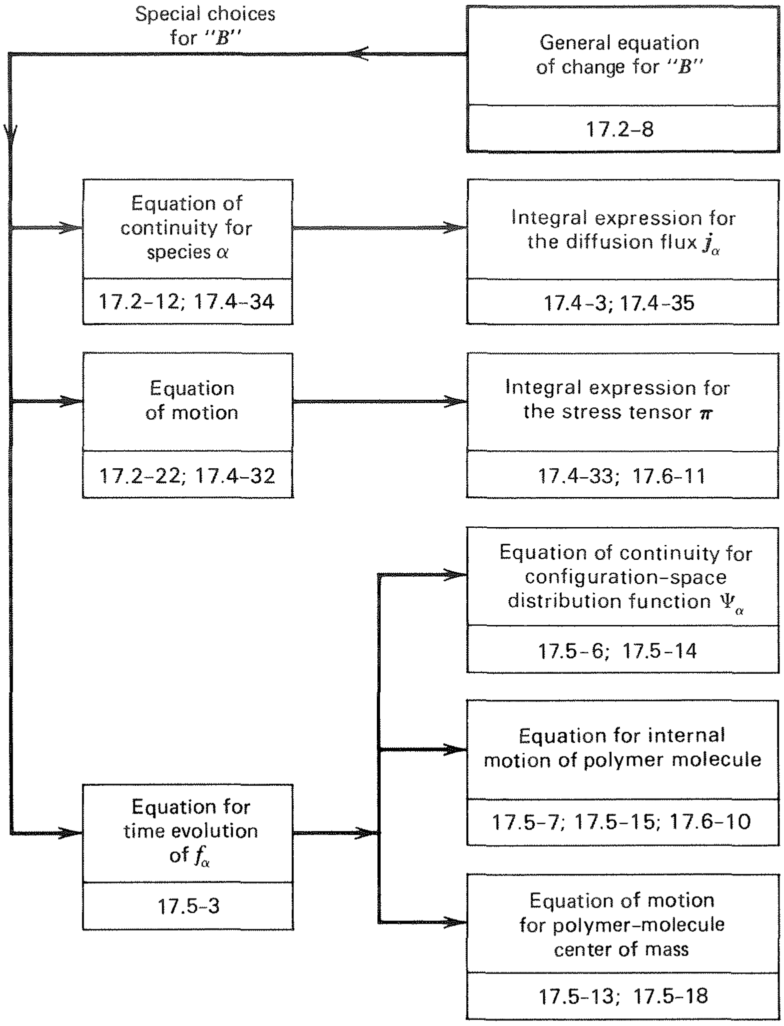
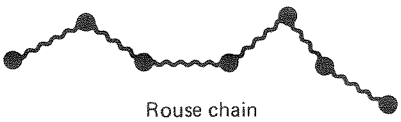


FIGURE 17.0-1. "Flow chart" for Chapter 17, showing how the key results follow from the general equation of change.

§17.1 CLASSICAL DYNAMICS OF A COMPLEX SYSTEM

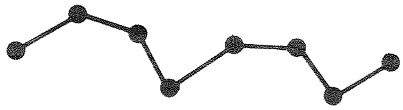
The discussions of this chapter are based on a very general model of a polymeric solution or undiluted polymer, visualized as a collection of a large number of molecules of various kinds. Each molecule is modeled as a collection of "finite beads" of arbitrary shape. These finite beads are then joined in an arbitrary manner by "springs" or "massless rods." In Fig. 17.1-1 several such molecular models of varying degrees of complexity are illustrated. Note that the "beads" in Chapters 11 through 16 are taken to be point masses (or spheres of finite size in some of the hydrodynamic interaction studies), whereas here the "finite beads" may be "needles" or arbitrary rigid bodies. At certain points in the development we may wish to restrict the model to the point masses considered earlier, in which case we will refer to "structureless beads."

To describe, at any instant, the orientation of the νth finite bead with respect to a fixed coordinate system we introduce a set of generalized coordinates, $q_{\nu\sigma}$. If the bead is a



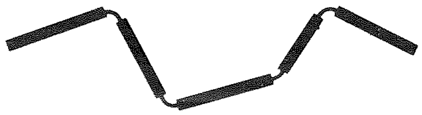
Rouse chain

(*a*)



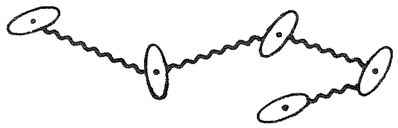
Kramers chain

(*b*)



Freely jointed
chain of "needles"

(*c*)



Rouse chain with
ellipsoidal beads

(*d*)

FIGURE 17.1-1. Examples of molecular models for use in kinetic theory.

"needle," then $\sigma = 1, 2$ and two such coordinates (θ_ν, ϕ_ν) are needed to describe the orientation; if it is an arbitrary rigid body, then $\sigma = 1, 2, 3$ and three Euler angles $(\alpha_\nu, \beta_\nu, \gamma_\nu)$ are required. If the bead is simply a mass point, there are no such coordinates.

The kinetic energy of a finite bead, with respect to a coordinate system translating with its own center of mass, is a quadratic form in the time derivatives, $\dot{q}_{\nu\sigma}$, of the generalized coordinates

$$\mathscr{K}_\nu = \tfrac{1}{2} \sum_\sigma \sum_\tau g_{\nu,\sigma\tau} \dot{q}_{\nu\sigma} \dot{q}_{\nu\tau} \tag{17.1-1}$$

where the $g_{\nu,\sigma\tau}$ are the elements of the "metric matrix" of the finite bead; these are, in general, functions of the coordinates $q_{\nu\sigma}$. As an example, if the finite bead is a "needle" of moment of inertia, I, the two coordinates may be taken to be the usual polar angles describing the orientation: $q_{\nu 1} = \theta_\nu$; $q_{\nu 2} = \phi_\nu$. The diagonal elements of the metric matrix are then

$$g_{\nu,11} = I \tag{17.1-2}$$

$$g_{\nu,22} = I \sin^2 q_{\nu 1} = I \sin^2 \theta_\nu \tag{17.1-3}$$

and the off-diagonal elements are zero.

The internal kinetic energy, $\mathscr{K}_{\text{int}}$, of the entire molecular model is then the sum of the rotational kinetic energies $\mathscr{K}_\nu$ and the translational kinetic energies $\frac{1}{2}m_\nu \dot{\boldsymbol{R}}_\nu^2$ of the finite beads

$$\mathscr{K}_{\text{int}} = \sum_\nu \left(\tfrac{1}{2}m_\nu \dot{\boldsymbol{R}}_\nu^2 + \mathscr{K}_\nu\right) \tag{17.1-4}$$

Here m_ν is the mass of the νth finite bead, and $\boldsymbol{R}_\nu$ is the vector from the center of mass of the entire molecular model to the center of mass of the νth finite bead; the vector $\dot{\boldsymbol{R}}_\nu$ is the bead velocity.

The molecular models being considered here may contain constraints; for example, the connectors between the finite beads may have fixed lengths or may have fixed angles between them. Hence there may be relations among the $\boldsymbol{R}_\nu$ and $q_{\nu\sigma}$. It is therefore necessary to introduce a set of generalized coordinates Q_s, which are *independent* and sufficient in number to describe the orientation of the molecular model in space, the relative locations of the finite beads, and the orientations of all the finite beads. The number of required generalized coordinates is fixed by the model, but the detailed choice of the coordinates is arbitrary. Various choices that may be made for chain models are discussed in §11.6

We next introduce the base vectors, $\boldsymbol{b}_{\nu s}$, defined in Eq. 12.1-6 as well as a set of similar quantities $b_{\nu\sigma s}$ associated with the finite bead orientations

$$\boldsymbol{b}_{\nu s} = \sqrt{m_\nu}\,\frac{\partial}{\partial Q_s}\boldsymbol{R}_\nu \tag{17.1-5}$$

$$b_{\nu\sigma s} = \frac{\partial}{\partial Q_s} q_{\nu\sigma} \tag{17.1-6}$$

so that the time derivatives may be written

$$\dot{\boldsymbol{R}}_\nu = \frac{1}{\sqrt{m_\nu}} \sum_s \dot{Q}_s \boldsymbol{b}_{\nu s} \tag{17.1-7}$$

$$\dot{q}_{\nu\sigma} = \sum_s \dot{Q}_s b_{\nu\sigma s} \tag{17.1-8}$$

Using the last two relations, we may rewrite the expression for the kinetic energy of a molecule in a coordinate system moving with its center of mass, Eq. 17.1-4, as a quadratic form in the time derivatives, $\dot{Q}_s$, of the generalized coordinates

$$\mathscr{K}_{\text{int}} = \tfrac{1}{2}\sum_s \sum_t g_{st}\dot{Q}_s\dot{Q}_t \tag{17.1-9}$$

where the coefficients are defined as

$$g_{st} = g_{st}^{(1)} + g_{st}^{(2)} \tag{17.1-10}$$

and

$$g_{st}^{(1)} = \sum_\nu (\boldsymbol{b}_{\nu s} \cdot \boldsymbol{b}_{\nu t}) \tag{17.1-11}$$

$$g_{st}^{(2)} = \sum_\nu \sum_\sigma \sum_\tau g_{\nu,\sigma\tau} b_{\nu\sigma s} b_{\nu\tau t} \tag{17.1-12}$$

The g_{st} are the elements of the metric matrix of the molecule and are in general functions of the generalized coordinates Q_s. The first term in the expression for the metric matrix $g_{st}^{(1)}$, defined by Eq. 17.1-11, is given by Eq. 12.1-7. In Chapter 12 the polymer molecules were modeled as collections of structureless beads, and for this reason the second term, $g_{st}^{(2)}$, did not arise.

As discussed in §12.1 the momentum conjugate to Q_s is defined as

$$\begin{aligned} P_s &= \frac{\partial}{\partial \dot{Q}_s} \mathscr{K}_{\text{int}} \\ &= \sum_t g_{st} \dot{Q}_t \end{aligned} \tag{17.1-13}$$

Also as discussed earlier these equations may always be inverted formally to give

$$\dot{Q}_s = \sum_t G_{st} P_t \tag{17.1-14}$$

where the G_{st} are the elements of the matrix which is the inverse of the metric matrix, g_{st}.

The last set of equations may be used to transform the expression for the kinetic energy of a molecule in a center of mass coordinate system as given by Eq. 17.1-9 to the form

$$\mathscr{K}_{\text{int}} = \tfrac{1}{2} \sum_s \sum_t G_{st} P_s P_t \tag{17.1-15}$$

The *Hamiltonian of a single molecule* in the same coordinate system is then a function of the coordinates Q_s and momenta P_s, given by

$$\mathscr{H}_{\text{int}} = \mathscr{K}_{\text{int}} + \phi \tag{17.1-16}$$

where ϕ, the intramolecular potential, is a function of the generalized coordinates Q_s.

The system which we study from the point of view of statistical mechanics is a collection of a large number of molecules—in general, of different types. If we consider a solution, the solvent molecules are modeled simply as mass points without structure although more complex models could be used. Such a system is illustrated in Fig. 17.1-2. In this discussion, we use Greek indices ($\alpha, \beta, \gamma, \ldots$) to indicate the molecular species, followed when necessary by italic indices ($i, j, k, \ldots$) to label the various molecules of the species. For example we use $\boldsymbol{r}^{\alpha i}$ as the vector from a space-fixed origin to the center of mass of molecule i of species α, which may be a polymer or a solvent molecule. The linear momentum of this molecule is then $\boldsymbol{p}^{\alpha i}$. Indices such as α and αi are omitted whenever they appear to be cumbersome and when no confusion can occur.

The *Hamiltonian of the entire system* in Fig. 17.1-2 is the sum of the energies of the separate molecules (each of which in turn is the sum of the kinetic energy of the motion of the center of mass, the internal Hamiltonian, and the potential $\phi^{(e)\alpha i}$ which describes the "external" force on a molecule of species α) and the intermolecular potential, Φ, associated with the forces between the molecules. This Hamiltonian may be written as

$$\mathscr{H}^{(T)} = \sum_\alpha \sum_i \left[\frac{1}{2m^\alpha} (\boldsymbol{p}^{\alpha i})^2 + \mathscr{H}_{\text{int}}^{\alpha i} + \phi^{(e)\alpha i} \right] + \Phi \tag{17.1-17}$$

where m^α is the mass of a molecule of species α.

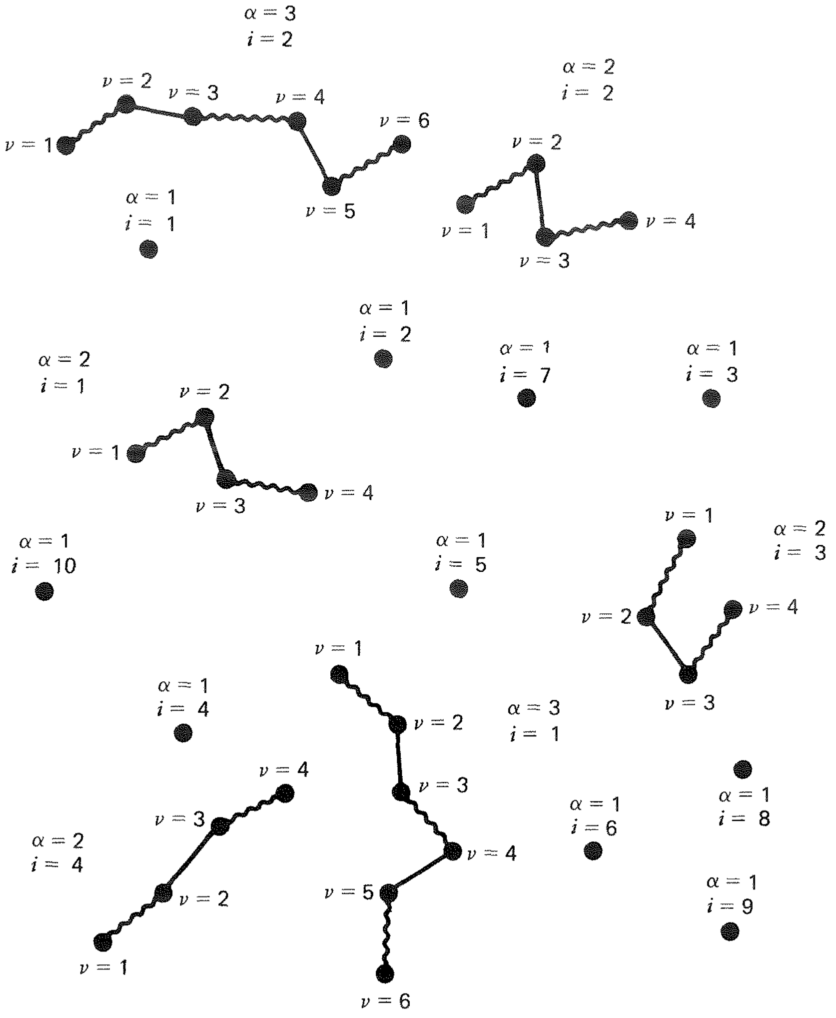


FIGURE 17.1-2. Sketch of a polymer solution containing a solvent ($\alpha = 1$) and two polymer species ($\alpha = 2, \alpha = 3$). Both polymer species have "constraints" (rigid portions indicated by an inflexible rod).

Hamilton's equations of motion, which describe the time derivatives of the coordinates and momenta, are given by Eqs. 12.2-6 and 12.2-7. Before writing these equations, we define several quantities. First, the force on the center of mass of molecule i of species α due to the external force is

$$\boldsymbol{F}^{(e)\alpha i} = -\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} \phi^{(e)\alpha i} \tag{17.1-18}$$

and that due to all the other molecules is

$$\boldsymbol{F}^{\alpha i} = -\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} \Phi \tag{17.1-19}$$

In a similar manner we define four generalized forces associated with the coordinate Q_s,

$$\mathscr{F}_s^{(k)\alpha i} = -\tfrac{1}{2} \sum_{tu} P_t^{\alpha i} P_u^{\alpha i} \frac{\partial}{\partial Q_s^{\alpha i}} G_{tu}^{\alpha i} \tag{17.1-20}$$

$$\mathscr{F}_s^{(\phi)\alpha i} = -\frac{\partial}{\partial Q_s^{\alpha i}} \phi^{\alpha i} \tag{17.1-21}$$

$$\mathscr{F}_s^{(e)\alpha i} = -\frac{\partial}{\partial Q_s^{\alpha i}} \phi^{(e)\alpha i} \tag{17.1-22}$$

$$\mathscr{F}_s^{(d)\alpha i} = -\frac{\partial}{\partial Q_s^{\alpha i}} \Phi \tag{17.1-23}$$

The first of these is associated with generalized forces arising from the use of non-Cartesian coordinates; the remaining three are associated with intramolecular, external, and intermolecular forces. In addition it is convenient to define

$$\mathscr{F}_s^{\alpha i} = \mathscr{F}_s^{(k)\alpha i} + \mathscr{F}_s^{(\phi)\alpha i} + \mathscr{F}_s^{(e)\alpha i} + \mathscr{F}_s^{(d)\alpha i} \tag{17.1-24}$$

as the sum of all four contributions.

In terms of the real forces and generalized forces, *Hamilton's equations of motion* are (cf. Eqs. 12.2-6 and 12.2-7)

$$\boxed{\begin{aligned}
\dot{\boldsymbol{r}}^{\alpha i} &= \frac{\partial \mathscr{H}^{(T)}}{\partial \boldsymbol{p}^{\alpha i}} = \frac{1}{m^\alpha} \boldsymbol{p}^{\alpha i} && (17.1\text{-}25)\\
\dot{Q}_s^{\alpha i} &= \frac{\partial \mathscr{H}^{(T)}}{\partial P_s^{\alpha i}} = \sum_t G_{st}^{\alpha i} P_t^{\alpha i} && (17.1\text{-}26)\\
\dot{\boldsymbol{p}}^{\alpha i} &= -\frac{\partial \mathscr{H}^{(T)}}{\partial \boldsymbol{r}^{\alpha i}} = \boldsymbol{F}^{(e)\alpha i} + \boldsymbol{F}^{\alpha i} && (17.1\text{-}27)\\
\dot{P}_s^{\alpha i} &= -\frac{\partial \mathscr{H}^{(T)}}{\partial Q_s^{\alpha i}} = \mathscr{F}_s^{\alpha i} && (17.1\text{-}28)
\end{aligned}}$$

These equations describe the time evolution of the dynamical state of an entire system.

The concept of a phase space is discussed in §12.3. This is a multidimensional space, the coordinates of which are the configuration and momentum coordinates of a system. In this case, it is convenient to consider a phase space described by the coordinates of all of the molecules making up the macroscopic system of interest—the polymer solution or melt. As time evolves, the coordinates of the system change and trace out a "trajectory" in this space. The derivatives of these coordinates along such a trajectory are described by the last set of equations. From Eqs. 17.1-7 and 17.1-14, it follows that the time derivative, along such a trajectory, of the vector $\boldsymbol{R}_\nu^{\alpha i}$ is

$$\dot{\boldsymbol{R}}_\nu^{\alpha i} = \frac{1}{\sqrt{m_\nu^\alpha}} \sum_{st} G_{st}^{\alpha i} P_t^{\alpha i} \boldsymbol{b}_{\nu s}^{\alpha i} \tag{17.1-29}$$

A "dynamical variable" is any function of the coordinates and momenta of a system, that is, a function "in the phase space," which in general varies along a particular trajectory. The right side of the last equation may be considered to be such a dynamical variable, and we note that the derivatives with respect to the phase space variables of this function are

$$\frac{\partial}{\partial Q_s^{\alpha i}} \dot{\boldsymbol{R}}_\nu^{\alpha i} = \frac{1}{\sqrt{m_\nu^\alpha}} \sum_{tu} P_u^{\alpha i} \left[\frac{\partial}{\partial Q_s^{\alpha i}} (G_{tu}^{\alpha i} \boldsymbol{b}_{\nu t}^{\alpha i}) \right] \tag{17.1-30}$$

$$\frac{\partial}{\partial P_s^{\alpha i}} \dot{\boldsymbol{R}}_\nu^{\alpha i} = \frac{1}{\sqrt{m_\nu^\alpha}} \sum_{t} G_{st}^{\alpha i} \boldsymbol{b}_{\nu t}^{\alpha i} \tag{17.1-31}$$

These results are used in the next section in developing the equation of motion.

EXAMPLE 17.1-1 The Two-Needle Model

Obtain the elements of the metric matrices, g_{st} and G_{st}, and the determinant, g, for the molecular model consisting of two needles joined as illustrated in Fig. 17.1-3.

SOLUTION Let θ_ν and ϕ_ν be the angles describing the directions of the unit vectors, $\boldsymbol{u}_\nu$, in the directions of the two needles. The length of each needle is l, and the center of mass of the needle is located a distance ωl from the end at which the needles just touch (with $\omega \neq 0$). Thus,

$$\boldsymbol{R}_2 - \boldsymbol{R}_1 = \omega l(\boldsymbol{u}_1 + \boldsymbol{u}_2) \tag{17.1-32}$$

and

$$\begin{aligned} \boldsymbol{R}_1 &= -\tfrac{1}{2}\omega l(\boldsymbol{u}_1 + \boldsymbol{u}_2) \\ \boldsymbol{R}_2 &= \tfrac{1}{2}\omega l(\boldsymbol{u}_1 + \boldsymbol{u}_2) \end{aligned} \tag{17.1-33}$$

These relations among the $\boldsymbol{R}_\nu$ and $q_{\nu\sigma}$ are the constraints associated with the condition that the ends of the needles just touch.

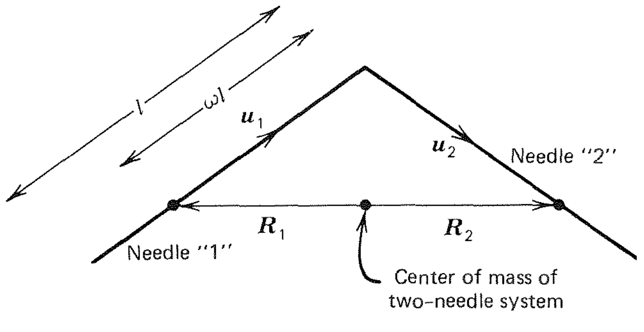


FIGURE 17.1-3. The two-needle model. The needles are joined head to tail, and the center of mass of a needle is a distance ωl from the joint.

The coordinates Q_s, with $s = 1, 2, 3, 4$, are now taken to be θ_1, ϕ_1, θ_2, and ϕ_2, respectively. One then finds from the definitions of the $\boldsymbol{b}_{\nu s}$, Eq. 17.1-5, and the last equations that

$$\begin{aligned}
\boldsymbol{b}_{11} &= -\tfrac{1}{2}\sqrt{m\omega}l\boldsymbol{s}_1 \\
\boldsymbol{b}_{12} &= -\tfrac{1}{2}\sqrt{m\omega}l\boldsymbol{t}_1 \sin\theta_1 \\
\boldsymbol{b}_{13} &= -\tfrac{1}{2}\sqrt{m\omega}l\boldsymbol{s}_2 \\
\boldsymbol{b}_{14} &= -\tfrac{1}{2}\sqrt{m\omega}l\boldsymbol{t}_2 \sin\theta_2 \\
\boldsymbol{b}_{2s} &= -\boldsymbol{b}_{1s}
\end{aligned} \tag{17.1-34}$$

where $\boldsymbol{s}_\nu$ and $\boldsymbol{t}_\nu$ are unit vectors normal to $\boldsymbol{u}_\nu$ described in Table E.5-1. Since the Q_s are the $q_{\nu\sigma}$ renumbered, it follows from the definition of the $b_{\nu\sigma s}$, Eq. 17.1-6, that

$$\begin{aligned}
b_{111} &= 1 \\
b_{122} &= 1 \\
b_{213} &= 1 \\
b_{224} &= 1
\end{aligned} \tag{17.1-35}$$

and the other $b_{\nu\sigma s}$ are zero.

Next, one finds from the definition of $g_{st}^{(1)}$, Eq. 17.1-11, that

$$(\tfrac{1}{2}ml^2\omega^2)^{-1}g_{st}^{(1)} = \begin{pmatrix} 1 & 0 & (\boldsymbol{s}_2\cdot\boldsymbol{s}_1) & (\boldsymbol{t}_2\cdot\boldsymbol{s}_1)S_2 \\ 0 & S_1^2 & (\boldsymbol{s}_2\cdot\boldsymbol{t}_1)S_1 & (\boldsymbol{t}_2\cdot\boldsymbol{t}_1)S_2S_1 \\ (\boldsymbol{s}_1\cdot\boldsymbol{s}_2) & (\boldsymbol{t}_1\cdot\boldsymbol{s}_2)S_1 & 1 & 0 \\ (\boldsymbol{s}_1\cdot\boldsymbol{s}_2)S_2 & (\boldsymbol{t}_1\cdot\boldsymbol{t}_2)S_1S_2 & 0 & S_2^2 \end{pmatrix} \tag{17.1-36}$$

where $S_1 = \sin\theta_1$, $S_2 = \sin\theta_2$ and from Eqs. 17.1-2, 3, and 12 that

$$\frac{1}{I}g_{st}^{(2)} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & S_1^2 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & S_2^2 \end{pmatrix} \tag{17.1-37}$$

The metric matrix, g_{st}, is given by Eq. 17.1-10 as the sum of these two matrices. This matrix may be written as

$$(\tfrac{1}{2}ml^2\omega^2)^{-1}g_{st} = \begin{pmatrix} A & 0 & (\boldsymbol{s}_1\cdot\boldsymbol{s}_2) & (\boldsymbol{s}_1\cdot\boldsymbol{t}_2)S_2 \\ 0 & AS_1^2 & (\boldsymbol{t}_1\cdot\boldsymbol{s}_2)S_1 & (\boldsymbol{t}_1\cdot\boldsymbol{t}_2)S_1S_2 \\ (\boldsymbol{s}_1\cdot\boldsymbol{s}_2) & (\boldsymbol{t}_1\cdot\boldsymbol{s}_2)S_1 & A & 0 \\ (\boldsymbol{s}_1\cdot\boldsymbol{t}_2)S_2 & (\boldsymbol{t}_1\cdot\boldsymbol{t}_2)S_1S_2 & 0 & AS_2^2 \end{pmatrix} \tag{17.1-38}$$

where

$$A = 1 + \frac{2I}{ml^2\omega^2} \tag{17.1-39}$$

The square root of the determinant of the matrix is

$$g^{1/2} = (\tfrac{1}{2}ml^2\omega^2)^2 A(A^2 - 1)^{1/2} S_1 S_2 h^{1/2} \tag{17.1-40}$$

where

$$h = 1 - \frac{(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)^2}{A^2} \tag{17.1-41}$$

As discussed in §12.3, the equilibrium distribution in configuration space, of molecular models with no intramolecular potential is $g^{1/2}$. Thus the factor $h^{1/2}$ describes the deviation of the equilibrium distribution for this model from that arising from a "random" distribution of angles.

A needle with a fraction $(1 - \omega)$ of its mass at the "head" end and a fraction ω of its mass at the "tail" end would have a moment of inertia of

$$I = \omega(1 - \omega)ml^2 \tag{17.1-42}$$

It is interesting to note that if $\omega = \frac{2}{3}$ this model is similar to the "three-bead, two-rod" model discussed in Example 16.1-2, and since $A = 2$ the equilibrium distribution of angles is the same. On comparing Eq. 17.1-39 with Eq. 12.1-16 one finds that indeed the two models lead to identical metric matrices, if $l = (\frac{3}{2})^{1/2}a$.

The inversion of the metric matrix leads to the values

$$\begin{aligned}
QG_{11} &= AS_1^2S_2^2[A^2 - 1 + (\boldsymbol{t}_1 \cdot \boldsymbol{u}_2)^2] \\
QG_{12} &= -AS_1S_2^2(\boldsymbol{s}_1 \cdot \boldsymbol{u}_2)(\boldsymbol{t}_1 \cdot \boldsymbol{u}_2) \\
QG_{13} &= -S_1^2S_2^2[A^2(\boldsymbol{s}_1 \cdot \boldsymbol{s}_2) + (\boldsymbol{t}_1 \cdot \boldsymbol{t}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{14} &= -S_1^2S_2[A^2(\boldsymbol{s}_1 \cdot \boldsymbol{t}_2) - (\boldsymbol{t}_1 \cdot \boldsymbol{s}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{22} &= AS_2^2[A^2 - 1 + (\boldsymbol{s}_1 \cdot \boldsymbol{u}_2)^2] \\
QG_{23} &= -S_1S_2^2[A^2(\boldsymbol{t}_1 \cdot \boldsymbol{s}_2) - (\boldsymbol{s}_1 \cdot \boldsymbol{t}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{24} &= -S_1S_2[A^2(\boldsymbol{t}_1 \cdot \boldsymbol{s}_2) + (\boldsymbol{s}_1 \cdot \boldsymbol{s}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{33} &= AS_1^2S_2^2[A^2 - 1 + (\boldsymbol{t}_2 \cdot \boldsymbol{u}_1)^2] \\
QG_{34} &= -AS_1^2S_2(\boldsymbol{s}_2 \cdot \boldsymbol{u}_1)(\boldsymbol{t}_2 \cdot \boldsymbol{u}_1) \\
QG_{44} &= AS_1^2[A^2 - 1 + (\boldsymbol{s}_2 \cdot \boldsymbol{u}_1)^2]
\end{aligned} \tag{17.1-43}$$

where

$$Q = \tfrac{1}{2}ml^2\omega^2A^2(A^2 - 1)hS_1^2S_2^2 \tag{17.1-44}$$

From these expressions one may obtain the elements of the metric matrix, G_{st}, for the three-bead two-rod model by setting $\omega = \frac{2}{3}$, $A = 2$, and $l = (\frac{3}{2})^{1/2}a$.

§17.2 ENSEMBLE AVERAGES AND EQUATIONS OF CHANGE

In the foregoing section, it is pointed out that the dynamical state of a single macroscopic system consisting of many solvent and polymer molecules may be described by a "system point" in the associated phase space. In general, the dynamical state changes with time and the point traces out a trajectory in the phase space. For convenience in the next few paragraphs, we use the single symbol x to describe a point in the phase space, that is, the full set of coordinates that describe the space. A trajectory is then described by the time evolution of the point $x(t)$.

In the statistical treatment, it is shown that the actual or "probable" behavior of a physical system is described by the average behavior of a large number, or "ensemble," of identical systems. The dynamical state of such an ensemble is described by a distribution of system points in the phase space, $f(x, t)$, and the average behavior is described by the time evolution of such a distribution. In the present discussion, the distribution function, $f(x, t)$, is normalized so that the integral over all of the phase space is unity

$$\int f(x, t)dx = 1 \tag{17.2-1}$$

Thus $f(x, t)dx$ is the fraction of system points that lies in the multidimensional hypercube dx in the phase space. Note that the distribution function introduced here is a generalization of that used in Eq. 12.3-1.

The development of the equation for the time evolution of the phase-space distribution function $f(x, t)$ is similar to that given in §13.2 for the "equation of continuity" of the configuration-space distribution function for a single dumbbell. The essential point in the development is that no system points are lost or created: as time evolves they simply move through the phase space describing the time evolution of the dynamical state of each system in the ensemble. Thus, by analogy with Eq. 13.2-10 we have

$$\frac{\partial f}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}(\dot{x}_i f) \tag{17.2-2}$$

where the x_i are the generalized coordinates and conjugate momenta.

Next we continue the analogy with the derivation of the "diffusion equation" in §13.2 and introduce the expressions for the time derivatives of the phase-space coordinates given by Hamilton's equations of motion, Eqs. 17.1-25 to 28. When these are substituted into Eq. 17.2-2 we obtain the *Liouville equation*[1]

$$\boxed{\frac{\partial f}{\partial t} = -\mathscr{L}f} \tag{17.2-3}$$

in which $\mathscr{L}$ is the Liouville operator

$$\mathscr{L} = \sum_\alpha \sum_i \left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i}\cdot\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} + \sum_s \sum_t G_{st}^{\alpha i} P_t^{\alpha i}\frac{\partial}{\partial Q_s^{\alpha i}} + [\boldsymbol{F}^{(e)\alpha i} + \boldsymbol{F}^{\alpha i}]\cdot\frac{\partial}{\partial \boldsymbol{p}^{\alpha i}} + \sum_s \mathscr{F}_s^{\alpha i}\frac{\partial}{\partial P_s^{\alpha i}}\right) \tag{17.2-4}$$

In obtaining this last equation many of the terms cancelled since mixed second derivatives of the full Hamiltonian of the system with respect to a coordinate and a momentum do not depend on the order of differentiation.

The physical properties of a macroscopic system are ensemble averages of certain dynamical variables or functions in the phase space. Let us denote an arbitrary dynamical

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[1] J. Liouville, *Journ. de Math. Pures et Appliquées*, 1. Sér., **3**, 342–349 (1838).

variable by $B(x)$, an arbitrary function in the phase space that does not depend explicitly on the time. The average over the ensemble is then denoted by the angular brackets:

$$\langle B\rangle = \int B(x)f(x, t)dx \tag{17.2-5}$$

by analogy with the use of angular brackets in §12.4.

An equation for the time evolution of the average value of an arbitrary dynamical variable B may be obtained by using the continuity equation in Eq. 17.2-2 in the following way:

$$\begin{aligned}\frac{\partial}{\partial t}\langle B\rangle &= \int B(x)\frac{\partial}{\partial t}f(x, t)dx\\ &= -\sum_i \int B(x)\frac{\partial}{\partial x_i}(\dot{x}_i f)dx\\ &= \sum_i \int \dot{x}_i f\frac{\partial}{\partial x_i}B(x)dx\end{aligned} \tag{17.2-6}$$

In the last step an integration by parts was performed, and use was made of the fact that for dynamical variables $B(x)$ of physical interest, $B(x)\dot{x}f$ evaluated at the limits of the variables is zero or, for periodic coordinates, the terms at the two ends cancel. If, now, use is made of Hamilton's equations of motion of the previous section, then we obtain

$$\frac{\partial}{\partial t}\langle B\rangle = \int f(x, t)[\mathscr{L}B(x)]dx \tag{17.2-7}$$

or

$$\boxed{\frac{\partial}{\partial t}\langle B\rangle = \langle \mathscr{L}B\rangle} \tag{17.2-8}$$

This is called the *general equation of change* for an arbitrary dynamical variable $B(x)$. We shall now use this result to obtain the equations of continuity and motion for the polymer solution, and in §17.5 it will be used again to obtain equations for the time evolution of lower-order distribution functions.

a. The Equations of Continuity

As particularly simple examples of the general equation of change, we consider the equations of continuity of each species. For this purpose we take as the dynamical variable

$$B = \sum_i \sum_\nu m_\nu^\alpha \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r}) \tag{17.2-9}$$

This dynamical variable is a function in the phase space, which depends only on a subset of the phase space variables (the configuration coordinates of all the molecules of species α) and depends parametrically on the vector $\boldsymbol{r}$. A particular term in the sum is zero unless the center of mass of bead ν of molecule i of this species is at position $\boldsymbol{r}$. Our statistical treatment begins with interpretation of the average of this dynamical variable

$$\rho_\alpha(\boldsymbol{r}, t) = \left\langle \sum_i \sum_\nu m_\nu^\alpha \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r}) \right\rangle \tag{17.2-10}$$

as the mass concentration at $\boldsymbol{r}$ of species α. It is to be pointed out that in making this identification, we note, explicitly, that the mass of a polymer molecule is distributed in space and is not simply located at the center of mass of the molecule, as is usually assumed, implicitly, in the statistical treatment of systems of small molecules. On the other hand, we have assumed implicitly, that all of the mass of a finite bead is located at the center of mass of the bead.

The mass concentration ρ_α, as defined by Eq. 17.2-10, is a function of $\boldsymbol{r}$ because the dynamical variable B depends parametrically on $\boldsymbol{r}$ and a function of time because in general the distribution function used to obtain the average varies with time. To make use of the general equation of change, Eq. 17.2-8, we next consider the operation of the Liouville operator given by Eq. 17.2-4 on one term in the expression for the dynamical variable B defined by Eq. 17.2-9. Thus we find that

$$\begin{aligned}
\mathscr{L}\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r}) &= \left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} \cdot \frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} + \sum_s \sum_t G_{st}^{\alpha i} P_t^{\alpha i} \frac{\partial}{\partial Q_s^{\alpha i}}\right)\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r}) \\
&= -\left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} + \frac{1}{\sqrt{m_\nu^\alpha}} \sum_s \sum_t G_{st}^{\alpha i} P_t^{\alpha i} \boldsymbol{b}_{\nu s}^{\alpha i}\right) \cdot \nabla\, \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r}) \\
&= -\nabla \cdot \left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_\nu^{\alpha i}\right)\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r})
\end{aligned} \tag{17.2-11}$$

The general equation of change then becomes the *equation of continuity for species* α,

$$\boxed{\frac{\partial}{\partial t}\rho_\alpha = -(\nabla \cdot \rho_\alpha \boldsymbol{v}_\alpha)} \tag{17.2-12}$$

where

$$\boldsymbol{v}_\alpha(\boldsymbol{r}, t) = \frac{1}{\rho_\alpha}\left\langle \sum_i \sum_\nu m_\nu^\alpha \left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_\nu^{\alpha i}\right)\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r})\right\rangle \tag{17.2-13}$$

is the mass average velocity of molecules of species α. The product $\rho_\alpha \boldsymbol{v}_\alpha$ is the density of linear momentum associated with these molecules. This expression is analogous to that for the mass density, Eq. 17.2-10. In the expression for the momentum density the extension in space is again recognized (the $\boldsymbol{R}_\nu^{\alpha i}$ term); and the momentum of the beads relative to the motion of the center of mass of the molecule is also acknowledged (the $\dot{\boldsymbol{R}}_\nu^{\alpha i}$ term). On the other hand, in this expression the spatial extent of the finite beads is once again neglected.

The total density is the sum

$$\rho = \sum_\alpha \rho_\alpha \tag{17.2-14}$$

and the total momentum density is the sum

$$\rho \boldsymbol{v} = \sum_{\alpha} \rho_{\alpha} \boldsymbol{v}_{\alpha} \tag{17.2-15}$$

With these definitions, it readily follows from Eqs. 17.2-13 that

$$\boxed{\frac{\partial}{\partial t} \rho = -(\nabla \cdot \rho \boldsymbol{v})} \tag{17.2-16}$$

This is the overall *equation of continuity* (Eq. D.6-2 or Eq. 1.1-4); for an incompressible fluid it simplifies to

$$(\nabla \cdot \boldsymbol{v}) = 0 \tag{17.2-17}$$

The *mass flux of species* α relative to the stream velocity[2] is

$$\boldsymbol{j}_{\alpha} = \rho_{\alpha}(\boldsymbol{v}_{\alpha} - \boldsymbol{v}) \tag{17.2-18}$$

A kinetic theory expression for this flux leads to expressions for the (translational) diffusivities in polymeric liquids (see Eqs. 18.4-29 and 19.4-28).

b. The Equation of Motion

Next we proceed with an analogous development that leads to the equation of motion. In this development certain terms are ultimately identified as making up the stress tensor and in this way we obtain an expression for the stress tensor in terms of integrals over the distribution functions.

For this development, we take as the dynamical variable

$$\boldsymbol{B} = \sum_{\alpha i \nu} m_{\nu}^{\alpha} \left(\frac{1}{m^{\alpha}} \boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_{\nu}^{\alpha i} \right) \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_{\nu}^{\alpha i} - \boldsymbol{r}) \tag{17.2-19}$$

It follows directly from this definition and Eqs. 17.2-13 and 15 that the average of this dynamical variable is $\rho \boldsymbol{v}$ so that in this case the left side of the general equation of change, Eq. 17.2-8, is $\partial \rho \boldsymbol{v} / \partial t$.

In contrast with the previous development, in which we derived equations of continuity for each species, here we develop a single equation describing the conservation of linear momentum of the mixture. The reason for this difference lies in the basic dynamics of the system. Since we are considering a nonreacting mixture, collisions among the molecules do not alter the chemical constitution. On the other hand collisions do affect the amount of linear momentum associated with each species, but not the total amount of linear momentum. For this reason, it is only when the total momentum is considered that one is lead to a "conservation" equation with no source terms—other than those associated with external forces.

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[2] See Eq. D.6-1 for the equation of continuity in terms of $\boldsymbol{j}_{\alpha}$. For further information on various definitions of diffusion fluxes see R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960), §16.1.

The Liouville operator, $\mathscr{L}$, is a linear, first order, differential operator and hence the operation of $\mathscr{L}$ on $\boldsymbol{B}$ leads to terms analogous to those obtained in the development of the equation of continuity and additional terms arising from the differentiation of the additional factor $[(1/m^\alpha)\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_\nu^{\alpha i}]$. The result is

$$\begin{aligned}\mathscr{L}\boldsymbol{B} = {} & -\nabla\cdot\sum_{\alpha i\nu} m_\nu^\alpha\left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_\nu^{\alpha i}\right)\left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_\nu^{\alpha i}\right)\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r}) \\ & + \sum_{\alpha i\nu} m_\nu^\alpha\left[\frac{1}{m^\alpha}[\boldsymbol{F}^{(e)\alpha i} + \boldsymbol{F}^{\alpha i}] + \sum_{st} G_{st}^{\alpha i} P_t^{\alpha i}\left(\frac{\partial}{\partial Q_s^{\alpha i}}\dot{\boldsymbol{R}}_\nu^{\alpha i}\right)\right. \\ & \left. + \sum_s \mathscr{F}_s^{\alpha i}\left(\frac{\partial}{\partial P_s^{\alpha i}}\dot{\boldsymbol{R}}_\nu^{\alpha i}\right)\right]\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r})\end{aligned} \tag{17.2-20}$$

The derivatives of $\dot{\boldsymbol{R}}_\nu^{\alpha i}$ with respect to the phase space variables are given by Eqs. 17.1-30 and 31. When we use these we find that it is convenient to define an "effective force" on bead ν as

$$\boldsymbol{\mathscr{F}}_\nu = \frac{m_\nu}{m_p}[\boldsymbol{F}^{(e)} + \boldsymbol{F}] + \sqrt{m_\nu}\sum_s\sum_t\left[\mathscr{F}_s G_{st}\boldsymbol{b}_{\nu t} + \sum_u\sum_v G_{uv}P_v P_s\left(\frac{\partial}{\partial Q_u}G_{st}\boldsymbol{b}_{\nu t}\right)\right] \tag{17.2-21}$$

It is to be noted that in this expression and in a number of those that follow, we omit for convenience the superscripts α and i specifying the species and identifying a particular molecule of that species. When this is done we use m_p to indicate the total mass of a molecule (polymer or solvent) rather than the more explicit m^α.

With the results developed above the general equation of change, Eq. 17.2-8 may be written in the form of the *equation of motion*

$$\boxed{\frac{\partial}{\partial t}\rho\boldsymbol{v} = -[\nabla\cdot\rho\boldsymbol{v}\boldsymbol{v}] - [\nabla\cdot\boldsymbol{\pi}^{(k)}] + \boldsymbol{S}} \tag{17.2-22}$$

in which

$$\boldsymbol{\pi}^{(k)} = \left\langle\sum_{\alpha i\nu} m_\nu^\alpha\left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_\nu^{\alpha i} - \boldsymbol{v}\right)\left(\frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_\nu^{\alpha i} - \boldsymbol{v}\right)\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r})\right\rangle \tag{17.2-23}$$

$$\boldsymbol{S} = \left\langle\sum_{\alpha i\nu}\boldsymbol{\mathscr{F}}_\nu^{\alpha i}\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r})\right\rangle \tag{17.2-24}$$

Equation 17.2-22 is similar in form to the equation of motion as given by Eq. D.6-3 or Eq. 1.1-8. The first two terms on the right arise from the first term in the expression for $\mathscr{L}\boldsymbol{B}$, Eq. 17.2-20. This first term in $\mathscr{L}\boldsymbol{B}$ has been separated to give the term containing $\rho\boldsymbol{v}\boldsymbol{v}$, the convective term associated with the bulk flow of the fluid relative to the fixed frame, and another term, containing $\boldsymbol{\pi}^{(k)}$, which is usually referred to as the "kinetic contribution" to the stress tensor and describes the momentum transport due to the "Brownian" motion of the beads relative to a coordinate system moving with fluid velocity $\boldsymbol{v}$. The source term $\boldsymbol{S}$ describes the momentum transport associated with the effective force $\boldsymbol{\mathscr{F}}_\nu^{\alpha i}$, defined by Eq. 17.2-21. It will be shown that except for the term in $\boldsymbol{\mathscr{F}}_\nu^{\alpha i}$ containing the external force $\boldsymbol{F}^{(e)}$, the quantity $\boldsymbol{S}$ may also be written as the divergence of a tensor; this procedure will then lead to additional contributions to the stress tensor associated with the various real and effective forces (compare Eqs. 17.2-22 and 17.4-32).

As examples, we may consider the explicit form of the effective force that appears in the source term of the equation of motion for several specific models. In particular, if one considers the elastic dumbbell model which is discussed in Chapter 13, one finds that the expressions for the effective forces given by Eq. 17.2-21 become for beads "1" and "2"

$$\mathscr{F}_1 = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) + \frac{\partial \phi}{\partial Q}\boldsymbol{u} \tag{17.2-25}$$

$$\mathscr{F}_2 = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \frac{\partial \phi}{\partial Q}\boldsymbol{u} \tag{17.2-26}$$

where $\boldsymbol{F}^{(e)}$ and $\boldsymbol{F}$ are the forces on the center of mass of the dumbbell due to the external and intermolecular potentials, respectively. In each expression the last term is the force on the bead due to the intramolecular potential which is in the direction of the spring ($\boldsymbol{u}$ is the unit vector $\boldsymbol{Q}/Q$). The analogous expressions for the specific case of the rigid dumbbell discussed in Chapter 14 are

$$\mathscr{F}_{-1} = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) + \frac{2}{L}\mathscr{K}_{\text{int}}\boldsymbol{u} \tag{17.2-27}$$

$$\mathscr{F}_1 = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \frac{2}{L}\mathscr{K}_{\text{int}}\boldsymbol{u} \tag{17.2-28}$$

where $\mathscr{K}_{\text{int}}$ is the rotational kinetic energy of the dumbbell defined by the general expression, Eq. 17.1-15, and $\boldsymbol{F}^{(e)}$ and $\boldsymbol{F}$ are defined as in Eqs. 17.2-25 and 17.2-26. In these equations the last terms are effective forces arising from the constraints; these terms are obtained from the last G_{st}-term in Eq. 17.2-21 with the help of Example 16.1-1.

EXAMPLE 17.2-1 The Effective Force for Models with No Constraints

Simplify Eq. 17.2-21 for the effective force $\mathscr{F}_\nu$, for models with no constraints and with beads that are mass points.

SOLUTION For any model with mass points (structureless beads) joined together with springs in any kind of connectivity, one can specify the location of the beads relative to the center of mass of the molecule by a set of vectors $\boldsymbol{Q}_k$. For a linear chain the $\boldsymbol{Q}_k$ would be the "connector vectors," but for a model with branching or closed loops the $\boldsymbol{Q}_k$ may be selected arbitrarily. In either case, if the generalized coordinates Q_s are taken to be the Cartesian components of $\boldsymbol{Q}_k$, we know that the g_{st} and G_{st} matrices do not depend on the generalized coordinates (cf. Eqs. 12.1-23 and 12.1-24). If this choice is made, then in Eq. 17.2-21 the term containing the double sum on u and v vanishes.

The force $\mathscr{F}_s$ in Eq. 17.2-21 can be obtained from Eqs. 17.1-20 to 24 as

$$\begin{aligned}\mathscr{F}_s &= -\frac{\partial}{\partial Q_s}(\phi + \phi^{(e)} + \Phi) \\ &= -\sum_\mu \frac{1}{\sqrt{m_\mu}}\left(\boldsymbol{b}_{\mu s}\cdot\frac{\partial}{\partial \boldsymbol{r}_\mu}(\phi + \phi^{(e)} + \Phi)\right)\end{aligned} \tag{17.2-29}$$

the second line being obtained by using the chain rule of partial differentiation (see §E.1). When this expression for $\mathscr{F}_s$ is inserted into Eq. 17.2-21, then use of 12D.3-5, a relation valid for systems with no constraints, gives

$$\begin{aligned}\mathscr{F}_\nu &= \frac{m_\nu}{m_p}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \sqrt{m_\nu}\sum_\mu \frac{1}{\sqrt{m_\mu}}\left(\delta_{\nu\mu} - \frac{\sqrt{m_\nu m_\mu}}{m_p}\right)\frac{\partial}{\partial \boldsymbol{r}_\mu}(\phi + \phi^{(e)} + \Phi) \\ &= \frac{m_\nu}{m_p}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \frac{\partial}{\partial \boldsymbol{r}_\nu}(\phi + \phi^{(e)} + \Phi) + \frac{m_\nu}{m_p}\sum_\mu \frac{\partial}{\partial \boldsymbol{r}_\mu}(\phi + \phi^{(e)} + \Phi)\end{aligned} \tag{17.2-30}$$

Since the sum of the intramolecular forces on the beads of one molecule is zero, it follows that $-\sum_\mu (\partial/\partial \boldsymbol{r}_\mu)\phi$ is zero. In addition $-\sum_\mu (\partial/\partial \boldsymbol{r}_\mu)\phi^{(e)}$ is just the total external force on the molecule, $\boldsymbol{F}^{(e)}$, and $-\sum_\mu(\partial/\partial \boldsymbol{r}_\mu)\Phi$ is the total force $\boldsymbol{F}$ on the molecule due to all the other molecules. Therefore, some cancellation occurs and

$$\mathscr{F}_\nu = -\frac{\partial}{\partial \boldsymbol{r}_\nu}(\phi + \phi^{(e)} + \Phi) \tag{17.2-31}$$

Thus, we see that if the molecular model involves no constraints the effective force $\mathscr{F}_\nu$, is simply the sum of the true forces arising from the various potentials. This general result is clearly consistent with the explicit expression for the elastic dumbbell model given by Eqs. 17.2-25 and 26; but for the rigid dumbbell model, which involves a constraint, the expressions for $\mathscr{F}_\nu$ have a different form (Eqs. 17.2-27 and 28).

§17.3 CONTRACTED DISTRIBUTION FUNCTIONS

In the foregoing sections a distribution function $f(x, t)$ in the full phase space of the system was introduced. Then the physical quantities of interest ρ, $\rho\boldsymbol{v}$, $\boldsymbol{\pi}^{(k)}$, and $\boldsymbol{S}$ were written as ensemble averages involving this distribution function. It will, however, be more convenient to express these averages in terms of certain "contracted distribution functions:"

The singlet phase-space distribution functions.
The pair phase-space distribution functions.
The singlet configuration-space distribution functions.
The pair configuration-space distribution functions.

In this section we define these contracted distribution functions, and then in the next section we obtain expressions for the stress tensor and other physical quantities in terms of these functions.

The singlet phase-space distribution function is the nonequilibrium generalization of the phase-space distribution function f_{eq} discussed in §12.3. Here we define the function for species α as

$$f_\alpha(\boldsymbol{r}, Q, \boldsymbol{p}, P, t) = \left\langle \sum_i \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q)\delta(\boldsymbol{p}^{\alpha i} - \boldsymbol{p})\delta(P^{\alpha i} - P)\right\rangle \tag{17.3-1}$$

The argument Q is symbolic for the full set of generalized coordinates and $\delta(Q^{\alpha i} - Q)$ is symbolic for the corresponding product of δ-functions. Similar comments apply to P and

$\delta(P^{\alpha i} - P)$. The function $f_\alpha(\boldsymbol{r}, Q, \boldsymbol{p}, P, t)$ is the probable number density of molecules of species α in the phase-space; that is

$$f_\alpha(\boldsymbol{r}, Q, \boldsymbol{p}, P, t)d\boldsymbol{r}\, dQ\, d\boldsymbol{p}\, dP \tag{17.3-2}$$

is the probable number of molecules of this species with center of mass in the region $d\boldsymbol{r}$ about $\boldsymbol{r}$ and with momentum $\boldsymbol{p}$, internal coordinates Q, and conjugate momenta P in the ranges $d\boldsymbol{p}$, dQ, and dP about $\boldsymbol{p}$, Q, and P.

The second set of contracted distribution functions is defined in an analogous manner

$$\begin{aligned} f_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', \boldsymbol{p}', P', \boldsymbol{p}'', P'', t) = \Big\langle \sum_i \sum_j \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r}')\delta(Q^{\alpha i} - Q')\delta(\boldsymbol{r}^{\beta j} - \boldsymbol{r}'')\delta(Q^{\beta j} - Q'') \\ \times\, \delta(\boldsymbol{p}^{\alpha i} - \boldsymbol{p}')\delta(P^{\alpha i} - P')\delta(\boldsymbol{p}^{\beta j} - \boldsymbol{p}'')\delta(P^{\beta j} - P'')\Big\rangle \end{aligned} \tag{17.3-3}$$

These are functions in the two-molecule phase spaces. They are the joint probable number densities of molecules of the species indicated. If the two species are alike ($\alpha = \beta$), the terms in the double sum in which $i = j$ are to be omitted. These functions vary rapidly with the separation distance between the centers of mass of the molecules at separation distances of the order of molecular dimensions, but vary slowly with the position of the center of mass of the pair. For this reason it is convenient to change variables and define a related set of functions

$$\tilde{f}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q', Q'', \boldsymbol{p}', P', \boldsymbol{p}'', P'', t) = f_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', \boldsymbol{p}', P', \boldsymbol{p}'', P'', t) \tag{17.3-4}$$

where

$$\boldsymbol{r} = \frac{m_p' \boldsymbol{r}' + m_p'' \boldsymbol{r}''}{m_p' + m_p''} \tag{17.3-5}$$

$$\boldsymbol{R} = \boldsymbol{r}'' - \boldsymbol{r}' \tag{17.3-6}$$

In the new set of functions the variables $\boldsymbol{r}'$ and $\boldsymbol{r}''$ are replaced by $\boldsymbol{r}$, the vector to the center of mass of the pair, and $\boldsymbol{R}$, the vector from the center of mass of the "first" molecule to that of the "second."

Next we define the configuration-space distribution functions by integrating the various phase space distribution functions over the momentum coordinates. As in the development of §12.3, the integration of the singlet function leads to the single-molecule configuration-space distribution function:

$$\Psi_\alpha(\boldsymbol{r}, Q, t) = \iint f_\alpha(\boldsymbol{r}, Q, \boldsymbol{p}, P, t)d\boldsymbol{p}\, dP \tag{17.3-7}$$

The integral of this function over the internal coordinates

$$\int \Psi_\alpha(\boldsymbol{r}, Q, t)dQ = n_\alpha(\boldsymbol{r}, t) \tag{17.3-8}$$

is the number density of molecules of species α (cf. Eq. 12.3-2).

In a similar manner the distribution functions in the configuration spaces of pairs are defined by integrating the $f_{\alpha\beta}$ over the momenta

$$\Psi_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', t) = \iiiint f_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', \boldsymbol{p}', P', \boldsymbol{p}'', P'', t)d\boldsymbol{p}'\, dP'\, d\boldsymbol{p}''\, dP'' \tag{17.3-9}$$

The functions, $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q', Q'', t)$, are defined in a similar manner by integrating the corresponding phase-space functions over the momenta. If the two molecules are sufficiently far apart that they are statistically independent, that is, uncorrelated, the joint probability becomes a product of the separate probabilities, that is

$$\lim_{|\boldsymbol{r}''-\boldsymbol{r}'|\to\infty} \Psi_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', t) = \Psi_\alpha(\boldsymbol{r}', Q', t)\Psi_\beta(\boldsymbol{r}'', Q'', t) \tag{17.3-10}$$

Use is made of this later.

In the development of the next section, we make use of the symmetry of the pair distribution functions in configuration space. From the definitions, Eqs. 17.3-3 and 9, it follows that

$$\Psi_{\beta\alpha}(\boldsymbol{r}'', Q'', \boldsymbol{r}', Q', t) = \Psi_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', t) \tag{17.3-11}$$

and thus

$$\tilde{\Psi}_{\beta\alpha}(\boldsymbol{r}, \boldsymbol{R}, Q'', Q', t) = \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, -\boldsymbol{R}, Q', Q'', t) \tag{17.3-12}$$

We conclude this section with the introduction of a convenient notation for an average over the momentum space. For any function, B, defined in the phase space of the system, we define the average

$$\begin{aligned}[\![B]\!]^\alpha &= \frac{1}{\Psi_\alpha(\boldsymbol{r}, Q, t)} \iint \left\langle B \sum_i \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q)\delta(\boldsymbol{p}^{\alpha i} - \boldsymbol{p})\delta(P^{\alpha i} - P)\right\rangle d\boldsymbol{p}\, dP \\ &= \frac{1}{\Psi_\alpha(\boldsymbol{r}, Q, t)} \left\langle B \sum_i \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q)\right\rangle \end{aligned} \tag{17.3-13}$$

This average is a function in the configuration space of a single molecule of species α, and involves taking the ensemble average over all the momentum coordinates and over all configuration coordinates except those of a single molecule of species α. From the definition of the singlet phase space distribution function, Eq. 17.3-1, it follows that if B is a function, $b(\boldsymbol{r}, Q, \boldsymbol{p}, P)$, in the phase space of a single molecule of species α, this average reduces to

$$[\![b]\!]^\alpha = \frac{1}{\Psi_\alpha(\boldsymbol{r}, Q, t)} \iint b(\boldsymbol{r}, Q, \boldsymbol{p}, P) f_\alpha(\boldsymbol{r}, Q, \boldsymbol{p}, P, t)d\boldsymbol{p}\, dP \tag{17.3-14}$$

and becomes identical to the average in §12.4. In the applications of this chapter, the function B will, in general, depend on the momentum coordinates of a single molecule of species α only, but will depend on the configuration coordinates of several molecules.

§17.4 THE STRESS TENSOR IN TERMS OF THE CONFIGURATION SPACE DISTRIBUTION FUNCTIONS

We now return to the expressions for the various macroscopic properties and express them in terms of the singlet and pair distribution functions. From the expression, Eq. 17.2-10, for the *mass concentration* associated with molecules of species α and the definitions of the previous section, one finds that

$$\begin{aligned}\rho_\alpha(\boldsymbol{r}, t) &= \sum_\nu m_\nu^\alpha \iiint f_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, \boldsymbol{p}, P, t)dQ\, d\boldsymbol{p}\, dP \\ &= \sum_\nu m_\nu^\alpha \int \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t)dQ \qquad (17.4\text{-}1)\end{aligned}$$

The displaced position argument in the distribution function in the integrand arises from the finite extension of the polymer molecules in space.

In a similar manner one finds from Eq. 17.2-13, that the *momentum density* associated with molecules of a particular species α is

$$\begin{aligned}\rho_\alpha \boldsymbol{v}_\alpha &= \sum_\nu m_\nu^\alpha \iiint \left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu\right) f_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, \boldsymbol{p}, P, t)dQ\, d\boldsymbol{p}\, dP \\ &= \sum_\nu m_\nu^\alpha \int \left[\!\left[\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu\right]\!\right]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t)dQ \qquad (17.4\text{-}2)\end{aligned}$$

The *mass flux* of α is then

$$\boldsymbol{j}_\alpha = \sum_\nu m_\nu \int \left[\!\left[\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right]\!\right]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t)dQ \qquad (17.4\text{-}3)$$

Next we turn to the *kinetic contribution to the stress tensor* as given by Eq. 17.2-23. This may be written as the sum of integrals involving the singlet distribution functions:

$$\boldsymbol{\pi}^{(k)} = \sum_{\alpha\nu} m_\nu^\alpha \int \left[\!\left[\left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right)\left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right)\right]\!\right]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t)dQ \qquad (17.4\text{-}4)$$

Most of the remainder of this section will be concerned with the *source term* $\boldsymbol{S}$ in the equation of motion (Eq. 17.2-24). Before embarking on this discussion we introduce some additional notation for the effective forces.

Let us return to the expression for the effective force, $\mathscr{F}_\nu$, as given by Eq. 17.2-21, and separate the expression into terms involving the external forces, intramolecular effects, and intermolecular effects. Thus we first define

$$\mathscr{F}_\nu^{(e)} = \sqrt{m_\nu} \sum_{st} \mathscr{F}_s^{(e)} G_{st} \boldsymbol{b}_{\nu t} \tag{17.4-5}$$

$$\mathscr{F}_\nu^{(S)} = \sqrt{m_\nu} \sum_{st} \left[(\mathscr{F}_s^{(k)} + \mathscr{F}_s^{(\phi)}) G_{st} \boldsymbol{b}_{\nu t} + \sum_{uv} G_{uv} P_v P_s \left(\frac{\partial}{\partial Q_u} G_{st} \boldsymbol{b}_{\nu t} \right) \right] \tag{17.4-6}$$

$$\mathscr{F}_\nu^{(D)} = \frac{m_\nu}{m_p} \boldsymbol{F} + \sqrt{m_\nu} \sum_{st} \mathscr{F}_s^{(d)} G_{st} \boldsymbol{b}_{\nu t} \tag{17.4-7}$$

so that

$$\mathscr{F}_\nu = \left[\frac{m_\nu}{m_p} \boldsymbol{F}^{(e)} + \mathscr{F}_\nu^{(e)} \right] + \mathscr{F}_\nu^{(S)} + \mathscr{F}_\nu^{(D)} \tag{17.4-8}$$

The superscripts (S) and (D) stand for "single" and "double." The relation between these vector effective forces and the scalar forces introduced in §17.1 is summarized in Table 17.4-1.

The source term in the equation of motion as defined by Eq. 17.2-24 may be separated in an analogous manner and written as

$$\boldsymbol{S} = \boldsymbol{S}^{(e)} + \boldsymbol{S}^{(S)} + \boldsymbol{S}^{(D)} \tag{17.4-9}$$

Since $(m_\nu/m_p)\boldsymbol{F}^{(e)} + \mathscr{F}_\nu^{(e)}$ and $\mathscr{F}_\nu^{(S)}$ are functions of the phase-space coordinates of a single molecule only, the corresponding contributions to the source term are obtained by performing integrations over all momenta and the configuration coordinates of all other molecules. This leads directly to

$$\boldsymbol{S}^{(e)} = \sum_{\alpha\nu} \int \left(\frac{m_\nu^\alpha}{m^\alpha} \boldsymbol{F}^{(e)\alpha} + \mathscr{F}_\nu^{(e)\alpha} \right) \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t)\, dQ \tag{17.4-10}$$

$$\boldsymbol{S}^{(S)} = \sum_{\alpha\nu} \int [\![\mathscr{F}_\nu^{(S)\alpha}]\!]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t)\, dQ \tag{17.4-11}$$

In the treatment of $\boldsymbol{S}^{(D)}$, the contribution of the intermolecular effects, we assume that the intermolecular potential is the sum of contributions associated with pairs of molecules

$$\Phi = \tfrac{1}{2} \sum_{\alpha i \beta j} \Phi^{\alpha i, \beta j} \tag{17.4-12}$$

where $\Phi^{\alpha i, \beta j}$ depends only on the configuration coordinates of the pair of molecules αi and βj, and the terms with both $\alpha = \beta$ *and* $i = j$ are zero. With the above assumption the source term, $\boldsymbol{S}^{(D)}$, may be written in terms of integrals involving only the pair distribution functions.

TABLE 17.4-1

Generalized and Effective Forces

Generalized Forces			Effective Forces			
Symbol	Defining Equation	Expression	Symbol	Defining Equation	Expression	$\sum_{\nu} \mathscr{F}_{\nu}^{(\ldots)}$
$\mathscr{F}_s^{(k)}$	17.1-20	—	$\mathscr{F}_{\nu}^{(S)}$	17.4-6		$\mathbf{0}$
$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\dfrac{\partial}{\partial Q_s}\,\phi$				
$\mathscr{F}_s^{(e)}$	17.1-22	$-\dfrac{\partial}{\partial Q_s}\,\phi^{(e)}$	$\mathscr{F}_{\nu}^{(e)}$	17.4-5	$\sqrt{m_{\nu}} \sum_{st} G_{st} \mathscr{F}_s^{(e)} \boldsymbol{b}_{\nu t}$	$\mathbf{0}$
$\mathscr{F}_s^{(d)}$	17.1-23	$-\dfrac{\partial}{\partial Q_s}\,\Phi$	$\mathscr{F}_{\nu}^{(D)}$	17.4-7	$\dfrac{m_{\nu}}{m_p} \boldsymbol{F} + \sqrt{m_{\nu}} \sum_{st} G_{st} \mathscr{F}_s^{(d)} \boldsymbol{b}_{\nu t}$	$\boldsymbol{F}$
$\mathscr{F}_s$	17.1-24	$\sum \mathscr{F}_s^{(\ldots)}$	$\mathscr{F}_{\nu}$	17.2-21	$\left[\dfrac{m_{\nu}}{m_p} \boldsymbol{F}^{(e)} + \mathscr{F}_{\nu}^{(e)}\right] + \mathscr{F}_{\nu}^{(S)} + \mathscr{F}_{\nu}^{(D)}$	$\boldsymbol{F} + \boldsymbol{F}^{(e)}$

With the assumption of "two-molecule" forces (Eq. 17.4-12) it follows from the definition of $\mathscr{F}_\nu^{(D)}$ in Eq. 17.4-7, and Eq. 17.1-23 that

$$\mathscr{F}_\nu^{(D)\alpha i} = \sum_{\beta j} \mathscr{F}_\nu^{\alpha i, \beta j} \tag{17.4-13}$$

That is, the effective intermolecular force on a bead of molecule i of species α is the sum of contributions from all of the other molecules of the same or different species. If we abbreviate αi by α and βj by β, a typical term in the sum is given by

$$\mathscr{F}_\nu^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta) = \frac{m_\nu^\alpha}{m^\alpha} \boldsymbol{F}^{\alpha\beta} + \sqrt{m_\nu^\alpha} \sum_{st} \mathscr{F}_s^{\alpha\beta} G_{st}^\alpha \boldsymbol{b}_{\nu t}^\alpha \tag{17.4-14}$$

where $\boldsymbol{R}_{\alpha\beta} = \boldsymbol{r}_\beta - \boldsymbol{r}_\alpha$ and

$$\boldsymbol{F}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta) = -\frac{\partial}{\partial \boldsymbol{r}^\alpha} \Phi^{\alpha\beta} \tag{17.4-15}$$

$$\mathscr{F}_s^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta) = -\frac{\partial}{\partial Q_s^\alpha} \Phi^{\alpha\beta} \tag{17.4-16}$$

The contribution of the intermolecular effects to the source term is given by

$$\boldsymbol{S}^{(D)} = \sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\alpha\beta} \Psi_{\alpha\beta}(\boldsymbol{r} - \boldsymbol{R}_\nu^\alpha, Q_\alpha, \boldsymbol{r}_\beta, Q_\beta, t) dQ_\alpha \, d\boldsymbol{r}_\beta \, dQ_\beta \tag{17.4-17}$$

where $\mathscr{F}_\nu^{\alpha\beta}$ may be interpreted as the effective force on bead ν of a molecule of species α with the center of mass at $\boldsymbol{r} - \boldsymbol{R}_\nu$ due to a molecule of species β with center of mass at $\boldsymbol{r}_\beta$. The right side may be written using the alternate form of the pair distribution function as

$$\sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}) \tilde{\Psi}_{\alpha\beta}\left(\boldsymbol{r} - \boldsymbol{R}_\nu^\alpha + \frac{m^\beta}{m^\alpha + m^\beta} \boldsymbol{R}_{\alpha\beta}, \boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta, t\right) dQ_\alpha \, dQ_\beta \, d\boldsymbol{R}_{\alpha\beta} \tag{17.4-18}$$

where the effective force is now that associated with a pair of molecules with the center of mass of the pair at the position indicated by the first argument of the distribution function and with the vector from α to β being $\boldsymbol{R}_{\alpha\beta}$.

Next, we develop an alternate form of the last result. To do this we first interchange the summation labels to obtain

$$\sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\beta\alpha}(\boldsymbol{R}_{\beta\alpha}) \tilde{\Psi}_{\beta\alpha}\left(\boldsymbol{r} - \boldsymbol{R}_\nu^\beta + \frac{m^\alpha}{m^\alpha + m^\beta} \boldsymbol{R}_{\beta\alpha}, \boldsymbol{R}_{\beta\alpha}, Q_\beta, Q_\alpha, t\right) dQ_\alpha \, dQ_\beta \, d\boldsymbol{R}_{\beta\alpha} \tag{17.4-19}$$

and second make use of the symmetry of the pair distribution functions. We change the integration variable, implying integration from $-\infty$ to $+\infty$ in both expressions:

$$\sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta}) \tilde{\Psi}_{\alpha\beta}\left(\boldsymbol{r} - \boldsymbol{R}_\nu^\beta - \frac{m^\alpha}{m^\alpha + m^\beta} \boldsymbol{R}_{\alpha\beta}, \boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta, t\right) dQ_\alpha \, dQ_\beta \, d\boldsymbol{R}_{\alpha\beta} \tag{17.4-20}$$

Finally, $\boldsymbol{S}^{(D)}$ may be written as one-half the sum of the expressions given by Eqs. 17.4-18 and 20,

$$\frac{1}{2}\sum_{\alpha\beta\nu}\iiint \mathscr{F}_\nu^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta})\,\tilde{\Psi}_{\alpha\beta}\!\left(\boldsymbol{r}-\boldsymbol{R}_\nu^\alpha+\frac{m^\beta}{m^\alpha+m^\beta}\boldsymbol{R}_{\alpha\beta},\boldsymbol{R}_{\alpha\beta},Q_\alpha,Q_\beta,t\right)dQ_\alpha\,dQ_\beta\,d\boldsymbol{R}_{\alpha\beta}$$
$$+\frac{1}{2}\sum_{\alpha\beta\nu}\iiint \mathscr{F}_\nu^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta})\,\tilde{\Psi}_{\alpha\beta}\!\left(\boldsymbol{r}-\boldsymbol{R}_\nu^\beta-\frac{m^\alpha}{m^\alpha+m^\beta}\boldsymbol{R}_{\alpha\beta},\boldsymbol{R}_{\alpha\beta},Q_\alpha,Q_\beta,t\right)dQ_\alpha\,dQ_\beta\,d\boldsymbol{R}_{\alpha\beta} \quad (17.4\text{-}21)$$

We have now completed the task of rewriting a number of macroscopic quantities (ρ_α, $\rho_\alpha \boldsymbol{v}_\alpha$, $\boldsymbol{j}_\alpha$, $\boldsymbol{\pi}^{(k)}$, and the three contributions to $\boldsymbol{S}$) in terms of the lower-order distribution functions Ψ_α and $\tilde{\Psi}_{\alpha\beta}$.

One final job remains, namely that of writing $\boldsymbol{S}^{(S)}$, $\boldsymbol{S}^{(D)}$, and part of $\boldsymbol{S}^{(e)}$ as divergences of tensors, so that the equation of motion (Eq. 17.2-22) can be put into the standard form given in Eq. D.6-3. This is accomplished by expanding Ψ_α and $\tilde{\Psi}_{\alpha\beta}$ about the position coordinate $\boldsymbol{r}$, which appears in the first independent variable of the distribution functions; to do this we use a generalized Taylor expansion given in §E.2. It turns out that the first term in the Taylor expansion is exactly zero for $\boldsymbol{S}^{(S)}$ and $\boldsymbol{S}^{(D)}$ as may be easily seen from the following arguments. If in Eq. 17.4-11 we replace $\Psi_\alpha(\boldsymbol{r}-\boldsymbol{R}_\nu, Q, t)$ by $\Psi_\alpha(\boldsymbol{r}, Q, t)$, then the summation on ν can be performed to give

$$\sum_\nu \mathscr{F}_\nu^{(S)\alpha} = \boldsymbol{0} \quad (17.4\text{-}22)$$

where we have made use of Eq. 17.4-6 and the fact that $\sum_\nu \sqrt{m_\nu}\,\boldsymbol{b}_{\nu t} = \boldsymbol{0}$; consequently with this replacement $\boldsymbol{S}^{(S)} = \boldsymbol{0}$. Similarly when in Eq. 17.4-21 we replace the distribution functions by $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)$, then the summations on ν give

$$\sum_\nu\left[\mathscr{F}_\nu^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta})+\mathscr{F}_\nu^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta})\right]=\boldsymbol{F}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta})+\boldsymbol{F}^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta}) \quad (17.4\text{-}23)$$

where Eq. 17.4-14 has been used. Since $\boldsymbol{F}^{\alpha\beta}$ is the total force on a molecule of α exerted by a molecule of β, it is evident that

$$\boldsymbol{F}^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta}) = -\boldsymbol{F}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}) \quad (17.4\text{-}24)$$

As a result in this approximation the two terms in Eq. 17.4-21 cancel one another and $\boldsymbol{S}^{(D)} = \boldsymbol{0}$.

Now we transform the expressions for $\boldsymbol{S}^{(e)}$, $\boldsymbol{S}^{(S)}$, and $\boldsymbol{S}^{(D)}$ by applying the generalized Taylor theorem of Eq. E.2-2 to Ψ_α and $\tilde{\Psi}_{\alpha\beta}$ as functions of their first variable. When this theorem is applied to $\boldsymbol{S}^{(e)}$ in Eq. 17.4-10 we find that

$$\boldsymbol{S}^{(e)} = n\bar{\boldsymbol{F}}^{(e)} - [\nabla\cdot\boldsymbol{\pi}^{(e)}] \quad (17.4\text{-}25)$$

where

$$\bar{\boldsymbol{F}}^{(e)} = \frac{1}{n}\sum_\alpha \int \boldsymbol{F}^{(e)\alpha}\,\Psi_\alpha(\boldsymbol{r}, Q, t)\,dQ \quad (17.4\text{-}26)$$

$$\boldsymbol{\pi}^{(e)} = \sum_\alpha\sum_\nu \iint_0^1 \boldsymbol{R}_\nu\left(\frac{m_\nu^\alpha}{m_\alpha}\boldsymbol{F}^{(e)\alpha}+\mathscr{F}_\nu^{(e)\alpha}\right)\Psi_\alpha(\boldsymbol{r}-\xi\boldsymbol{R}_\nu, Q, t)\,d\xi\,dQ \quad (17.4\text{-}27)$$

In the expansion of $\mathbb{S}^{(e)}$ the first term does not vanish, and this term $n\bar{\boldsymbol{F}}^{(e)}$, corresponds to the external force term in the equation of motion ($\sum_i \rho_i \boldsymbol{g}_i$ in Eq. D.6-3).

In a similar manner one finds from Eq. 17.4-11, the expression for the contribution of the intramolecular effects, $\mathbb{S}^{(S)}$, that

$$\mathbb{S}^{(S)} = -[\boldsymbol{\nabla} \cdot \boldsymbol{\pi}^{(S)}] \tag{17.4-28}$$

where

$$\boldsymbol{\pi}^{(S)} = \sum_{\alpha} \sum_{\nu} \iint_0^1 \boldsymbol{R}_\nu [\![\mathscr{F}_\nu^{(S)\alpha}]\!]^\alpha \Psi_\alpha(\boldsymbol{r} - \xi \boldsymbol{R}_\nu, Q, t)\, d\xi\, dQ \tag{17.4-29}$$

In this case, the term analogous to $\bar{\boldsymbol{F}}^{(e)}$ is zero because of Eq. 17.4-22 as just discussed.

The theorem is next applied to the "two-molecule" contribution, $\mathbb{S}^{(D)}$, as given by Eq. 17.4-21. Again for the reasons discussed above the first term is zero and

$$\mathbb{S}^{(D)} = -[\boldsymbol{\nabla} \cdot \boldsymbol{\pi}^{(D)}] \tag{17.4-30}$$

Before writing the expression for $\boldsymbol{\pi}^{(D)}$, however, it is convenient to use the symmetry argument as discussed above to write the expression in the somewhat simpler unsymmetrized form

$$\begin{aligned} \boldsymbol{\pi}^{(D)} = \sum_{\alpha\beta\nu} \iiiint_0^1 & \left(\boldsymbol{R}_\nu^\alpha - \frac{m^\beta}{m^\alpha + m^\beta} \boldsymbol{R}_{\alpha\beta} \right) \mathscr{F}_\nu^{\alpha\beta} \\ & \times \tilde{\Psi}_{\alpha\beta}\left(\boldsymbol{r} - \xi \boldsymbol{R}_\nu^\alpha + \frac{m^\beta}{m^\alpha + m^\beta} \xi \boldsymbol{R}_{\alpha\beta}, \boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta, t \right) d\xi\, dQ_\alpha\, dQ_\beta\, d\boldsymbol{R}_{\alpha\beta} \end{aligned} \tag{17.4-31}$$

We see finally that the *equation of motion*, Eq. 17.2-22 now can be written in the form of Eq. D.6-3 or Eq. 1.1-8,

$$\boxed{\frac{\partial}{\partial t} \rho \boldsymbol{v} = -[\boldsymbol{\nabla} \cdot \rho \boldsymbol{v}\boldsymbol{v}] - [\boldsymbol{\nabla} \cdot \boldsymbol{\pi}] + n\bar{\boldsymbol{F}}^{(e)}} \tag{17.4-32}$$

where $\boldsymbol{\pi}$ is the *stress tensor*, which may be written as

$$\boxed{\boldsymbol{\pi} = \boldsymbol{\pi}^{(k)} + \boldsymbol{\pi}^{(e)} + \boldsymbol{\pi}^{(S)} + \boldsymbol{\pi}^{(D)}} \tag{17.4-33}$$

The four contributions to the stress tensor are those associated with the molecular motion, external forces, intramolecular potentials, and intermolecular potentials (see Fig. 17.4-1).

Finally let us write down the analogous results for the *equation of continuity for species* α (cf. Eq. 17.2-12)

$$\boxed{\frac{\partial}{\partial t} \rho_\alpha = -(\boldsymbol{\nabla} \cdot \rho_\alpha \boldsymbol{v}) - (\boldsymbol{\nabla} \cdot \boldsymbol{j}_\alpha)} \tag{17.4-34}$$

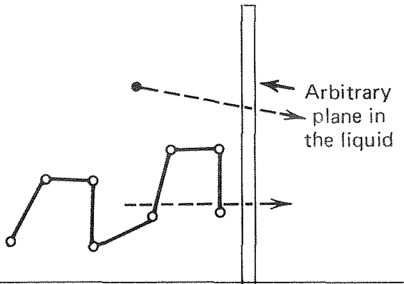
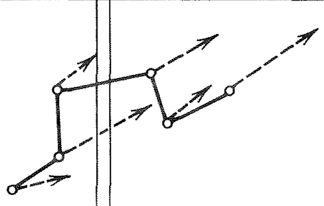
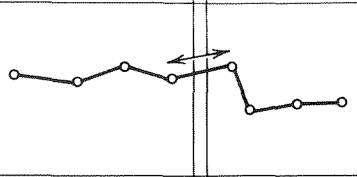
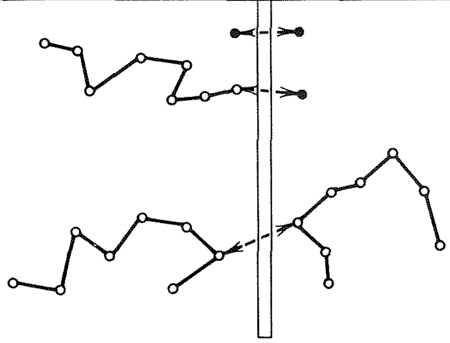
ntribution	Formal Expression	Pictorial Representation	Mechanism Involved
$\pi^{(k)}$	17.4-4		Momentum transport across plane by motion of solvent and polymer species (the "kinetic" contribution).
$\pi^{(e)}$	17.4-27		Force transmitted across plane because of the exertion of external forces on the solvent and polymer species (the "external force" contribution).
$\pi^{(S)}$	17.4-29		Force transmitted across plane by *intra*molecular forces in a polymer molecule straddling the plane (the "singlet" contribution).
$\pi^{(D)}$	17.4-31		Force transmitted across plane because of *inter*molecular forces between molecules of the same or different species (the "doublet" distribution).

FIGURE 17.4-1. Contributions to the stress tensor π in Eq. 17.4-33, pictured here for a liquid containing one solvent species and one polymer species.

in which the mass flux j_α is

$$j_\alpha = m_p \int \left[\frac{1}{m_p}\boldsymbol{p} - \boldsymbol{v}\right]^{\alpha} \Psi_\alpha(\boldsymbol{r}, Q, t)\,dQ$$
$$- \nabla \cdot \sum_\nu m_\nu \iint_0^1 \boldsymbol{R}_\nu \left[\frac{1}{m_p}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right]^{\alpha} \Psi_\alpha(\boldsymbol{r} - \xi \boldsymbol{R}_\nu, Q, t)\,d\xi\,dQ \qquad (17.4\text{-}35)$$

This result is obtained by applying the generalized Taylor theorem to Eq. 17.4-3. The first term in this expression may be interpreted as the product of the mass of a molecule and the difference between the average velocity of the center of mass and the stream velocity of the fluid. This is the principal term. The second term is a correction which arises from the finite extent of the molecules.

This completes the formal development of the equations of change for momentum and mass and the derivation of integral expressions for the fluxes π and j_α in terms of the contracted distribution functions.

§17.5 EQUATIONS OF CONTINUITY FOR CONFIGURATIONAL DISTRIBUTION FUNCTIONS

In the foregoing section, we developed integral expressions for the various contributions to the stress tensor that involve the low-order distribution functions. The next step is the development of methods for evaluating or approximating these functions. For this purpose we return to the general equation of change, Eq. 17.2-8, and take as the dynamical variable of interest,

$$B = \sum_i B_i \tag{17.5-1}$$

$$B_i = \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q)\delta(\boldsymbol{p}^{\alpha i} - \boldsymbol{p})\delta(P^{\alpha i} - P) \tag{17.5-2}$$

From the definition in Eq. 17.3-1, it is seen that the average of this dynamical variable is a singlet phase-space distribution function. Making use of the expression for the Liouville operator, Eq. 17.2-4, we then find that the general equation of change, Eq. 17.2-8 becomes for this special choice of the dynamical variable

$$\boxed{\begin{aligned} &\frac{\partial}{\partial t} f_\alpha + \left(\frac{1}{m^\alpha}\boldsymbol{p}\cdot\nabla f_\alpha\right) + \sum_{st} P_s \frac{\partial}{\partial Q_t}(G_{st} f_\alpha) + \left(\boldsymbol{F}^{(e)}\cdot\frac{\partial}{\partial \boldsymbol{p}} f_\alpha\right) \\ &\qquad + \left(\frac{\partial}{\partial \boldsymbol{p}}\cdot\left\langle\sum_i \boldsymbol{F}^{\alpha i} B_i\right\rangle\right) + \sum_s \frac{\partial}{\partial P_s}\left\langle\sum_i \mathscr{F}_s^{\alpha i} B_i\right\rangle = 0 \end{aligned}} \tag{17.5-3}$$

This is the *equation for the time evolution of* f_α. The first four terms on the left of this equation along with the portion of the last term arising from the external and intramolecular potentials would occur in the "one-molecule Liouville equation." Setting the sum of these terms equal to zero gives an equation that would describe the time evolution of the singlet distribution for molecules moving independently and not interacting with any other molecules. The remaining terms describe the effect of interactions with the other molecules of the system. If we assume that the intermolecular potential energy Φ is the sum of two-molecule terms as given by Eq. 17.4-12, then these interaction terms may be written in terms of the pair distribution functions. First, we find that the fifth term involves

$$\left\langle\sum_i \boldsymbol{F}^{\alpha i} B_i\right\rangle = \sum_\beta \int \boldsymbol{F}^{\alpha\beta} f_{\alpha\beta}(\boldsymbol{r}, Q, \boldsymbol{r}_\beta, Q_\beta, \boldsymbol{p}, P, \boldsymbol{p}_\beta, P_\beta, t)\,d\boldsymbol{r}_\beta\, dQ_\beta\, d\boldsymbol{p}_\beta\, dP_\beta \tag{17.5-4}$$

where $\boldsymbol{F}^{\alpha\beta}$, as defined by Eq. 17.4-15,, is the net force on a molecule of species α due to a molecule of species β.

In treating the last term in Eq. 17.5-3, we again, in a manner similar to the treatment of the source term in the equation of motion (see Eqs. 17.4-5 to 8), partition $\mathscr{F}_s^{\alpha i}$ into contributions due to the effects of external, intramolecular, and intermolecular forces. Thus we find from Eq. 17.1-24 that

$$\left\langle \sum_i \mathscr{F}_s^{\alpha i} B_i \right\rangle = (\mathscr{F}_s^{(e)} + \mathscr{F}_s^{(k)} + \mathscr{F}_s^{(\phi)}) f_\alpha + \sum_\beta \int \mathscr{F}_s^{\alpha\beta} f_{\alpha\beta}(r, Q, r_\beta, Q_\beta, p, P, p_\beta, P_\beta, t) dr_\beta \, dQ_\beta \, dp_\beta \, dP_\beta \tag{17.5-5}$$

where $\mathscr{F}_s^{\alpha\beta}$ is the generalized force defined by Eq. 17.4-16. These terms describe the effects of the various forces on the orientation and other internal coordinates of a molecule.

If the expressions given by Eqs. 17.5-4 and 5 are used in Eq. 17.5-3, we obtain an equation for the time evolution of the singlet distribution function. This equation, however, involves the pair distribution functions and hence cannot be solved without a knowledge of these functions. This type of problem is typical of statistical treatments of non-equilibrium systems, and a "truncation" scheme is usually resorted to in order to obtain a "closed" set of equations. In the present treatment three major approximations are introduced to accomplish this truncation. One of these is the "short range force" approximation which we use to reduce the problem to one in the phase space of a single molecule (see §18.1 and Eq. 18.1-4); the second is an approximation, resembling Stokes' law for the average force on a bead (see §18.2, Eq. 18.2-1, and §19.2, Eq. 19.1-4); and the third is an approximation concerning the momentum dependence of the singlet distribution function which leads to an expression for the "Brownian" forces and further reduces the problem to one in the configuration space of a single molecule (see §§18.3 and 19.2).

When the differential equation, Eq. 17.5-3, for the singlet phase-space distribution function is integrated over all of the momentum coordinates, we obtain the *equation of continuity for the configuration-space distribution function*

$$\frac{\partial}{\partial t} \Psi_\alpha + \frac{1}{m^\alpha} \nabla \cdot (\llbracket p \rrbracket^\alpha \Psi_\alpha) + \sum_s \sum_t \frac{\partial}{\partial Q_s} (G_{st} \llbracket P_t \rrbracket^\alpha \Psi_\alpha) = 0 \tag{17.5-6}$$

In doing the integration the terms involving the pair distribution function drop out.

Another set of equations may be obtained from Eq. 17.5-3 by first multiplying by P_s and then integrating over all the momenta. This procedure gives the *equations of motion for the internal coordinates of a polymer molecule*

$$\frac{\partial}{\partial t} (\llbracket P_s \rrbracket^\alpha \Psi_\alpha) + \frac{1}{m^\alpha} \nabla \cdot (\llbracket p P_s \rrbracket^\alpha \Psi_\alpha) = (\mathscr{F}_s^{(e)\alpha} + \mathscr{F}_s^{(\phi)\alpha} + \mathscr{F}_s^{(b)\alpha} + \mathscr{F}_s^{(h)\alpha}) \Psi_\alpha \tag{17.5-7}$$

where

$$\mathscr{F}_s^{(b)\alpha} = \llbracket \mathscr{F}_s^{(k)} \rrbracket^\alpha - \frac{1}{\Psi_\alpha} \sum_t \frac{\partial}{\partial Q_t} (\llbracket \dot{Q}_t P_s \rrbracket^\alpha \Psi_\alpha) \tag{17.5-8}$$

$$\mathscr{F}_s^{(h)\alpha} = \frac{1}{\Psi_\alpha} \sum_\beta \iint \mathscr{F}_s^{\alpha\beta} \Psi_{\alpha\beta}(r, Q, r_\beta, Q_\beta, t) \, dr_\beta \, dQ_\beta \tag{17.5-9}$$

TABLE 17.5-1

Generalized Forces

Symbol	Defining Equation	Expression	Symbol	Defining Equation	Expression
$\mathscr{F}_s^{(k)}$	17.1-20	—	$\mathscr{F}_s^{(b)}$	17.5-8	$[\![\mathscr{F}_s^{(k)}]\!]^\alpha + \cdots$
$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\frac{\partial}{\partial Q_s}\phi$	$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\frac{\partial}{\partial Q_s}\phi$
$\mathscr{F}_s^{(e)}$	17.1-22	$-\frac{\partial}{\partial Q_s}\phi^{(e)}$	$\mathscr{F}_s^{(e)}$	17.1-22	$-\frac{\partial}{\partial Q_s}\phi^{(e)}$
$\mathscr{F}_s^{(d)}$	17.1-23	$-\frac{\partial}{\partial Q_s}\Phi$	$\mathscr{F}_s^{(h)}$	17.5-9	$\frac{1}{\Psi_\alpha}\sum_\beta \iint \mathscr{F}_s^{\alpha\beta}\Psi_{\alpha\beta}d\boldsymbol{r}_\beta\, dQ_\beta$

The quantity $\mathscr{F}_s^{(b)\alpha}$ is a generalized force associated with Brownian forces, and $\mathscr{F}_s^{(h)\alpha}$ is related to the hydrodynamic forces. The generalized forces appearing in Eq. 17.5-7 are summarized in Table 17.5-1.

A similar set of equations associated with the motion of the center of mass of a molecule may be obtained by first multiplying Eq. 17.5-3 by $\boldsymbol{p}$ and integrating over the momenta. Before writing this equation, however, we define a force $\boldsymbol{F}^{(h)\alpha}$, which may be interpreted as the total hydrodynamic force on a molecule of species α, as

$$\boldsymbol{F}^{(h)\alpha} = \frac{1}{\bar{N}\Psi_\alpha}\sum_\beta \iint \boldsymbol{F}^{\alpha\beta}\Psi_{\alpha\beta}(\boldsymbol{r}, Q, \boldsymbol{r}_\beta, Q_\beta, t)d\boldsymbol{r}_\beta\, dQ_\beta \tag{17.5-10}$$

where

$$\bar{N} = \sum_\alpha x_\alpha N_\alpha \tag{17.5-11}$$

$$x_\alpha = \frac{n_\alpha}{\sum_\beta n_\beta} \tag{17.5-12}$$

In this definition we have introduced[1] the average number, $\bar{N}$, of beads per molecule (*including* the solvent, if any) in terms of the number of beads, N_α, making up a molecule of species α, and the mole fraction, x_α, of this species. With these definitions we find from Eq. 17.5-3 that the *equation of motion for the centers of mass of molecules of species* α is

$$\frac{\partial}{\partial t}([\![\boldsymbol{p}]\!]^\alpha\Psi_\alpha) + \frac{1}{m_p}\nabla\cdot([\![\boldsymbol{pp}]\!]^\alpha\Psi_\alpha) + \sum_{st}\frac{\partial}{\partial Q_t}(G_{st}[\![P_s\boldsymbol{p}]\!]^\alpha\Psi_\alpha) = (\boldsymbol{F}^{(e)\alpha} + \bar{N}\boldsymbol{F}^{(h)\alpha})\Psi_\alpha \tag{17.5-13}$$

---

[1] In later developments we approximate $\boldsymbol{F}^{(h)\alpha}$ by a Stokes' law type of expression involving a friction coefficient. It should be emphasized that the introduction of $\bar{N}$ at this point along with the physical interpretation of the friction coefficient leads directly to $D_{\text{tr}} \propto M^{-1/2}$ for the diffusion of a solute in a dilute solution with hydrodynamic interaction, $D_{\text{tr}} \propto M^{-1}$ for solutions with no hydrodynamic interaction, and $D_{\text{tr}} \propto M^{-2}$ for self diffusion in an undiluted polymer (see §§18.4 and 19.4). Note also that $\bar{N}$ is introduced in an analogous fashion in Eq. 18.1-8 for the hydrodynamic force $\boldsymbol{F}_\nu^{(h)\alpha}$ on a single bead ν, and this plays a crucial role in the description of the molecular-weight dependence of the rheological properties of polymer melts (see Example 19.6-1).

The equation of motion discussed in §17.2 results from integrating this equation over the configuration coordinates Q_s and summing the equations over the species index α.

Equations 17.5-6 (equation of continuity for Ψ_α), 17.5-7 (equation of internal motion), and 17.5-13 (equation of center-of-mass motion) are key equations in the kinetic theory. Up to this point these equations are free from assumptions, but somewhat too general for most purposes. We now show that the introduction of a small number of minor assumptions simplifies the equations considerably. It is these slightly less rigorous equations that we use in subsequent chapters; in addition they are written in forms reminiscent of the equations given in Chapters 13–16.

It is to be expected that the distribution function, f_α, varies slowly with the position variable, $\boldsymbol{r}$, and that this variation over distances of the order of molecular dimensions may be neglected. This approximation allows us to neglect the second term in the equation of continuity, Eq. 17.5-6, and write the *equation of continuity for* Ψ_α as

$$\boxed{\begin{aligned} \frac{\partial}{\partial t}\Psi_\alpha &= -\sum_{st}\frac{\partial}{\partial Q_s}\left(G_{st}[\![P_t]\!]^\alpha\Psi_\alpha\right) \\ &= -\sum_{s}\frac{\partial}{\partial Q_s}\left([\![\dot{Q}_s]\!]^\alpha\Psi_\alpha\right) \end{aligned}} \tag{17.5-14}$$

Once an expression is introduced for the momentum space averages, $[\![P_t]\!]^\alpha$ or $[\![\dot{Q}_s]\!]^\alpha$, this equation becomes the "diffusion" equation for the distribution function.

The terms on the left of the equation of motion, Eq. 17.5-7 may be interpreted as "acceleration terms" and those on the right as force terms. If we neglect the acceleration terms, as we have done in Chapters 13–16, then the equation of motion becomes a simple *generalized force balance*

$$\boxed{\mathscr{F}_s^{(e)\alpha} + \mathscr{F}_s^{(\phi)\alpha} + \mathscr{F}_s^{(b)\alpha} + \mathscr{F}_s^{(h)\alpha} = 0} \tag{17.5-15}$$

The first two terms are related to the external and intramolecular or "connector" forces and, as previously mentioned, $\mathscr{F}_s^{(b)\alpha}$ and $\mathscr{F}_s^{(h)\alpha}$ are related to the Brownian and hydrodynamic forces. The manner in which these generalized forces are related to those introduced in §17.1 in the discussion of the Liouville equation is summarized in Table 17.5-1.

Equation 17.5-13 may be written in a form analogous to Eq. 17.5-7,

$$\begin{aligned} m^\alpha\left[\frac{\partial}{\partial t}(\boldsymbol{v}\Psi_\alpha) + \nabla\cdot(\boldsymbol{v}\boldsymbol{v}\Psi_\alpha)\right] &+ \frac{\partial}{\partial t}\left([\![\boldsymbol{p} - m^\alpha\boldsymbol{v}]\!]^\alpha\Psi_\alpha\right) + \nabla\cdot\left(\boldsymbol{v}[\![\boldsymbol{p} - m^\alpha\boldsymbol{v}]\!]^\alpha\Psi_\alpha\right) \\ &+ \nabla\cdot\left([\![\boldsymbol{p} - m^\alpha\boldsymbol{v}]\!]^\alpha\boldsymbol{v}\Psi_\alpha\right) = \left(\bar{N}\boldsymbol{F}^{(h)\alpha} + \boldsymbol{F}^{(b)\alpha} + \boldsymbol{F}^{(e)\alpha}\right)\Psi_\alpha \end{aligned} \tag{17.5-16}$$

where

$$\boldsymbol{F}^{(b)\alpha} = -\frac{1}{m^\alpha\Psi_\alpha}\nabla\cdot\left([\![(\boldsymbol{p} - m^\alpha\boldsymbol{v})(\boldsymbol{p} - m^\alpha\boldsymbol{v})]\!]^\alpha\Psi_\alpha\right) - \frac{1}{\Psi_\alpha}\sum_{st}\frac{\partial}{\partial Q_s}\left(G_{st}[\![P_t\boldsymbol{p}]\!]^\alpha\Psi_\alpha\right) \tag{17.5-17}$$

is interpreted as the total Brownian force on a molecule. The first term on the left of Eq. 17.5-16 is an acceleration term which we neglect; if, in addition, we neglect those terms which contain the momentum-space average of the linear expression $(\boldsymbol{p} - m^\alpha \boldsymbol{v})$, then this equation also reduces to a *force balance*,

$$\boxed{\tilde{N}\boldsymbol{F}^{(h)\alpha} + \boldsymbol{F}^{(b)\alpha} + \boldsymbol{F}^{(e)\alpha} = \boldsymbol{0}} \tag{17.5-18}$$

involving the total forces on a molecule: the hydrodynamic force $\boldsymbol{F}^{(h)\alpha}$ (Eq. 17.5-10), the Brownian force $\boldsymbol{F}^{(b)\alpha}$ (17.5-17) and the external force $\boldsymbol{F}^{(e)\alpha}$ (Eq. 17.1-18). The neglect of the terms containing $\llbracket \boldsymbol{p} - m^\alpha \boldsymbol{v} \rrbracket^{(\alpha)}$ is possible if f_α is an even function of $\boldsymbol{p} - m^\alpha \boldsymbol{v}$, as is indeed true at equilibrium; the validity of this assumption away from equilibrium needs further investigation.

§17.6 SIMPLIFIED EXPRESSIONS FOR THE STRESS TENSOR AND THE MASS FLUX

Now that we have simplified the equations of continuity and motion, the next task is to introduce some minor simplifications in the expressions for the contributions to the stress tensor: $\boldsymbol{\pi}^{(k)}$, $\boldsymbol{\pi}^{(e)}$, $\boldsymbol{\pi}^{(S)}$, and $\boldsymbol{\pi}^{(D)}$. In the arguments of the distribution functions we make the following simplifications:

In Eq. 17.4-4:	replace $\boldsymbol{r} - \boldsymbol{R}_\nu$ by $\boldsymbol{r}$
In Eq. 17.4-27 and 29:	replace $\boldsymbol{r} - \xi \boldsymbol{R}_\nu$ by $\boldsymbol{r}$
In Eq. 17.4-31:	replace $\boldsymbol{r} - \xi \boldsymbol{R}_\nu + [m^\beta/(m^\alpha + m^\beta)]\xi \boldsymbol{R}$ by $\boldsymbol{r}$

These approximations correspond to expanding the distribution functions about r, using the generalized Taylor theorem in Eq. E.2-2, and neglecting all higher order terms, which would contain spatial gradients. From a molecular point of view this corresponds to neglecting the variation of Ψ_α and $\tilde{\Psi}_{\alpha\beta}$ over distances comparable to molecular dimensions.

When one makes the above assumptions, the stress tensor contributions can be simplified as follows:

$$\boldsymbol{\pi}^{(k)} = \sum_{\alpha\nu} m_\nu^\alpha \int \left\llbracket \left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right)\left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right)\right\rrbracket^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t)dQ \tag{17.6-1}$$

$$\boldsymbol{\pi}^{(e)} = \sum_{\alpha\nu} \int \boldsymbol{R}_\nu \mathscr{F}_\nu^{(e)\alpha} \Psi_\alpha(\boldsymbol{r}, Q, t)dQ \tag{17.6-2}$$

$$\boldsymbol{\pi}^{(S)} = \sum_{\alpha\nu} \int \boldsymbol{R}_\nu \llbracket \mathscr{F}_\nu^{(S)\alpha} \rrbracket^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t)\, dQ \tag{17.6-3}$$

$$\begin{aligned} \boldsymbol{\pi}^{(D)} = & -\tfrac{1}{2}\sum_{\alpha\beta} \iiint \boldsymbol{R}\boldsymbol{F}^{\alpha\beta}\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)dQ_\alpha\, dQ_\beta\, d\boldsymbol{R} \\ & + \sum_{\alpha\beta\nu st} \sqrt{m_\nu^\alpha} \iiint \mathscr{F}_s^{\alpha\beta} G_{st}^\alpha \boldsymbol{R}_\nu^\alpha \boldsymbol{b}_{\nu t}^\alpha \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)dQ_\alpha\, dQ_\beta\, d\boldsymbol{R} \end{aligned} \tag{17.6-4}$$

In the first term of the expression for $\boldsymbol{\pi}^{(D)}$, we have made use of the symmetry of the pair distribution function in a manner similar to that used in the discussion of $\boldsymbol{\pi}^{(D)}$ in §17.4 to replace the factor $m^{\beta}/(m^{\alpha} + m^{\beta})$ by simply $\frac{1}{2}$.

We now show how the above contributions can be combined with the result that some cancellations occur, and then a remarkably simple expression for the stress tensor emerges. In the development it is convenient to introduce the effective forces defined on the right side of Table 17.6-1; since the effective forces $\mathscr{F}_{\nu}^{(\cdots)}$ are all related to the generalized forces $\mathscr{F}_{s}^{(\cdots)}$ in the same way, their use should cause no confusion. We start by rewriting the kinetic contribution, Eq. 17.6-1, as the sum of two terms:

$$\boldsymbol{\pi}^{(k)} = \boldsymbol{\pi}_k + \sum_{\alpha\nu} m_{\nu}^{\alpha} \int [\![\dot{\boldsymbol{R}}_{\nu}\dot{\boldsymbol{R}}_{\nu}]\!]^{\alpha}\Psi_{\alpha}(\boldsymbol{r}, Q, t)dQ \tag{17.6-5}$$

$$\boldsymbol{\pi}_k = \sum_{\alpha} m^{\alpha} \int \left[\!\!\left[\left(\frac{1}{m^{\alpha}}\boldsymbol{p} - \boldsymbol{v}\right)\left(\frac{1}{m^{\alpha}}\boldsymbol{p} - \boldsymbol{v}\right)\right]\!\!\right]^{\alpha} \Psi_{\alpha}(\boldsymbol{r}, Q, t)dQ \tag{17.6-6}$$

The first term on the right side of Eq. 17.6-5 describes the effect of the Brownian motion of the centers of mass of the molecules and the second that due to the motion of the beads relative to center of mass of the molecule.

Next let us consider the term in the expression for $\boldsymbol{\pi}^{(S)}$, as given by Eq. 17.6-3, resulting from the last term in the expression for $\mathscr{F}_{\nu}^{(S)}$, Eq. 17.4-6. This term may be written by performing an integration by parts:

$$\begin{aligned}
&\sum_{\alpha\nu stu} \sqrt{m_{\nu}^{\alpha}} \int [\![\dot{Q}_u P_s]\!]^{\alpha}\boldsymbol{R}_{\nu}\left(\frac{\partial}{\partial Q_u} G_{st}^{\alpha}\, \boldsymbol{b}_{\nu t}^{\alpha}\right)\Psi_{\alpha}(\boldsymbol{r}, Q, t)dQ \\
&\quad = -\sum_{\alpha\nu stu} \sqrt{m_{\nu}^{\alpha}} \int \left\{\frac{\partial}{\partial Q_u} \boldsymbol{R}_{\nu}[\![\dot{Q}_u P_s]\!]^{\alpha}\Psi_{\alpha}(\boldsymbol{r}, Q, t)\right\}G_{st}^{\alpha}\boldsymbol{b}_{\nu t}^{\alpha}\, dQ \\
&\quad = -\sum_{\alpha\nu stu} \int \boldsymbol{b}_{\nu u}^{\alpha}\, [\![\dot{Q}_u P_s]\!]^{\alpha}\Psi_{\alpha}(\boldsymbol{r}, Q, t)G_{st}^{\alpha}\boldsymbol{b}_{\nu t}^{\alpha}\, dQ \\
&\qquad - \sum_{\alpha\nu stu} \sqrt{m_{\nu}^{\alpha}} \int \boldsymbol{R}_{\nu}\left\{\frac{\partial}{\partial Q_u}\, [\![\dot{Q}_u P_s]\!]^{\alpha}\Psi_{\alpha}(\boldsymbol{r}, Q, t)\right\}G_{st}^{\alpha}\boldsymbol{b}_{\nu t}^{\alpha}\, dQ
\end{aligned} \tag{17.6-7}$$

The term in the next to last line of the last equation differs from the second term in the expression for $\boldsymbol{\pi}^{(k)}$, Eq. 17.6-5, only in the sign and hence cancels this term. It is then convenient to combine the last term in Eq. 17.6-7 with $\boldsymbol{\pi}^{(S)}$ (as given by Eq. 17.6-3). This then gives for the sum of the two contributions to the stress tensor:

$$\boldsymbol{\pi}^{(k)} + \boldsymbol{\pi}^{(S)} = \boldsymbol{\pi}_k + \sum_{\alpha\nu} \int \boldsymbol{R}_{\nu}(\mathscr{F}_{\nu}^{(\phi)\alpha} + \mathscr{F}_{\nu}^{(b)\alpha})\Psi_{\alpha}(\boldsymbol{r}, Q, t)dQ \tag{17.6-8}$$

Next, one returns to Eq. 17.5-9, which defines $\mathscr{F}_{s}^{(h)\alpha}$, rewrites the integral in terms of $\tilde{\Psi}_{\alpha\beta}$ and approximates $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r} + \frac{1}{2}\boldsymbol{R}, \boldsymbol{R}, t)$ by $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, t)$. Then, in the second term in $\boldsymbol{\pi}^{(D)}$, as given in Eq. 17.6-4, $\tilde{\Psi}_{\alpha\beta}$ can be eliminated in favor of Ψ_{α} by means of Eq. 17.5-9; in the process $\mathscr{F}_{s}^{(h)\alpha}$

TABLE 17.6-1

Generalized and Effective Forces

Symbol	Defining Equation	Expression	Symbol	Defining Equation
$\mathscr{F}_s^{(b)}$	17.5-8	—	$\boldsymbol{\mathscr{F}}_\nu^{(b)}$	$\sqrt{m_\nu} \sum_{st} \mathscr{F}_s^{(b)} G_{st} \boldsymbol{b}_{\nu t}$
$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\dfrac{\partial}{\partial Q_s} \phi$	$\boldsymbol{\mathscr{F}}_\nu^{(\phi)}$	$\sqrt{m_\nu} \sum_{st} \mathscr{F}_s^{(\phi)} G_{st} \boldsymbol{b}_{\nu t}$
$\mathscr{F}_s^{(e)}$	17.1-22	$-\dfrac{\partial}{\partial Q_s} \phi^{(e)}$	$\boldsymbol{\mathscr{F}}_\nu^{(e)}$	$\sqrt{m_\nu} \sum_{st} \mathscr{F}_s^{(e)} G_{st} \boldsymbol{b}_{\nu t}$
$\mathscr{F}_s^{(h)}$	17.5-9	$\dfrac{1}{\Psi_\alpha} \sum_\beta \iint \mathscr{F}_s^{\alpha\beta} \Psi_{\alpha\beta}\, d\boldsymbol{r}_\beta\, dQ_\beta$	$\boldsymbol{\mathscr{F}}_\nu^{(h)}$	$\sqrt{m_\nu} \sum_{st} \mathscr{F}_s^{(h)} G_{st} \boldsymbol{b}_{\nu t}$

appears, and this scalar force can be expressed in terms of the vector force $\boldsymbol{\mathscr{F}}_\nu^{(h)\alpha}$ according to Table 17.6-1. These substitutions then enable us to rewrite the second term in $\boldsymbol{\pi}^{(D)}$ as

$$\sum_{\alpha\nu} \int \boldsymbol{R}_\nu \boldsymbol{\mathscr{F}}_\nu^{(h)\alpha} \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \tag{17.6-9}$$

This has the same form as the integrals in Eq. 17.6-2 and 8.

Finally we note that the generalized force balance in Eq. 17.5-15 can be written, using Table 17.6-1, as an effective force balance

$$\boxed{\boldsymbol{\mathscr{F}}_\nu^{(e)\alpha} + \boldsymbol{\mathscr{F}}_\nu^{(\phi)\alpha} + \boldsymbol{\mathscr{F}}_\nu^{(b)\alpha} + \boldsymbol{\mathscr{F}}_\nu^{(h)\alpha} = \boldsymbol{0}} \tag{17.6-10}$$

When we now add together the various contributions to the stress tensor (Eqs. 17.6-8, 17.6-2, 17.6-9, and the first term in Eq. 17.6-4) and use the force balance, we obtain the following extraordinarily simple expression for the stress tensor of a polymeric liquid:[1]

$$\boxed{\boldsymbol{\pi} = \boldsymbol{\pi}_k - \tfrac{1}{2} \sum_{\alpha\beta} \iiint \boldsymbol{R}\boldsymbol{F}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t) dQ_\alpha\, dQ_\beta\, d\boldsymbol{R}} \tag{17.6-11}$$

The first term, which is given by Eq. 17.6-6, is the kinetic contribution (i.e., the effect of the Brownian motion of the centers of mass of the molecules). The second term describes the effects of the net intermolecular forces between the centers of mass of the molecules. The evaluation of this term requires a knowledge of the pair distribution functions $\tilde{\Psi}_{\alpha\beta}$.

---

[1] This equation seems to be a generalization of Eq. 5.15 of J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 817–829 (1950); see also M. Fixman, *J. Chem. Phys.*, **42**, 3831–3837 (1965).

We conclude by pointing out that the mass flux $\boldsymbol{j}_\alpha$ can be simplified in a manner analogous to the treatment of the contributions to $\boldsymbol{\pi}$ in Eqs. 17.6-1 to 4. From Eq. 17.4-35 we obtain

$$\boxed{\boldsymbol{j}_\alpha = m_p \int \left[\!\!\left[\frac{1}{m_p}\boldsymbol{p} - \boldsymbol{v} \right]\!\!\right]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t)dQ - \nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t)dQ} \tag{17.6-12}$$

It is shown in the next two chapters that the first term is the principal contribution, linear in the concentration gradient and the external force.

PROBLEMS

17B.1 Effective Forces in Models with No Constraints

Show that for a molecular model with no constraints each of the effective forces listed in Table 17.4-1 is the negative of the derivative of a potential (that is, a *true* force).

17B.2 Metric Matrix of a Special Two-Needle Model

Show that the metric matrix, g_{st}, of the "two-needle" molecular model described in Example 17.1-1 with $\omega = \frac{2}{3}$ is identical to the metric matrix of the three-bead, two-rod model described in Example 12.1-1, if the needles are idealized as mass points separated by massless rods.

17C.1 Three-Bead Models

Develop explicit expressions for each of the forces listed in Table 17.4-1 for the two related molecular models: (a) the three-bead, two-spring model (see Example 12.1-2) and (b) the three-bead, two-rod model (see Example 12.1-1).

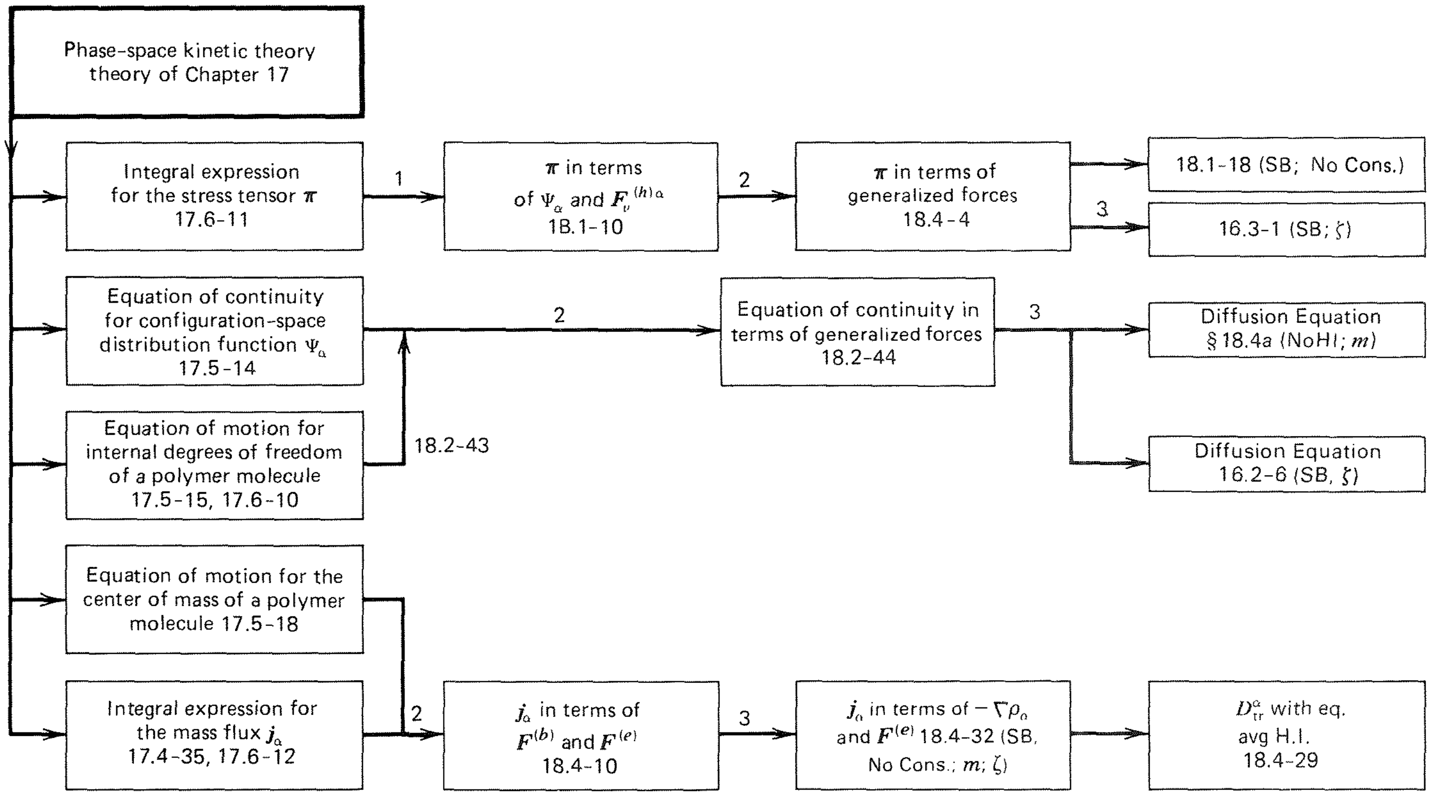
CHAPTER 18

PHASE-SPACE THEORY FOR DILUTE SOLUTIONS

In the foregoing chapter we obtained the five major results listed at the left of Fig. 18.0-1. These key equations, which are all obtained from a common source (the general equation of change), contain only the minor assumptions listed in the opening paragraph of Chapter 17. However, in order to evaluate various quantities appearing in these general results we would have to know not only the configurational distribution function Ψ_α for a single molecule, but also the pair distribution function $\Psi_{\alpha\beta}$ and the single-molecule phase-space distribution function f_α (needed for the calculation of the $[\![\quad]\!]$-averages). If we can avoid the necessity of obtaining $\Psi_{\alpha\beta}$ and f_α, considerable simplification ensues, and the theoretical results are more easily applied. This chapter is devoted primarily to the introduction of three major approximations, which we believe to be appropriate for dilute polymer solutions, that do indeed eliminate $\Psi_{\alpha\beta}$ and f_α from further consideration. These approximations are:

1. The *short-range force approximation*, which states that the only non-negligible contributions from the *inter*molecular forces are those occuring when "beads" belonging to two different molecules are in very close proximity. We feel that this approximation is quite reasonable.
2. The *Stokes' law empiricism* for the hydrodynamic drag on a bead (or some modification of this linear relation between the drag force and the bead velocity); this assumption may be less defensible but, as we have seen in Chapters 13–16, it has been used in all of the theories discussed so far. The version of Stokes' law introduced here includes the possibility of a tensor friction coefficient.
3. The *equilibration-in-momentum-space approximation*, which has also been used in the earlier developments and which leads to the standard results for the terms ascribed to Brownian motion; very little has been done to explore deviations from the Maxwellian velocity distribution.

These three major approximations are discussed in the above order in §§18.1, 2, and 3 respectively; their roles in the theoretical developments are made clear in Fig. 18.0-1. In the treatment of undiluted polymers discussed in Chapter 19 the short-range force approximation as discussed in this chapter is used, but a different form of the Stokes' law empiricism is introduced (see §19.1) and the assumption of equilibration-in-momentum-space is replaced by an approximation describing "reptation" (see §19.2).


Phase-space kinetic theory theory of Chapter 17
Integral expression for the stress tensor $\boldsymbol{\pi}$ 17.6-11
1
$\boldsymbol{\pi}$ in terms of Ψ_α and $\boldsymbol{F}_\nu^{(h)\alpha}$ 1B.1-10
2
$\boldsymbol{\pi}$ in terms of generalized forces 18.4-4
18.1-18 (SB; No Cons.)
3
16.3-1 (SB; ζ)
Equation of continuity for configuration-space distribution function Ψ_α 17.5-14
2
Equation of continuity in terms of generalized forces 18.2-44
3
Diffusion Equation §18.4a (NoHI; m)
Diffusion Equation 16.2-6 (SB, ζ)
Equation of motion for internal degrees of freedom of a polymer molecule 17.5-15, 17.6-10
18.2-43
Equation of motion for the center of mass of a polymer molecule 17.5-18
Integral expression for the mass flux $\boldsymbol{j}_\alpha$ 17.4-35, 17.6-12
2
$\boldsymbol{j}_\alpha$ in terms of $\boldsymbol{F}^{(b)}$ and $\boldsymbol{F}^{(e)}$ 18.4-10
3
$\boldsymbol{j}_\alpha$ in terms of $-\nabla\rho_\alpha$ and $\boldsymbol{F}^{(e)}$ 18.4-32 (SB, No Cons.; m; ζ)
D_{tr}^{α} with eq. avg H.I. 18.4-29

The first three sections of this chapter are written in such a way that a variety of physical ideas are included:

Hydrodynamic interaction.
Finite beads.
Constraints.
External forces.
Non-isotropic friction tensors in the Stokes' law relation.
Beads with different masses and friction tensors.

This means that the results given in §§18.1-3 can provide the description of a variety of different "models" of polymeric fluids. We have in these equations the starting point for studying the effects of hydrodynamic interaction or anisotropic Brownian motion; bead-spring models with no constraints or bead-rod models with constraints; models with structureless beads or models with finite beads; models with all beads alike or with beads that may have different masses and friction coefficients. Many of the models that can be generated have yet to be explored.

In the last section of this chapter, §18.4, we summarize certain key results for the kinetic theory of dilute solutions: the diffusion equation for Ψ_α; the stress tensor π; and the mass flux j_α and the translational diffusivity $D^\alpha_{\rm tr}$. We also point out connections with Chapter 16 and other earlier chapters.

§18.1 THE SHORT-RANGE FORCE APPROXIMATION

The first major approximation of the development is made as a first step towards eliminating the need for the pair distribution function and thereby reduces the problem to one in the phase space of a single molecule. For this purpose we first assume that the potential energy of a pair of molecules is the sum of the potential energies associated with pairs of beads on different molecules

$$\Phi^{\alpha\beta} = \sum_\nu \sum_\mu \Phi^{\alpha\beta}_{\nu\mu} \tag{18.1-1}$$

Then the force between the centers of mass, introduced in Eq. 17.4-15, is a similar sum

$$\boldsymbol{F}^{\alpha\beta} = \sum_\nu \sum_\mu \boldsymbol{F}^{\alpha\beta}_{\nu\mu} \tag{18.1-2}$$

FIGURE 18.0-1. "Flow chart" for Chapter 18 showing how the key results are obtained from Chapter 17.

MAJOR APPROXIMATIONS

1. Short-range force approximation
2. Modified Stokes' law empiricism
3. Equilibration in momentum space approximation

SIMPLIFICATION OF MODEL

NoHI – no hydrodynamic interaction
No Cons. – no constraints
SB – structureless beads
ζ – scalar friction coefficient
m – all beads have same mass

where

$$F^{\alpha\beta}_{\nu\mu} = -\frac{\partial}{\partial r^{\alpha}}\Phi^{\alpha\beta}_{\nu\mu} \tag{18.1-3}$$

is the contribution to the force on the center of mass of a molecule of species α due to the force on bead ν arising from bead μ on a molecule of species β. This force depends on the vector between the centers of mass of the two beads $\alpha\nu$ and $\beta\mu$ as well as any additional coordinates that may be required to specify the orientation of the finite beads.

According to the *short-range force approximation* the force $F^{\alpha\beta}_{\nu\mu}$ is small unless the beads ν (of molecule α) and μ (of molecule β) are very close to one another (see Fig. 18.1-1). Thus, as an approximation in the integral of the second term of the expression for the stress tensor π (Eq. 17.6-11), we can say that $F^{\alpha\beta}_{\nu\mu}$ is zero unless

$$\boldsymbol{R} = \boldsymbol{R}^{\alpha}_{\nu} - \boldsymbol{R}^{\beta}_{\mu} \tag{18.1-4}$$

so that

$$\pi = \pi_k - \tfrac{1}{2}\sum_{\alpha\beta\nu\mu}\iiint(\boldsymbol{R}^{\alpha}_{\nu} - \boldsymbol{R}^{\beta}_{\mu})\boldsymbol{F}^{\alpha\beta}_{\nu\mu}\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_{\alpha}, Q_{\beta}, t)\,dQ_{\alpha}\,dQ_{\beta}\,d\boldsymbol{R} \tag{18.1-5}$$

It then follows from the symmetry of the pair distribution function (§17.3) that

$$\pi = \pi_k - \sum_{\alpha\beta\nu}\iiint \boldsymbol{R}^{\alpha}_{\nu}\boldsymbol{F}^{\alpha\beta}_{\nu}\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_{\alpha}, Q_{\beta}, t)\,dQ_{\alpha}\,dQ_{\beta}\,d\boldsymbol{R} \tag{18.1-6}$$

where

$$\boldsymbol{F}^{\alpha\beta}_{\nu} = \sum_{\mu}\boldsymbol{F}^{\alpha\beta}_{\nu\mu} \tag{18.1-7}$$

is the force on the center of mass of a molecule of species α due to forces on bead ν arising from interactions with a molecule of species, β.

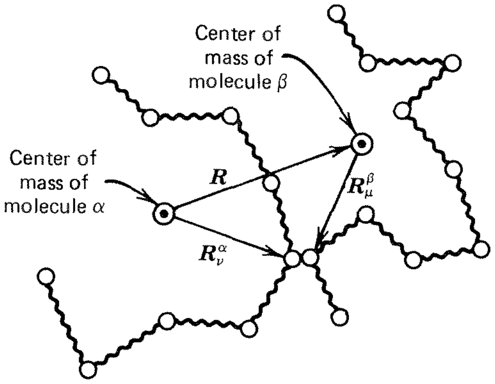


FIGURE 18.1-1. Bead ν of molecule α and bead μ of molecule β are located at the same point in space, so that $\boldsymbol{R} = \boldsymbol{R}^{\alpha}_{\nu} - \boldsymbol{R}^{\beta}_{\mu}$.

Next, by analogy with the definition of $\boldsymbol{F}^{(h)\alpha}$ given in Eq. 17.5-10 we define the hydrodynamic force on bead ν of molecule α by

$$\boldsymbol{F}_\nu^{(h)\alpha} = \frac{1}{\bar{N}\Psi_\alpha} \sum_\beta \iint \boldsymbol{F}_\nu^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)dQ_\beta\, d\boldsymbol{R} \tag{18.1-8}$$

in which $\bar{N} = \sum x_\alpha N_\alpha$ is the average number of beads per molecule in the mixture with mole fractions x_α (Eq. 17.5-11). From this definition and Eqs. 18.1-2 and 7, it follows that the total hydrodynamic force on a molecule is:

$$\boldsymbol{F}^{(h)\alpha} = \sum_\nu \boldsymbol{F}_\nu^{(h)\alpha} \tag{18.1-9}$$

The definitions of hydrodynamic forces are summarized in Table 18.1-1.

With the definition of $\boldsymbol{F}_\nu^{(h)\alpha}$ above we can rewrite the expression for the stress tensor, Eq. 18.1-6, as:

$$\boxed{\boldsymbol{\pi} = \boldsymbol{\pi}_k - \bar{N} \sum_{\alpha\nu} \int \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} \Psi_\alpha(\boldsymbol{r}, Q, t)dQ} \tag{18.1-10}$$

where $\boldsymbol{\pi}_k$ is given by Eq. 17.6-6. In this form the single-molecule distribution function Ψ_α appears explicitly. Of course, the pair distribution function $\tilde{\Psi}_{\alpha\beta}$ is contained in the definition of $\boldsymbol{F}_\nu^{(h)\alpha}$; however, in the next section, after we introduce an empirical expression for $\boldsymbol{F}_\nu^{(h)\alpha}$, the pair distribution function no longer appears in any of the working equations. In addition we point out that Eq. 18.1-10 is a generalization of Eqs. 13.3-16 (elastic dumbbells) and 15.2-2 (bead-spring chains).

TABLE 18.1-1

Hydrodynamic Forces

Symbol	Defining Equation	Expression	Symbol	Defining Equation	Expression
$\mathscr{F}_s^{\alpha\beta}$	17.4-16	$-\frac{\partial}{\partial Q_s^\alpha} \Phi^{\alpha\beta}$	$\mathscr{F}_s^{(h)\alpha}$	17.5-9	$\frac{1}{\Psi_\alpha} \sum_\beta \iint \mathscr{F}_s^{\alpha\beta} \Psi_{\alpha\beta}\, d\boldsymbol{r}_\beta\, d$
$\mathscr{F}_\nu^{\alpha\beta} - \frac{m_\nu^\alpha}{m^\alpha} \boldsymbol{F}^{\alpha\beta}$	17.4-14	$\sqrt{m_\nu^\alpha} \sum_s \sum_t \mathscr{F}_s^{\alpha\beta} G_{st}^\alpha \boldsymbol{b}_{\nu t}^\alpha$	$\mathscr{F}_\nu^{(h)\alpha}$	See Table 17.6-1	$\sqrt{m_\nu^\alpha} \sum_s \sum_t \mathscr{F}_s^{(h)\alpha} G_{st}^\alpha \boldsymbol{b}_\nu^\alpha$
$\boldsymbol{F}_\nu^{\alpha\beta}$	18.1-3 18.1-7	$\sum_\mu \left(-\frac{\partial}{\partial \boldsymbol{r}^\alpha} \Phi_{\nu\mu}^{\alpha\beta} \right)$ $= \sum_\mu \boldsymbol{F}_{\nu\mu}^{\alpha\beta}$	$\boldsymbol{F}_\nu^{(h)\alpha}$	18.1-8	$\frac{1}{\bar{N}\Psi_\alpha} \sum_\beta \iint \boldsymbol{F}_\nu^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}\, dQ_\beta$
$\boldsymbol{F}^{\alpha\beta}$	17.4-15	$-\frac{\partial}{\partial \boldsymbol{r}^\alpha} \Phi^{\alpha\beta} = \sum_\nu \boldsymbol{F}_\nu^{\alpha\beta}$	$\boldsymbol{F}^{(h)\alpha}$	17.5-10	$\sum_\nu \boldsymbol{F}_\nu^{(h)\alpha}$

We conclude this section by developing formulas for the generalized and effective forces that are needed in subsequent developments. The hydrodynamic force $\boldsymbol{F}_\nu^{(h)\alpha}$ can be related to the generalized hydrodynamic force $\mathscr{F}_s^{(h)\alpha}$ of Eq. 17.5-9. To show this, we return to the definition of $\mathscr{F}_s^{\alpha\beta}$ in Eq. 17.4-16 and introduce the restriction to pairwise additive forces between beads, Eq. 18.1-1. We then find that

$$\begin{aligned}\mathscr{F}_s^{\alpha\beta} &= -\sum_\nu\sum_\mu \frac{\partial}{\partial Q_s^\alpha}\Phi_{\nu\mu}^{\alpha\beta}\\ &= \sum_\nu\sum_\mu \frac{1}{\sqrt{m_\nu^\alpha}}(\boldsymbol{b}_{\nu s}^\alpha\cdot\boldsymbol{F}_{\nu\mu}^{\alpha\beta}) + \sum_{\nu\mu\sigma} b_{\nu\sigma s}T_{\nu\mu,\sigma}^{\alpha\beta}\end{aligned} \tag{18.1-11}$$

where

$$T_{\nu\mu,\sigma}^{\alpha\beta} = -\frac{\partial}{\partial q_{\nu\sigma}^\alpha}\Phi_{\nu\mu}^{\alpha\beta} \tag{18.1-12}$$

The second term is associated with the effects of the orientation coordinates of a finite bead. If this expression is used in the definition of the generalized hydrodynamic force, Eq. 17.5-9, one finds that

$$\mathscr{F}_s^{(h)} = \bar{N}\sum_\nu \frac{1}{\sqrt{m_\nu}}(\boldsymbol{b}_{\nu s}\cdot\boldsymbol{F}_\nu^{(h)}) + \bar{N}\sum_{\nu\sigma} b_{\nu\sigma s}T_{\nu\sigma}^{(h)} \tag{18.1-13}$$

where

$$T_{\nu\sigma}^{(h)\alpha} = \frac{1}{\bar{N}\Psi_\alpha}\sum_{\beta\mu}\iint T_{\nu\mu,\sigma}^{\alpha\beta}\,\Psi_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)\,dQ_\beta\,d\boldsymbol{R} \tag{18.1-14}$$

One then finds from Table 17.6-1 that the effective hydrodynamic force is

$$\mathscr{F}_\nu^{(h)} = \bar{N}\sqrt{m_\nu}\sum_{st\mu} G_{st}\boldsymbol{b}_{\nu t}\left[\frac{1}{\sqrt{m_\mu}}(\boldsymbol{b}_{\mu s}\cdot\boldsymbol{F}_\mu^{(h)}) + \sum_\sigma b_{\mu\sigma s}T_{\mu\sigma}^{(h)}\right] \tag{18.1-15}$$

Only in special situations however, is it possible—even in principle—to solve this set of equations and express the $\boldsymbol{F}_\mu^{(h)}$ in terms of the $\mathscr{F}_\nu^{(h)}$; the following example illustrates this point. Note that Eqs. 18.1-13 and 15, simplified for structureless beads, appear in Eq. A of Table 16.1-3.

EXAMPLE 18.1-1 The Stress Tensor for Models with Structureless Beads and No Constraints

If the molecular model is made up of beads which are mass points, and if there are no constraints in the model, Eq. 18.1-15 may be solved for the hydrodynamic forces, $\boldsymbol{F}_\mu^{(h)}$. Obtain this solution and use it to obtain an alternative expression for the stress tensor applicable to this restricted molecular model.

SOLUTION For structureless beads $T_{\mu\sigma}^{(h)} = 0$, and for models with no constraints Eq. 12D.3-5 applies. This enables us to simplify Eq. 18.1-15 to

$$\boldsymbol{F}_\nu^{(h)} = \frac{m_\nu}{m_p}\boldsymbol{F}^{(h)} + \frac{1}{N}\boldsymbol{\mathscr{F}}_\nu^{(h)} \tag{18.1-16}$$

One then finds from Eq. 18.1-10 that

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k - \sum_{\alpha\nu}\int \boldsymbol{R}_\nu \boldsymbol{\mathscr{F}}_\nu^{(h)\alpha}\Psi_\alpha(\boldsymbol{r}, Q, t)dQ \tag{18.1-17}$$

It then follows from the force balance, Eq. 17.6-10, that

$$\begin{aligned}\boldsymbol{\pi} &= \boldsymbol{\pi}_k + \sum_{\alpha\nu}\int \boldsymbol{R}_\nu(\boldsymbol{\mathscr{F}}_\nu^{(e)\alpha} + \boldsymbol{\mathscr{F}}_\nu^{(\phi)\alpha} + \boldsymbol{\mathscr{F}}_\nu^{(b)\alpha})\Psi_\alpha(\boldsymbol{r}, Q, t)dQ \\ &= \boldsymbol{\pi}_k + \sum_{\alpha\nu}\int \boldsymbol{R}_\nu\,(\boldsymbol{F}_\nu^{(e)\alpha} + \boldsymbol{F}_\nu^{(\phi)\alpha} + \boldsymbol{F}_\nu^{(b)\alpha})\Psi_\alpha(\boldsymbol{r}, Q, t)dQ\end{aligned} \tag{18.1-18}$$

This result should be compared with Eqs. 16.3-16, 15.2-1, and 13.3-14. In §18.4 we obtain a generalization of this result for less restricted models (see Eq. 18.4-4).

§18.2 MODIFIED STOKES' LAW EMPIRICISMS FOR THE HYDRODYNAMIC FORCES

We begin this section with the introduction of the second major approximation in the development—an approximation which resembles Stokes' law for the force on a sphere moving through a fluid (see Example 1.4-1). We follow the tradition of the older kinetic theories and assume that the hydrodynamic force $\boldsymbol{F}_\nu^{(h)\alpha}$ on bead ν depends linearly on the difference between the statistically averaged velocity of the bead, $[\![\dot{\boldsymbol{r}}_\nu^\alpha]\!]^\alpha$, and the local velocity of the continuum background at the position of the bead, $\boldsymbol{v}(\boldsymbol{r}_\nu^\alpha) + \boldsymbol{v}'(\boldsymbol{r}_\nu^\alpha)$; here $\boldsymbol{v}$ is the mass-averaged velocity imposed on the fluid mixture by external forces and bounding surfaces, and $\boldsymbol{v}'$ is the perturbation of this velocity field by hydrodynamic interaction (if it is desired to include this effect in dilute solution modeling). In writing this linear relation we allow the coefficient of proportionality to be a tensor, $\boldsymbol{\zeta}_\nu^\alpha$, which we call the *friction tensor*, and it may be different for different beads; a non-isotropic tensor coefficient is particularly appropriate when finite, nonspherical beads are used in the modeling. Hence we write:

$$\boxed{\boldsymbol{F}_\nu^{(h)\alpha} = -\boldsymbol{\zeta}_\nu^\alpha\cdot[[\![\dot{\boldsymbol{r}}_\nu^\alpha]\!]^\alpha - \boldsymbol{v}(\boldsymbol{r}_\nu^\alpha) - \boldsymbol{v}'(\boldsymbol{r}_\nu^\alpha)]} \tag{18.2-1}$$

Whereas Stokes' law in classical fluid-dynamics is derived from the creeping flow equations of motion for a sphere moving at constant velocity through a quiescent Newtonian fluid, Eq. 18.2-1 is set forth as an empirical conjecture to describe the resistance encountered by a portion of a macromolecule as it moves about in an irregular way among the various solvent and solute molecules in the liquid. Note that Eq. 18.2-1 is the same as Eq. 13.2-2.

In dilute solutions it is customary to account for hydrodynamic interactions as we have done earlier (see §§13.6, 14.6, 15.4, and 16.1) by writing

$$\boldsymbol{v}'(\boldsymbol{r}_\nu^\alpha) = -\sum_\mu[\boldsymbol{\Omega}_{\nu\mu}^\alpha\cdot\boldsymbol{F}_\mu^{(h)\alpha}] \tag{18.2-2}$$

in terms of the matrix of *hydrodynamic interaction tensors* $\mathbf{\Omega}^{\alpha}_{\nu\mu}$; the quantity $\boldsymbol{v}'(\boldsymbol{r}^{\alpha}_{\nu})$ describes the perturbation of the velocity field due to the motion of the other beads of the same molecule. In dilute solutions hydrodynamic interaction involving beads on other molecules is neglected. We do not specify, here, the form of $\mathbf{\Omega}^{\alpha}_{\nu\mu}$, but point out that the Oseen-Burgers and Rotne–Prager–Yamakawa expressions have been used in earlier chapters (see §§13.6, 14.6, 15.4).

The velocity $\boldsymbol{v}(\boldsymbol{r}^{\alpha}_{\nu})$ appearing in Eq. 18.2-1 may be expanded in a Taylor series about the center of mass. If we keep only the first two terms we get:

$$\boldsymbol{v}(\boldsymbol{r}^{\alpha}_{\nu}) = \boldsymbol{v}(\boldsymbol{r}^{\alpha}) + [\boldsymbol{\kappa} \cdot \boldsymbol{R}^{\alpha}_{\nu}] \tag{18.2-3}$$

where $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^{\dagger}$ is the transpose of the velocity gradient evaluated at the center of mass of the molecule of species α. The use of Eq. 18.2-3 is the same as the restriction to *homogeneous flow*, which was used throughout Chapters 13–16.

The main task of this section is to use Eq. 18.2-1 to obtain an expression for $[\![\dot{Q}^{\alpha}_{s}]\!]$ (Eq. 18.2-43) that can be substituted into Eq. 17.5-14 to obtain the diffusion equation, Eq. 18.2-44. The derivation is rather long and tedious, because we wish to retain the capability of including hydrodynamic interaction (using Eq. 18.2-2), and/or a tensorial friction coefficient ($\boldsymbol{\zeta}^{\alpha}_{\nu}$ in Eq. 18.2-1), and/or different friction coefficients for each bead. Before embarking on the derivation, it is useful to define some additional tensors, closely related to those used in §15.4 and §16.1.

As in §15.4 we use the matrix of tensors $\mathbf{\Upsilon}_{\nu\mu}$, which we call the *dimensionless diffusion tensors*[1]

$$\mathbf{\Upsilon}_{\nu\mu} = \delta_{\nu\mu}\boldsymbol{\delta} + \{\boldsymbol{\zeta}_{\nu} \cdot \mathbf{\Omega}_{\nu\mu}\} \tag{18.2-4}$$

Next, we define[2] the matrix of *dimensionless mobility tensors* $\mathbf{B}_{\nu\mu}$ by

$$\sum_{\mu} \{\mathbf{B}_{\nu\mu} \cdot \mathbf{\Upsilon}_{\mu\eta}\} = \delta_{\nu\eta}\boldsymbol{\delta} \tag{18.2-5}$$

and the matrix of *effective friction tensors* $\boldsymbol{\zeta}_{\nu\mu}$ by

$$\boldsymbol{\zeta}_{\nu\mu} = \{\mathbf{B}_{\nu\mu} \cdot \boldsymbol{\zeta}_{\mu}\} \tag{18.2-6}$$

Finally we define a set of *weight tensors* $\boldsymbol{\lambda}_{\nu}$ (a generalization of the l_{ν} of §15.4) by

$$\boldsymbol{\lambda}_{\nu} = \{\mathbf{Z}^{-1} \cdot \sum_{\mu} \boldsymbol{\zeta}_{\mu\nu}\} \tag{18.2-7}$$

where $\mathbf{Z}^{-1}$ is the tensor inverse to the *total effective friction tensor*

$$\mathbf{Z} = \sum_{\nu} \sum_{\mu} \boldsymbol{\zeta}_{\mu\nu} \tag{18.2-8}$$

The definition of the $\boldsymbol{\lambda}_{\nu}$ insures that $\sum_{\nu} \boldsymbol{\lambda}_{\nu} = \boldsymbol{\delta}$. These tensors are encountered again in the discussion of translational diffusion in §18.4.

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[1] These tensors are closely related to the *diffusion tensors* used by J. G. Kirkwood [*Rec. Trav. Chim.*, **68**, 649–660 (1949), Eq. 14]; see also J. J. Erpenbeck and J. G. Kirkwood, *J. Chem. Phys.*, **38**, 1023–1024 (1963).

[2] See Problem 18B.1 for a proof that this may be done.

It is convenient to require that the friction tensors be symmetric

$$\boldsymbol{\zeta}_\nu^\dagger = \boldsymbol{\zeta}_\nu \tag{18.2-9}$$

and to take the hydrodynamic interaction tensors to have the related property that

$$\boldsymbol{\Omega}_{\nu\mu}^\dagger = \boldsymbol{\Omega}_{\mu\nu} \tag{18.2-10}$$

The Oseen-Burgers tensors (Eq. 15.4-3) and the Rotne-Prager-Yamakawa tensors (Eq. 14.6-2) both have this property. With these restrictions it may be shown that

$$\boldsymbol{\zeta}_{\nu\mu}^\dagger = \boldsymbol{\zeta}_{\mu\nu} \tag{18.2-11}$$

It may further be shown from Eqs. 18.2-7 and 8 that

$$\mathbf{Z}^\dagger = \mathbf{Z} \tag{18.2-12}$$

$$\boldsymbol{\lambda}_\nu^\dagger = \left(\sum_\mu \boldsymbol{\zeta}_{\nu\mu}\right)\cdot\mathbf{Z}^{-1} \tag{18.2-13}$$

These relations, which follow from the assumed symmetry of $\boldsymbol{\zeta}_\nu$, lead to considerable simplification of a number of the relations developed in this section.

When the expressions for $\boldsymbol{v}$ and $\boldsymbol{v}'$ (Eqs. 18.2-2 and 3) are inserted into Eq. 18.2-1, and when the hydrodynamic force terms are all collected together on the left side, this equation becomes

$$\sum_\mu \{\boldsymbol{\Upsilon}_{\nu\mu}\cdot\boldsymbol{F}_\mu^{(h)}\} = -\boldsymbol{\zeta}_\nu\cdot[\llbracket\dot{\boldsymbol{r}}_c\rrbracket - \boldsymbol{v}(\boldsymbol{r}_c) + \llbracket\dot{\boldsymbol{R}}_\nu\rrbracket - \boldsymbol{\kappa}\cdot\boldsymbol{R}_\nu] \tag{18.2-14}$$

Then with the definitions of the dimensionless mobility tensors and the effective friction tensors, Eq. 18.2-14 can be solved for the hydrodynamic force on bead ν:

$$\boldsymbol{F}_\nu^{(h)} = -\sum_\mu \boldsymbol{\zeta}_{\nu\mu}\cdot[\llbracket\dot{\boldsymbol{r}}_c\rrbracket - \boldsymbol{v}(\boldsymbol{r}_c) + \llbracket\dot{\boldsymbol{R}}_\mu\rrbracket - \boldsymbol{\kappa}\cdot\boldsymbol{R}_\mu] \tag{18.2-15}$$

Therefore the total hydrodynamic force on a molecule, $\boldsymbol{F}^{(h)} = \sum_\nu \boldsymbol{F}_\nu^{(h)}$, is

$$\boldsymbol{F}^{(h)} = -\mathbf{Z}\cdot[\llbracket\dot{\boldsymbol{r}}_c\rrbracket - \boldsymbol{v}(\boldsymbol{r}_c) + \sum_\nu \boldsymbol{\lambda}_\nu\cdot[\llbracket\dot{\boldsymbol{R}}_\nu\rrbracket - \boldsymbol{\kappa}\cdot\boldsymbol{R}_\nu]] \tag{18.2-16}$$

We can now use the force balance in Eq. 17.5-18 and solve for the "drift velocity" $\llbracket\dot{\boldsymbol{r}}_c\rrbracket - \boldsymbol{v}(\boldsymbol{r}_c)$ to get

$$\llbracket\dot{\boldsymbol{r}}_c\rrbracket - \boldsymbol{v}(\boldsymbol{r}_c) = \frac{1}{N}[\mathbf{Z}^{-1}\cdot(\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] - \sum_\nu [\boldsymbol{\lambda}_\nu\cdot(\llbracket\dot{\boldsymbol{R}}_\nu\rrbracket - [\boldsymbol{\kappa}\cdot\boldsymbol{R}_\nu])] \tag{18.2-17}$$

where $\boldsymbol{F}^{(b)}$ is the total Brownian force on a molecule, given by Eq. 17.5-17. This equation may be rearranged into the form

$$\sum_\nu [\boldsymbol{\lambda}_\nu\cdot\llbracket\dot{\boldsymbol{r}}_\nu\rrbracket] - \boldsymbol{v}(\boldsymbol{r}_c) + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_c] - \sum_\nu [\boldsymbol{\lambda}_\nu\cdot\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu] = \frac{1}{N}[\mathbf{Z}^{-1}\cdot(\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] \tag{18.2-18}$$

In this form the equation may be compared with Eq. 15.4-16. If there are no concentration gradients, so that the total Brownian force $\boldsymbol{F}^{(b)}$ is zero, and if the total external force $\boldsymbol{F}^{(e)}$ is zero, then the right side of Eq. 18.2-18 is zero. If, in addition, the $\boldsymbol{\zeta}_\nu$ are isotropic, and if the hydrodynamic interaction tensors $\boldsymbol{\Omega}_{\nu\mu}$ are equilibrium averaged (and hence isotropic), then the $\boldsymbol{\lambda}_\nu$ are isotropic, and it follows that the quantity $\sum_\nu [\boldsymbol{\lambda}_\nu \cdot \boldsymbol{r}_\nu]$ is convected with the fluid; that is, in the notation of Eq. 15.4-16, we have $\sum_\nu [\boldsymbol{\lambda}_\nu \cdot \llbracket \dot{\boldsymbol{r}}_\nu \rrbracket] = \boldsymbol{v}_0 + \boldsymbol{\kappa} \cdot \sum_\nu [\boldsymbol{\lambda}_\nu \cdot \boldsymbol{r}_\nu]$. Thus we see that, with the restrictions just cited, the quantity $\sum_\nu [\boldsymbol{\lambda}_\nu \cdot \boldsymbol{r}_\nu]$ is the hydrodynamic center of resistance $\boldsymbol{r}_h = \sum_\nu l_\nu \boldsymbol{r}_\nu$, and the weight tensors $\boldsymbol{\lambda}_\nu$ are generalizations of the l_ν.

Making use of Eq. 18.2-17, we may rewrite the expression for the hydrodynamic force, Eq. 18.2-15, in the form

$$\boldsymbol{F}_\nu^{(h)} = -\sum_\mu \tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot [\llbracket \dot{\boldsymbol{R}}_\mu \rrbracket - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu] - \frac{1}{\bar{N}} [\boldsymbol{\lambda}_\nu^\dagger \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] \tag{18.2-19}$$

where the $\tilde{\boldsymbol{\zeta}}_{\nu\mu}$ are the modified effective friction tensors

$$\tilde{\boldsymbol{\zeta}}_{\nu\mu} = \boldsymbol{\zeta}_{\nu\mu} - \left\{\left(\sum_\eta \boldsymbol{\zeta}_{\nu\eta}\right) \cdot \boldsymbol{\lambda}_\mu\right\} = \boldsymbol{\zeta}_{\nu\mu} - \{\boldsymbol{\lambda}_\nu^\dagger \cdot \mathbf{Z} \cdot \boldsymbol{\lambda}_\mu\} \tag{18.2-20}$$

In going to the second form of the last expression, we have made use of Eq. 18.2-13. It is to be noted from the last relation that

$$\tilde{\boldsymbol{\zeta}}_{\nu\mu}^\dagger = \tilde{\boldsymbol{\zeta}}_{\mu\nu} \tag{18.2-21}$$

$$\sum_\nu \tilde{\boldsymbol{\zeta}}_{\nu\mu} = \mathbf{0} \tag{18.2-22}$$

Then making use of Eq. 18.2-13 again, along with the definition of the base vectors $\boldsymbol{b}_{\nu s}$, we find that

$$\boldsymbol{F}_\nu^{(h)} = -\sum_{\mu s} \frac{1}{\sqrt{m_\mu}} \llbracket \dot{Q}_s \rrbracket [\tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{b}_{\mu s}] + \sum_\mu [\tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu]] - \frac{1}{\bar{N}} [\boldsymbol{\lambda}_\nu^\dagger \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] \tag{18.2-23}$$

This is the expression for $\boldsymbol{F}_\nu^{(h)}$ in terms of the $\llbracket \dot{Q}_s \rrbracket$. Next we obtain the effective hydrodynamic force $\mathscr{F}_s^{(h)}$ in terms of the $\llbracket \dot{Q}_s \rrbracket$ and then solve for the latter. For this purpose, we return to the expression for $\mathscr{F}_s^{(h)}$, as given by Eq. 18.1-13, and consider the term on the right involving the force $\boldsymbol{F}_\nu^{(h)}$. From Eq. 18.2-23, we find that

$$\bar{N} \sum_\nu \frac{1}{\sqrt{m_\nu}} (\boldsymbol{b}_{\nu s} \cdot \boldsymbol{F}_\nu^{(h)}) = -\sum_t \tilde{g}_{st}^{(1)} \llbracket \dot{Q}_t \rrbracket + (\mathbf{M}_s^{(1)} : \boldsymbol{\kappa}) - \mathscr{F}_s^{(b,e)} \tag{18.2-24}$$

where

$$\tilde{g}_{st}^{(1)} = \bar{N} \sum_{\nu\mu} \frac{1}{\sqrt{m_\nu m_\mu}} (\boldsymbol{b}_{\nu s} \cdot \tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{b}_{\mu t}) \tag{18.2-25}$$

$$\mathbf{M}_s^{(1)} = \bar{N} \sum_{\nu\mu} \frac{1}{\sqrt{m_\nu}} \{\boldsymbol{R}_\mu \boldsymbol{b}_{\nu s} \cdot \tilde{\boldsymbol{\zeta}}_{\nu\mu}\} \tag{18.2-26}$$

$$\mathscr{F}_s^{(b,e)} = \sum_\nu \frac{1}{\sqrt{m_\nu}} (\boldsymbol{\lambda}_\nu : \boldsymbol{b}_{\nu s}(\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})) \tag{18.2-27}$$

The Brownian force $\boldsymbol{F}^{(b)}$ was defined in Eq. 17.5-17; in the absence of hydrodynamic interaction $\mathscr{F}_s^{(b,e)}$ is zero.

The second term in the expression for the hydrodynamic force $\mathscr{F}_s^{(h)}$, as given by Eq. 18.1-13, depends on the model used for the *finite* beads. As an example of a finite bead we consider a cylindrically symmetric body. The potential field acting on such a body does not involve the angle associated with rotation about the symmetry axis and one may use as two of the coordinates, $q_{\nu\sigma}$, the polar angles $q_{\nu 1} = \theta_\nu$ and $q_{\nu 2} = \phi_\nu$ describing the unit vector, $\boldsymbol{u}_\nu$, along the symmetry axis. The averages, $T_{\nu\sigma}^{(h)\alpha}$, defined by Eqs. 18.1-12 and 14, may then be written

$$T_{\nu\sigma}^{(h)\alpha} = -\frac{\partial}{\partial q_{\nu\sigma}^\alpha} \Phi_\nu^{(h)\alpha} \tag{18.2-28}$$

where

$$\Phi_\nu^{(h)\alpha} = \frac{1}{\bar{N}\Psi_\alpha} \sum_{\beta\mu} \iint \Phi_{\nu\mu}^{\alpha\beta}\, \tilde{\Psi}_{\alpha\beta}(r, \boldsymbol{R}, Q_\alpha, Q_\beta, t)\, dQ_\beta\, d\boldsymbol{R} \tag{18.2-29}$$

is an average potential due to interactions with the surrounding molecules. These derivatives are closely related to the torque on the bead.

The torque on a cylindrical bead oriented in the direction $\boldsymbol{u}$ in an external potential Φ is given by

$$\boldsymbol{T} = -\left[\boldsymbol{u} \times \frac{\partial}{\partial \boldsymbol{u}} \Phi\right] \tag{18.2-30}$$

Thus, one finds from Eq. 18.2-28 that if the finite bead is modeled as a cylindrical body,

$$T_{\nu 1}^{(h)} = (\boldsymbol{t}_\nu \cdot \boldsymbol{T}_\nu^{(h)}), \qquad T_{\nu 2}^{(h)} = -\sin\theta_\nu\, (\boldsymbol{s}_\nu \cdot \boldsymbol{T}_\nu^{(h)}) \tag{18.2-31}$$

where $\boldsymbol{T}_\nu^{(h)}$ is an average torque on the bead due to the surrounding molecules.

Brenner[3] has shown that the hydrodynamic torque on a cylindrically symmetric body with "fore-aft" symmetry is

$$\boldsymbol{T}_\nu^{(h)} = -\boldsymbol{\xi}_\nu \cdot ([\boldsymbol{u}_\nu \times [\![\dot{\boldsymbol{u}}_\nu]\!]] - \tfrac{1}{2}[\nabla \times \boldsymbol{v}]) + \tilde{\xi}_\nu [\boldsymbol{u}_\nu \times [\boldsymbol{u}_\nu \cdot \dot{\boldsymbol{\gamma}}]] \tag{18.2-32}$$

where

$$\boldsymbol{\xi}_\nu = \xi_{\nu\|} \boldsymbol{u}_\nu \boldsymbol{u}_\nu + \xi_{\nu\perp}(\boldsymbol{\delta} - \boldsymbol{u}_\nu \boldsymbol{u}_\nu) \tag{18.2-33}$$

and $\xi_{\nu\|}$, $\xi_{\nu\perp}$, $\tilde{\xi}_\nu$ are three scalar constants, the rotational friction coefficients. By combining this expression with Eq. 18.2-31, one finds that the second term in the expression for $\mathscr{F}_s^{(h)}$ as given by Eq. 18.1-13 becomes

$$\begin{aligned} \bar{N} \sum_{\nu\sigma} b_{\nu\sigma s} T_{\nu\sigma}^{(h)} = & -\bar{N} \sum_{\nu} \xi_{\nu\perp} (b_{\nu 1 s} [\![\dot{\theta}_\nu]\!] + b_{\nu 2 s} (\sin\theta_\nu)^2 [\![\dot{\phi}_\nu]\!]) \\ & + \tfrac{1}{2} \bar{N} \sum_{\nu} \sum_{\sigma} b_{\nu\sigma s} \boldsymbol{c}_{\nu\sigma} \boldsymbol{u}_\nu : \{\xi_{\nu\perp} \boldsymbol{\omega} + \tilde{\xi}_\nu \dot{\boldsymbol{\gamma}}\} \end{aligned} \tag{18.2-34}$$

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[3] H. Brenner, *Int. J. Multiphase Flow*, **1**, 195 341 (1974).

Then using Eq. 17.1-8 for the $\dot{q}_{\nu\sigma}$, one finds that this equation may be written in a form similar to Eq. 18.2-24

$$\bar{N}\sum_{\nu}\sum_{\sigma} b_{\nu\sigma s} T_{\nu\sigma}^{(h)} = -\sum_{t} \tilde{g}_{st}^{(2)} [\![\dot{Q}_t]\!] + (\mathbf{M}_s^{(2)}:\boldsymbol{\kappa}) \qquad (18.2\text{-}35)$$

where

$$\tilde{g}_{st}^{(2)} = \bar{N}\sum_{\nu} \zeta_{\nu\perp}[b_{\nu 1s} b_{\nu 1t} + (\sin\theta_\nu)^2 b_{\nu 2s} b_{\nu 2t}] \qquad (18.2\text{-}36)$$

$$\begin{aligned} \mathbf{M}_s^{(2)} &= \tfrac{1}{2}\bar{N}\sum_{\nu}\sum_{\sigma} \zeta_{\nu\perp} b_{\nu\sigma s}(\boldsymbol{u}_\nu \boldsymbol{c}_{\nu\sigma} - \boldsymbol{c}_{\nu\sigma}\boldsymbol{u}_\nu) \\ &\quad + \tfrac{1}{2}\bar{N}\sum_{\nu}\sum_{\sigma} \tilde{\zeta}_\nu b_{\nu\sigma s}(\boldsymbol{u}_\nu \boldsymbol{c}_{\nu\sigma} + \boldsymbol{c}_{\nu\sigma}\boldsymbol{u}_\nu) \end{aligned} \qquad (18.2\text{-}37)$$

We will assume that even if the *finite* beads are modeled as more general rigid bodies the expression may be written in the form of Eq. 18.2-35, with more general expressions for $\tilde{g}_{st}^{(2)}$ and $\mathbf{M}_s^{(2)}$.

When Eqs. 18.2-24 and 35 are used in Eq. 18.1-13 one finds that

$$\mathscr{F}_s^{(h)} = -\sum_{t} \tilde{g}_{st}[\![\dot{Q}_t]\!] + (\mathbf{M}_s:\boldsymbol{\kappa}) - \mathscr{F}_s^{(b,e)} \qquad (18.2\text{-}38)$$

where

$$\tilde{g}_{st} = \tilde{g}_{st}^{(1)} + \tilde{g}_{st}^{(2)} \qquad (18.2\text{-}39)$$

$$\mathbf{M}_s = \mathbf{M}_s^{(1)} + \mathbf{M}_s^{(2)} \qquad (18.2\text{-}40)$$

To solve these equations for the $[\![\dot{Q}_s]\!]$, we introduce a matrix with elements, $\tilde{G}_{st}$, which is the inverse of the $\tilde{g}_{st}$ matrix

$$\sum_{t} \tilde{G}_{st}\tilde{g}_{tu} = \delta_{su} \qquad (18.2\text{-}41)$$

In terms of this matrix,

$$[\![\dot{Q}_s]\!] = \sum_{t} \tilde{G}_{st}\,((\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(h)} + \mathscr{F}_t^{(b,e)}) \qquad (18.2\text{-}42)$$

The effective force balance, Eq. 17.5-15, may then be used to rewrite this as

$$[\![\dot{Q}_s]\!] = \sum_{t} \tilde{G}_{st}(\mathscr{F}_t^{(e)} + \mathscr{F}_t^{(\phi)} + \mathscr{F}_t^{(b)} + \mathscr{F}_t^{(b,e)} + (\mathbf{M}_t:\boldsymbol{\kappa})) \qquad (18.2\text{-}43)$$

Thus, we see that the generalized velocities are given by expressions involving sums of five generalized forces.

The last result may be used in the equation of continuity, Eq. 17.5-14, to give

$$\boxed{\frac{\partial \Psi_\alpha}{\partial t} + \sum_{st} \frac{\partial}{\partial Q_s}[\tilde{G}_{st}(\mathscr{F}_t^{(e)} + \mathscr{F}_t^{(\phi)} + \mathscr{F}_t^{(b)} + \mathscr{F}_t^{(b,e)} + (\mathbf{M}_t:\boldsymbol{\kappa}))\Psi_\alpha] = 0} \qquad (18.2\text{-}44)$$

After the expression for the generalized Brownian force $\mathscr{F}_t^{(b)}$ has been inserted into this equation, we have the second-order partial differential equation for Ψ_α known as the *diffusion equation.*

§18.3 POSSIBLE APPROXIMATIONS FOR THE BROWNIAN FORCES

The third major approximation in the development reduces the problem from one in the phase space of a single molecule to one in the configuration space only. This is an approximation for the momentum dependence of the distribution function, which enters into the evaluation of the generalized Brownian forces. The expression for the generalized Brownian force given by Eq. 17.5-8 may be rearranged to give

$$\mathscr{F}_s^{(b)} = -\frac{1}{\Psi_\alpha}\sum_{tu}\frac{\partial}{\partial Q_u}(G_{tu}[\![P_tP_s]\!]\Psi_\alpha) - \tfrac{1}{2}\sum_{tu}[\![P_tP_u]\!]\left(\frac{\partial}{\partial Q_s}G_{tu}\right) \tag{18.3-1}$$

The total Brownian force on a molecule is given by Eq. 17.5-17.

We consider three different assumptions for evaluating the $[\![\quad]\!]$ quantities in the Brownian force expression:

a. The *assumption of equilibration in momentum space*; this can be written down at once for any kind of model. It is this assumption that has heretofore been used universally for dilute solutions in all of the publications by Kirkwood, Zimm, Rouse, and others.

b. *The assumption that f_α is an even function of $\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}$ and independent of $\boldsymbol{r}_c$.* This assumption is used only for models with structureless beads and no constraints. It has been used to get the expression given in Eq. 13.2-3, which, in turn, has been used in studies on nonisotropic Brownian motion[1] (see §13.7) and studies on velocity distributions that are Maxwellian about the bead velocities rather than about the center of mass velocity of the bead-spring model.[2]

c. The *assumption of reptational motion*, which is used in the kinetic theory of concentrated polymer solutions and undiluted polymers; the discussion of this assumption is postponed until §19.2.

In this section we discuss the consequences of assumptions (a) and (b).

a. Equilibration in Momentum Space

If one assumes that the momentum dependence of the distribution function is that characteristic of equilibrium, then

$$[\![P_tP_s]\!] = kT\, g_{st} \tag{18.3-2}$$

$$[\![(\boldsymbol{p}_c - m_p\boldsymbol{v})(\boldsymbol{p}_c - m_p\boldsymbol{v})]\!] = m_pkT\,\boldsymbol{\delta} \tag{18.3-3}$$

$$[\![P_s\boldsymbol{p}_c]\!] = \boldsymbol{0} \tag{18.3-4}$$

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[1] R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983); R. B. Bird and J. M. Wiest, *J. Rheol.*, **29**, 519–532 (1985).

[2] R. B. Bird, X. J. Fan, and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **15**, 85–92 (1984); *errata*: in Eq. 4.7, change 6 to 12, and in Eq. 4.9 change $\frac{2}{9}$ to $\frac{1}{9}$.

In connection with Eq. 18.3-2, see Example 12.4-1. If one uses these relations, one finds[3] from Eq. 18.3-1 that the generalized Brownian force associated with the s-degree of freedom is

$$\boxed{\mathscr{F}_s^{(b)} = -kT \frac{\partial}{\partial Q_s} \ln \frac{\Psi_\alpha}{\sqrt{g}}} \tag{18.3-5}$$

and from Eq. 17.5-17, that the total Brownian force on the entire polymer molecule is

$$\boldsymbol{F}^{(b)} = -kT\, \nabla \ln \Psi_\alpha \tag{18.3-6}$$

It is these expressions that have traditionally been used in polymer kinetic theory. That is, we ignore the influence of the flow field on the velocity distribution.

b. Special Results for Structureless Beads and No Internal Constraints

Equation 18.3-1 for the generalized Brownian force may be written as follows:

$$\begin{aligned} \mathscr{F}_s^{(b)} = &-\frac{1}{\Psi_\alpha} \sum_{\nu t} \sqrt{m_\nu}\, \boldsymbol{b}_{\nu s} \cdot \frac{\partial}{\partial Q_t} (\llbracket \dot{\boldsymbol{R}}_\nu \dot{Q}_t \rrbracket \Psi_\alpha) \\ &- \frac{1}{\Psi_\alpha} \sum_{\nu t \sigma \tau} b_{\nu \sigma s} \frac{\partial}{\partial Q_t} (g_{\nu, \sigma\tau} \llbracket \dot{q}_{\nu\tau} \dot{Q}_t \rrbracket \Psi_\alpha) \\ &+ \tfrac{1}{2} \sum_{\nu\sigma\tau} \left(\frac{\partial}{\partial Q_s} g_{\nu, \sigma\tau} \right) \llbracket \dot{q}_{\nu\tau} \dot{q}_{\nu\sigma} \rrbracket \end{aligned} \tag{18.3-7}$$

In this form, approximations other than the equilibration approximation may be introduced for the momentum averages of the products of the time derivatives. It should be noted, however, that any approximation which does not reduce at equilibrium, that is, in the absence of a flow field, to the results just given in §18.3a, cannot be correct in this limit.

We now restrict the discussion to models with structureless beads, so that the last two terms in Eq. 18.3-7 can be discarded. Then using the defining equation for $\mathscr{F}_\nu^{(b)}$ in Table 17.6-1 we obtain

$$\mathscr{F}_\nu^{(b)} = -\frac{1}{\Psi_\alpha} \sum_{\mu s t u} \sqrt{m_\nu m_\mu}\, G_{st} \boldsymbol{b}_{\nu t} \boldsymbol{b}_{\mu s} \cdot \frac{\partial}{\partial Q_u} (\llbracket \dot{Q}_u \dot{\boldsymbol{R}}_\mu \rrbracket \Psi_\alpha) \tag{18.3-8}$$

For models with no constraints Eq. 12D.3-5 allows us to simplify this result to

$$\mathscr{F}_\nu^{(b)} = -\frac{m_\nu}{\Psi_\alpha} \sum_s \frac{\partial}{\partial Q_s} (\llbracket \dot{Q}_s \dot{\boldsymbol{R}}_\nu \rrbracket \Psi_\alpha) \tag{18.3-9}$$

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[3] In obtaining this result we use the standard result that, since the matrices (g_{uv}) and (G_{uv}) are inverse to one another

$$\sum_u \sum_v g_{uv} \frac{\partial}{\partial Q_t} G_{vu} = -\frac{\partial}{\partial Q_t} \ln g \tag{18.3-4a}$$

where g is the determinant of the g_{uv}.

For such a system the set of $\boldsymbol{r}_\nu$ may be used as the independent variables rather than the coordinates Q_s and the vector to the center of mass $\boldsymbol{r}_c$. Making such a transformation, we find from the last equation that

$$\mathscr{F}_\nu^{(b)} = -\frac{m_\nu}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial \boldsymbol{r}_\mu}\cdot(\llbracket \dot{\boldsymbol{R}}_\mu \dot{\boldsymbol{R}}_\nu \rrbracket \Psi_\alpha) \tag{18.3-10}$$

This force has been defined in such a manner that the sum on the index ν gives zero.

The total Brownian force on a molecule is given by Eq. 17.5-17. As long as f_α does not depend on $\boldsymbol{r}_c$ the first term on the right is zero and

$$\boldsymbol{F}^{(b)} = -\frac{1}{\Psi_\alpha}\sum_s \frac{\partial}{\partial Q_s}(\llbracket \dot{Q}_s \boldsymbol{p}_c \rrbracket \Psi_\alpha) \tag{18.3-11}$$

For models with structureless beads and no internal constraints this expression may be transformed in a similar manner to give

$$\boldsymbol{F}^{(b)} = -\frac{1}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial \boldsymbol{r}_\mu}\cdot(\llbracket \dot{\boldsymbol{R}}_\mu \boldsymbol{p}_c \rrbracket \Psi_\alpha) \tag{18.3-12}$$

By combining this result with Eq. 18.3-10 one finds that

$$\boldsymbol{F}_\nu^{(b)} = \frac{m_\nu}{m_p}\boldsymbol{F}^{(b)} + \mathscr{F}_\nu^{(b)} = -\frac{m_\nu}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial \boldsymbol{r}_\mu}\cdot(\llbracket \dot{\boldsymbol{R}}_\mu \dot{\boldsymbol{r}}_\nu \rrbracket \Psi_\alpha) \tag{18.3-13}$$

This may be interpreted as the total Brownian force on a bead.

Next, we note that for models with structureless beads and no internal constraints and with f_α independent of $\boldsymbol{r}_c$:

$$-\frac{m_\nu}{\Psi_\alpha}\frac{\partial}{\partial \boldsymbol{r}_c}\cdot\left(\left\llbracket\left(\frac{1}{m_p}\boldsymbol{p}_c - \boldsymbol{v}\right)\dot{\boldsymbol{r}}_\nu\right\rrbracket\Psi_\alpha\right) = -\frac{m_\nu}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial \boldsymbol{r}_\mu}\cdot\left(\left\llbracket\left(\frac{1}{m_p}\boldsymbol{p}_c - \boldsymbol{v}\right)\dot{\boldsymbol{r}}_\nu\right\rrbracket\Psi_\alpha\right) = \boldsymbol{0} \tag{18.3-14}$$

Then, adding the second form of this expression to the right of Eq. 18.3-13, one finds that

$$\boldsymbol{F}_\nu^{(b)} = -\frac{m_\nu}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial \boldsymbol{r}_\mu}\cdot(\llbracket (\dot{\boldsymbol{r}}_\mu - \boldsymbol{v})\dot{\boldsymbol{r}}_\nu \rrbracket \Psi_\alpha) \tag{18.3-15}$$

It is however reasonable to assume that the momentum dependence of the distribution function is an even function of the difference $(\dot{\boldsymbol{r}}_\mu - \boldsymbol{v})$. With this restriction the last expression reduces to

$$\boxed{\boldsymbol{F}_\nu^{(b)} = -\frac{m_\nu}{\Psi_\alpha}\frac{\partial}{\partial \boldsymbol{r}_\nu}\cdot[\llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rrbracket \Psi_\alpha]} \tag{18.3-16}$$

as the expression for the total Brownian force on a mass point. It is this form for the Brownian force that was used in Eqs. 13.2-3 and 13.7-2. Note that $\boldsymbol{F}_\nu^{(b)}$ is the negative of the divergence of the momentum flux associated with the νth bead; it is exactly this expression that appears as $\llbracket \dot{\boldsymbol{R}}_\nu \dot{\boldsymbol{R}}_\nu \rrbracket^\alpha \Psi_\alpha$ in the kinetic contribution to the stress tensor (Eq. 17.6-5).

§18.4 THE DIFFUSION EQUATION, THE STRESS TENSOR, AND THE MASS FLUX

The principal results of §§18.1, 18.2, and 18.3(a) are valid for quite general models including tensorial friction coefficients, internal constraints, and hydrodynamic interaction. In parts (a) and (b) of this section, we summarize these main results for the diffusion equation and the expression for the stress tensor. In part (c) we first consider translational diffusion for quite general models and then for models made up of structureless beads, involving no constraints, but with the effects of hydrodynamic interaction included.

a. The Diffusion Equation for Ψ_α

The diffusion equation as given by Eq. 18.2-44 involves the modified metric matrix elements, $\tilde{G}_{st}$, and the coupling tensors, $\mathbf{M}_t$. The modified metric matrix elements are those of the matrix inverse to that with elements $\tilde{g}_{st}$ given by Eq. 18.2-39 as the sum of two terms. The first term, $\tilde{g}_{st}^{(1)}$, is that associated with the structure of the molecule as a whole, and the second, $\tilde{g}_{st}^{(2)}$, is that associated with the structure of the finite beads.

The matrix elements $\tilde{g}_{st}^{(1)}$ are defined by Eq. 18.2-25. If one neglects hydrodynamic interaction and takes the masses of beads to be equal then this expression reduces to (m is the mass of a bead),

$$\tilde{g}_{st}^{(1)} = \frac{\bar{N}}{m}\sum_{\nu} \boldsymbol{\zeta}_\nu : \boldsymbol{b}_{\nu s}\boldsymbol{b}_{\nu t} - \frac{\bar{N}}{m}\left(\sum_{\nu} \boldsymbol{b}_{\nu s}\cdot\boldsymbol{\zeta}_\nu\right)\cdot\mathbf{Z}^{-1}\cdot\left(\sum_{\mu}\boldsymbol{\zeta}_\mu\cdot\boldsymbol{b}_{\mu t}\right) \tag{18.4-1}$$

where $\mathbf{Z} = \sum_\nu \boldsymbol{\zeta}_\nu$. For the example discussed in §18.2, in which the finite beads are taken to have cylindrical symmetry, the modified matrix elements, $\tilde{g}_{st}^{(2)}$, are given by Eq. 18.2-36. We now further restrict the model and take the beads to be "needles," that is, cylindrically symmetric bodies with zero moment of inertia about the symmetry axis. Then on comparing Eq. 18.2-36 with Eq. 17.1-12 one finds that

$$\tilde{g}_{st}^{(2)} = \frac{\bar{N}\xi_\perp}{I}\, g_{st}^{(2)} \tag{18.4-2}$$

Then $\tilde{g}_{st}$ is obtained by combining Eqs. 18.4-1 and 2.

In a similar manner the coupling tensor $\mathbf{M}_s$ is given by Eq. 18.2-40 as the sum of two terms. An expression for the first term, $\mathbf{M}_s^{(1)}$, which is also associated with the structure of the molecule as a whole is given by Eq. 18.2-26. If one again neglects hydrodynamic interaction and takes the masses of the beads to be equal, this expression reduces to

$$\mathbf{M}_s^{(1)} = \frac{\bar{N}}{\sqrt{m}}\left(\sum_{\nu} \boldsymbol{R}_\nu \boldsymbol{b}_{\nu s}\cdot\boldsymbol{\zeta}_\nu\right) - \frac{\bar{N}}{\sqrt{m}}\sum_{\nu\mu} \boldsymbol{R}_\mu(\boldsymbol{b}_{\nu s}\cdot\boldsymbol{\zeta}_\nu\cdot\mathbf{Z}^{-1}\cdot\boldsymbol{\zeta}_\mu) \tag{18.4-3}$$

An expression for the second contribution, $\mathbf{M}_s^{(2)}$, to the coupling tensor is given by Eq. 18.2-37.

The diffusion equation is given by Eq. 18.2-44 in terms of these quantities and $\mathscr{F}_t^{(b,e)}$. This latter quantity is defined by Eq. 18.2-27 in terms of the total Brownian and external forces, $\boldsymbol{F}^{(b)}$ and $\boldsymbol{F}^{(e)}$, on a molecule. If these forces are taken to be zero, then $\mathscr{F}_t^{(b,e)}$ is zero. An expression for the generalized intramolecular force, $\mathscr{F}_t^{(\phi)}$, is given by Eq. 17.1-21, and if one assumes equilibration in momentum space, the generalized Brownian force, $\mathscr{F}_t^{(b)}$, is given by 18.3-5. When these and the results of this subsection are used in Eq. 18.2-44 we have the *diffusion equation* for Ψ_α for models with identical beads (with structure), when hydrodynamic interaction is neglected. The development of this diffusion equation for a specific model is illustrated in Example 18.4-1.

In §16.2 we give the diffusion equation (Eq. 16.2-6) for models with structureless beads and scalar friction coefficients. For those models we retain the full hydrodynamic interaction and allow the beads to have different masses and friction coefficients. Equation 16.2-6 includes as special cases the diffusion equations used in Chapters 13–15.

b. The Stress Tensor

Let us now return to the general expression for the stress tensor given in Eq. 18.1-10 in terms of the hydrodynamic force $\boldsymbol{F}_\nu^{(h)}$. Although Eq. 18.1-10 is both very general and simple in form, it is not particularly useful until one inserts a specific expression for the $\boldsymbol{F}_\nu^{(h)}$. We use Eq. 18.2-19, a modified Stokes' law expression for $\boldsymbol{F}_\nu^{(h)}$, which includes hydrodynamic interaction and beads with structure (including anisotropic friction tensors). Insertion of $\boldsymbol{F}_\nu^{(h)}$ from Eq. 18.2-19 into Eq. 18.1-10 then gives

$$\boxed{\begin{aligned}\boldsymbol{\pi} = \boldsymbol{\pi}_k + \bar{N} \sum_{\alpha\nu\mu} \int \boldsymbol{R}_\nu(\llbracket \dot{\boldsymbol{R}}_\mu \rrbracket - \boldsymbol{\kappa}\cdot\boldsymbol{R}_\mu)\cdot\bar{\boldsymbol{\zeta}}_{\mu\nu}\Psi_\alpha(\boldsymbol{r}, Q, t)dQ \\ + \sum_\alpha \sum_\nu \int \boldsymbol{R}_\nu(\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})\cdot\boldsymbol{\lambda}_\nu\Psi_\alpha(\boldsymbol{r}, Q, t)dQ\end{aligned}} \tag{18.4-4}$$

To utilize this stress tensor formula we need an expression for $\llbracket \dot{\boldsymbol{R}}_\nu \rrbracket$; this is obtained by combining Eqs. 17.1-7 and 18.2-43 to get

$$\llbracket \dot{\boldsymbol{R}}_\nu \rrbracket = \frac{1}{\sqrt{m_\nu}} \sum_s \sum_t \tilde{G}_{st}\boldsymbol{b}_{\nu s}\left(\mathscr{F}_t^{(e)} + \mathscr{F}_t^{(\phi)} + \mathscr{F}_t^{(b)} + \mathscr{F}_t^{(b,e)} + (\mathbf{M}_t : \boldsymbol{\kappa})\right) \tag{18.4-5}$$

Insertion of this expression for $\llbracket \dot{\boldsymbol{R}}_\nu \rrbracket$ into Eq. 18.4-4 then gives the stress tensor $\boldsymbol{\pi}$ in terms of the generalized forces $\mathscr{F}_t^{(\ )}$ and the quantity $(\mathbf{M}_t : \boldsymbol{\kappa})$; this is then the generalization of the rather simple special result given in Eq. 18.1-18 (see Problem 18C.1). The use of Eqs. 18.4-4 and 5 is illustrated in Example 18.4-1 for a molecular model containing beads with structure.

In §16.3 several formulas for the stress tensor are given, which are less general than Eqs. 18.4-4 and 5. Equations 16.3-1, 11, 16, and 20 include, as special cases, the stress-tensor expressions used in Chapters 13–15.

c. The Mass Flux and the Translational Diffusivity

The mass flux of species α is given by Eq. 17.6-12. The first term on the right side of this equation is an average of the "drift velocity" of a molecule of species α, which in turn is related to the hydrodynamic force on the molecule. We may thus use the force balance equations for species α to express the drift velocity in terms of the Brownian and external forces, and to obtain an expression for the mass-flux vector in terms of the concentration gradient and the average external force. The second term on the right side of Eq. 17.6-12 results from the finite extension of the polymer molecules in space, and its role in various diffusional phenomena has not yet been explored.

We begin by working with very general molecular models and include the full effects of hydrodynamic interaction. We first form the dot product of $(m_\nu/m_p)\boldsymbol{\zeta}_\nu^{-1}$ with Eq. 18.2-14 to get the drift velocity for the molecule

$$\llbracket \dot{\boldsymbol{r}}_c \rrbracket - \boldsymbol{v}(\boldsymbol{r}_c) = -\sum_\nu \sum_\mu \frac{m_\nu}{m_p} [\boldsymbol{\zeta}_\nu^{-1} \cdot \boldsymbol{\Upsilon}_{\nu\mu} \cdot \boldsymbol{F}_\mu^{(h)}] \tag{18.4-6}$$

Insertion of this into Eq. 17.6-12 then gives

$$\begin{aligned} \boldsymbol{j}_\alpha = &-\sum_\nu \sum_\mu m_\nu \int [\boldsymbol{\zeta}_\nu^{-1} \cdot \boldsymbol{\Upsilon}_{\nu\mu} \cdot \boldsymbol{F}_\mu^{(h)}] \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \\ &-\nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu \llbracket \dot{\boldsymbol{R}}_\nu \rrbracket \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \end{aligned} \tag{18.4-7}$$

Next we substitute for $\boldsymbol{F}_\mu^{(h)}$ the expression given in Eq. 18.2-19. The result may be simplified by using two identities (see Problem 18D.1)

$$\left\{\boldsymbol{\zeta}_\nu^{-1} \cdot \sum_\mu \boldsymbol{\Upsilon}_{\nu\mu} \cdot \boldsymbol{\lambda}_\mu^\dagger\right\} = \mathbf{Z}^{-1} \tag{18.4-8}$$

$$\left\{\boldsymbol{\zeta}_\nu^{-1} \cdot \sum_\mu \boldsymbol{\Upsilon}_{\nu\mu} \cdot \tilde{\boldsymbol{\zeta}}_{\mu\eta}\right\} = \delta_{\nu\eta}\boldsymbol{\delta} - \boldsymbol{\lambda}_\eta \tag{18.4-9}$$

The mass flux of species α then becomes

$$\begin{aligned} \boldsymbol{j}_\alpha = &\frac{m_p}{\bar{N}} \int \mathbf{Z}^{-1} \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)}) \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \\ &-m_p \sum_\nu \int \boldsymbol{\lambda}_\nu \cdot (\llbracket \dot{\boldsymbol{R}}_\nu \rrbracket - [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\nu]) \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \\ &-\nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu \llbracket \dot{\boldsymbol{R}}_\nu \rrbracket \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \end{aligned} \tag{18.4-10}$$

To make use of this result, the expression for $\llbracket \dot{\boldsymbol{R}}_\nu \rrbracket$ in Eq. 18.4-5 has to be inserted. For further interpretation of this equation, see Problem 18B.2.

Having discussed the mass flux for a quite general model, we now turn to the much simpler models with structureless beads and no constraints. We start with Eq. 18.4-7 for $\boldsymbol{j}_\alpha$ and insert the appropriate expression for the hydrodynamic force $\boldsymbol{F}_\mu^{(h)}$ obtained from Eq. 18.1-16 and the force balances in Eqs. 17.5-18 and 17.6-10

$$\boldsymbol{F}_\mu^{(h)} = -\frac{1}{\bar{N}} (\boldsymbol{F}_\mu^{(b)} + \boldsymbol{F}_\mu^{(e)} + \boldsymbol{F}_\mu^{(\phi)}) \tag{18.4-11}$$

where $\boldsymbol{F}_\mu^{(b)}$ is the total Brownian force on a bead defined by Eq. 18.3-13; $\boldsymbol{F}_\mu^{(e)}$ is the total external force defined in an analogous manner

$$\boldsymbol{F}_\mu^{(e)} = \frac{m_\mu}{m_p} \boldsymbol{F}^{(e)} + \mathscr{F}_\mu^{(e)} \tag{18.4-12}$$

and $\bar{N}$ is the average number of beads per molecule defined by Eq. 17.5-11. Using Eq. 18.4-11 in Eq. 18.4-7, we find that

$$\begin{aligned} \boldsymbol{j}_\alpha = {} & \frac{1}{\bar{N}} \sum_\nu \sum_\mu m_\nu \int \boldsymbol{\zeta}_\nu^{-1} \cdot \boldsymbol{\Upsilon}_{\nu\mu} \cdot (\boldsymbol{F}_\mu^{(e)} + \boldsymbol{F}_\mu^{(b)} + \boldsymbol{F}_\mu^{(\phi)}) \Psi_\alpha \, dQ \\ & - \nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!] \Psi_\alpha \, dQ \qquad \text{(structureless beads, no constraints)} \end{aligned} \tag{18.4-13}$$

Equation 18.4-10 for general models and Eq. 18.4-13 for models with structureless beads and no constraints are the integral expressions for the mass fluxes involving the configurational distribution function Ψ_α.

We now make a specific assumption for the function Ψ_α in order to get mass flux expressions in terms of the translational diffusion tensors. Specifically we assume that the diffusion process is sufficiently slow that Ψ_α can be approximated by the equilibrium distribution function in the absence of external forces (§12.3):

$$\Psi_\alpha = \frac{n_\alpha}{J} \sqrt{g}\, e^{-\phi/kT} \tag{18.4-14}$$

where n_α is the number density of molecules of species α, and J is the normalization constant. Using this expression for the configurational distribution function in the expressions for the Brownian forces, Eqs. 18.3-5 and 6, and the definition of $\mathscr{F}_\mu^{(\phi)}$ in Table 17.6-1 one finds that

$$\mathscr{F}_s^{(b)} = -\mathscr{F}_s^{(\phi)} \tag{18.4-15}$$

$$\boldsymbol{F}_\mu^{(b)} = \frac{m_\mu}{m_p} \boldsymbol{F}^{(b)} - \mathscr{F}_\mu^{(\phi)} \tag{18.4-16}$$

$$\boldsymbol{F}^{(b)} = -kT \nabla \ln n_\alpha \tag{18.4-17}$$

These relations are valid for any choice of molecular model.

Next we consider the very general model used to derive $\boldsymbol{j}_\alpha$ in Eq. 18.4-10. To do this we return to Eq. 18.4-5 and the relations in Table 17.6-1 to obtain the expression for $[\![\dot{\boldsymbol{R}}_\nu]\!]$

$$\begin{aligned} [\![\dot{\boldsymbol{R}}_\nu]\!] = {} & \frac{1}{\sqrt{m_\nu}} \sum_{st\mu} \frac{1}{\sqrt{m_\mu}} \tilde{G}_{st} \boldsymbol{b}_{\nu s} \boldsymbol{b}_{\mu t} \cdot \boldsymbol{\lambda}_\mu^\dagger \cdot (-kT \nabla \ln n_\alpha + \boldsymbol{F}^{(e)}) \\ & + \frac{1}{\sqrt{m_\nu}} \sum_{st} \tilde{G}_{st} \boldsymbol{b}_{\nu s} (\mathscr{F}_t^{(e)} + \mathbf{M}_t : \boldsymbol{\kappa}) \end{aligned} \tag{18.4-18}$$

One then finds from Eq. 18.4-10 that

$$\begin{aligned} \boldsymbol{j}_\alpha = &-\bar{\boldsymbol{\Delta}}^\alpha \cdot \left(\nabla \rho_\alpha - \frac{\rho_\alpha}{kT} \bar{\boldsymbol{F}}^{(e)\alpha} \right) \\ &+ m^\alpha \sum_\nu \int \boldsymbol{\lambda}_\nu \cdot \left[\boldsymbol{\kappa} \cdot \boldsymbol{R}_\nu - \sum_s \sum_t \tilde{G}_{st} \boldsymbol{b}_{\nu s} (\mathscr{F}_t^{(e)} + \mathbf{M}_t : \boldsymbol{\kappa}) \right] \Psi_\alpha \, dQ \\ &- \nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!] \Psi_\alpha \, dQ \end{aligned} \tag{18.4-19}$$

Here $\bar{\boldsymbol{F}}^{(e)\alpha}$ is an average total external force on the molecule defined as

$$\bar{\boldsymbol{F}}^{(e)\alpha} = (\bar{\boldsymbol{\Delta}}^\alpha)^{-1} \cdot \langle \boldsymbol{\Delta}^\alpha \cdot \boldsymbol{F}^{(e)\alpha} \rangle_{\text{eq}} \tag{18.4-20}$$

in which $\bar{\boldsymbol{\Delta}}^\alpha$ is an average translational diffusion tensor

$$\bar{\boldsymbol{\Delta}}^\alpha = \langle \boldsymbol{\Delta}^\alpha \rangle_{\text{eq}} \tag{18.4-21}$$

where

$$\boldsymbol{\Delta}^\alpha = \frac{kT}{\bar{N}} \mathbf{Z}_\alpha^{-1} - kT \sum_{\nu\mu st} \frac{1}{\sqrt{m_\nu m_\mu}} \tilde{G}_{st} \{ \boldsymbol{\lambda}_\nu \cdot \boldsymbol{b}_{\nu s} \boldsymbol{b}_{\mu t} \cdot \boldsymbol{\lambda}_\mu^\dagger \} \tag{18.4-22}$$

It is interesting to note that the $\bar{\boldsymbol{F}}^{(e)\alpha}$ in Eq. 18.4-20 is a different average from that which appeared in the definition of $\bar{\boldsymbol{F}}^{(e)\alpha}$ in Eq. 17.4-26 in connection with the equation of motion.

Having obtained the general expression for the average translational diffusion tensor $\bar{\boldsymbol{\Delta}}^\alpha$, we now turn once again to the simple models with structureless beads and no constraints. For such models we find that the mass flux $\boldsymbol{j}_\alpha$ is given by an expression similar to Eq. 18.4-19, but with the second term on the right side missing and with different expressions for the average external force $\bar{\boldsymbol{F}}^{(e)\alpha}$ and the average translational diffusion tensor $\bar{\boldsymbol{\Delta}}^\alpha = \langle \boldsymbol{\Delta}^\alpha \rangle_{\text{eq}}$

$$\bar{\boldsymbol{F}}^{(e)\alpha} = (\bar{\boldsymbol{\Delta}}^\alpha)^{-1} \cdot \left\langle \sum_\mu \boldsymbol{\Delta}_\mu^\alpha \boldsymbol{F}_\mu^{(e)\alpha} \right\rangle_{\text{eq}} \qquad \text{(structureless beads, no constraints)} \tag{18.4-23}$$

$$\boldsymbol{\Delta}^\alpha = \sum_\mu \frac{m_\mu^\alpha}{m^\alpha} \boldsymbol{\Delta}_\mu^\alpha \qquad \text{(structureless beads, no constraints)} \tag{18.4-24}$$

where

$$\boldsymbol{\Delta}_\mu^\alpha = \frac{kT}{\bar{N}} \sum_\nu \frac{m_\nu^\alpha}{m^\alpha} \{ \boldsymbol{\zeta}_\nu^{-1} \cdot \boldsymbol{\Upsilon}_{\nu\mu} \} \tag{18.4-25}$$

This is as far as we go without making further simplifications of the model.

In order to conclude the section with some simple and well-known formulas, we now specialize to a dilute solution of one polymer species (α) in a solvent (a species with $N = 1$, so that $\bar{N} = 1$); furthermore we take all the beads to be alike, each one with an isotropic friction tensor $\zeta\boldsymbol{\delta}$. Then the diffusion tensor $\boldsymbol{\Delta}^{\alpha}$, given by Eqs. 18.4-24 and 25, is

$$\boldsymbol{\Delta}^{\alpha} = \frac{kT}{N_{\alpha}^{2}\zeta} \sum_{\nu} \sum_{\mu} \boldsymbol{\Upsilon}_{\nu\mu}^{\alpha} \tag{18.4-26}$$

Then, if we use the equilibrium configurational distribution function, Eq. 18.4-14, to evaluate the average of this expression for $\boldsymbol{\Delta}^{\alpha}$ we find that

$$\bar{\boldsymbol{\Delta}}^{\alpha} = D_{\text{tr}}^{\alpha}\boldsymbol{\delta} \tag{18.4-27}$$

in which D_{tr}^{α} is given by *Kirkwood's formula*[1]

$$D_{\text{tr}}^{\alpha} = \frac{kT}{3N_{\alpha}^{2}\zeta} \sum_{\nu} \sum_{\mu} \langle \boldsymbol{\delta} : \boldsymbol{\Upsilon}_{\nu\mu}^{\alpha} \rangle_{\text{eq}} \tag{18.4-28}$$

Using the definition of the dimensionless diffusion tensors, Eq. 18.2-4, we then find that the *translational diffusivity* of a polymer in which the molecular model involves only structureless beads with no constraints is

$$\boxed{D_{\text{tr}}^{\alpha} = \frac{kT}{N_{\alpha}^{2}\zeta} \sum_{\nu} \sum_{\mu} H_{\nu\mu}^{\alpha}} \tag{18.4-29}$$

where

$$H_{\nu\mu}^{\alpha} = \delta_{\nu\mu} + \tfrac{1}{3}\zeta\langle \boldsymbol{\delta} : \boldsymbol{\Omega}_{\nu\mu}^{\alpha} \rangle_{\text{eq}} \tag{18.4-30}$$

In obtaining this expression we have used the equilibrium distribution function, Eq. 18.4-14, to obtain the expression for the Brownian force, Eq. 18.4-15, and to carry out the average over the configuration space in Eq. 18.4-28. This result may be compared with that given by Eq. 15.4-40; in Problem 15D.2 it is further shown that the Zimm bead-spring model leads to $D_{\text{tr}}^{\alpha} \propto M_{\alpha}^{-1/2}$. When hydrodynamic interaction is neglected, Eq. 18.4-29 reduces to

$$D_{\text{tr}}^{\alpha} = \frac{kT}{N_{\alpha}\zeta} \tag{18.4-31}$$

as the expression for the diffusivity. When $\bar{\boldsymbol{\Delta}}^{\alpha}$ of Eq. 18.4-27 is used in Eq. 18.4-19, and when the last term in Eq. 18.4-19 is omitted (this is consistent with the use of the equilibrium distribution function), we find that

$$\boxed{\boldsymbol{j}_{\alpha} = D_{\text{tr}}^{\alpha}\left(\boldsymbol{\nabla}\rho_{\alpha} - \frac{\rho_{\alpha}}{kT}\bar{\boldsymbol{F}}^{(e)\alpha}\right)} \tag{18.4-32}$$

If the external forces on the beads are alike and independent of the internal coordinates, $\bar{\boldsymbol{F}}^{(e)\alpha}$ is the total force on a molecule. This result shows that the effects of a concentration

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[1] J. G. Kirkwood, *J. Polymer Sci.*, **12**, 1-14 (1954), see Eq. 9. See also J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967), pp. 13, 25, 41, 76, 101; H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 280.

gradient and an external force in producing a mass flux are both described[2] by the diffusivity D_{tr}^{α}. This relation is consistent with the prediction of irreversible thermodynamics in the linear approximation[3] and also with the Nernst–Einstein relation.

EXAMPLE 18.4-1 The Diffusion Equation for the Multirod-Rod Model

Develop the diffusion equation, Eq. 18.2-44, for a molecular model similar to the multibead-rod, but with the beads replaced by rods or "needles" of length $a = L/N$. Neglect hydrodynamic interaction, and consider dilute solutions so that $\bar{N} = 1$.

SOLUTION In this example we take as the molecular model a set of N "needles" aligned along a rod[4] (note that $N \geqslant 2$). As in the treatment of the multibead-rod in §14.1 (see Fig. 14.1-2) we take the centers of mass of the needles to be at the points

$$\boldsymbol{R}_{\nu} = \tfrac{1}{2}\,a\nu\boldsymbol{u} \qquad \nu = -(N-1), -(N-3), \ldots, +(N-1) \tag{18.4-33}$$

where a is the length of one needle. The model is such that the needles just touch, and hence the overall length of the rod is $L = Na$. The orientation of the rod (and all of the needles) is described by the unit vector $\boldsymbol{u}$ or the polar angles $\theta = Q_1$ and $\phi = Q_2$. One then finds from the definitions in Eqs. 17.1-5 and 6 that

$$\boldsymbol{b}_{\nu s} = \tfrac{1}{2}\nu a\sqrt{m}\,\boldsymbol{c}_s, \qquad b_{\nu\sigma s} = \delta_{\sigma s} \tag{18.4-34,35}$$

where m is the mass of one needle and the $\boldsymbol{c}_s$ are the vectors defined in §E.5.

We take the friction tensors of the needles to be alike and given by

$$\boldsymbol{\zeta}_{\nu} = \boldsymbol{\zeta} = \zeta_{\parallel}\,\boldsymbol{uu} + \zeta_{\perp}(\boldsymbol{\delta} - \boldsymbol{uu}) \tag{18.4-36}$$

where $\zeta_{\parallel}$ and $\zeta_{\perp}$ are the parallel and perpendicular components. We then find from Eq. 18.4-1 that

$$\tilde{g}_{st}^{(1)} = \tfrac{1}{4}\,a^2\left(\sum_{\nu} \nu^2\right)(\boldsymbol{\zeta}:\boldsymbol{c}_s\boldsymbol{c}_t) = \tfrac{1}{12}\,N(N^2-1)a^2\zeta_{\perp}(\boldsymbol{c}_s\cdot\boldsymbol{c}_t) \tag{18.4-37}$$

and from Eqs. 17.1-2, 3, and 12 and 18.4-2 that

$$\tilde{g}_{st}^{(2)} = N\xi_{\perp}(\boldsymbol{c}_s\cdot\boldsymbol{c}_t) \tag{18.4-38}$$

where $\xi_{\perp}$ is a "rotational friction coefficient" of a needle. Thus, the modified metric matrix is

$$\tilde{g}_{st} = X_{\perp}(\boldsymbol{c}_s\cdot\boldsymbol{c}_t), \qquad X_{\perp} = N[\xi_{\perp} + \tfrac{1}{12}(N^2-1)a^2\zeta_{\perp}] \tag{18.4-39,40}$$

The determinant of this matrix is

$$\tilde{g} = X_{\perp}^2 \sin^2\theta \tag{18.4-41}$$

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[2] It may be pointed out that the diffusivity D_{tr}^{α} is a property of the polymer–solvent mixture. In particular, the value of the friction coefficient ζ depends on the properties of both species.

[3] See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954, 1964), Section 11.2; and R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960), Eq. 18.4-15. Starting with the latter equation, one neglects the thermal- and pressure-diffusion terms and assumes a dilute (and ideal) solution of species α in the solvent, to obtain exactly Eq. 18.4-32 of the present text.

[4] The special case in which $N = 2$ has been treated by A. R. Altenberger and J. S. Dahler, *Macromolecules*, **18**, 1700–1710 (1985).

and the elements of the inverse matrix are

$$\tilde{G}_{st} = \frac{1}{X_{\perp}} (\boldsymbol{d}_s \cdot \boldsymbol{d}_t) \tag{18.4-42}$$

Next, one finds from Eqs. 18.4-3 and 18.2-37 that the two contributions to the coupling tensor are

$$\mathbf{M}_s^{(1)} = \tfrac{1}{2} N(N^2 - 1)a^2\zeta_{\perp} \boldsymbol{u}\boldsymbol{c}_s \tag{18.4-43a}$$

$$\mathbf{M}_s^{(2)} = \tfrac{1}{2} N\zeta_{\perp}(\boldsymbol{u}_s\boldsymbol{c}_s - \boldsymbol{c}_s\boldsymbol{u}_s) + \tfrac{1}{2} N\tilde{\xi}(\boldsymbol{u}\boldsymbol{c}_s + \boldsymbol{c}_s\boldsymbol{u}) \tag{18.4-43b}$$

The coupling tensors are thus,

$$\mathbf{M}_s = \tfrac{1}{2} \tilde{X}(\boldsymbol{u}_s\boldsymbol{c}_s + \boldsymbol{c}_s\boldsymbol{u}_s) + \tfrac{1}{2} X_{\perp}(\boldsymbol{u}\boldsymbol{c}_s - \boldsymbol{c}_s\boldsymbol{u}) \tag{18.4-44}$$

where

$$\tilde{X} = N[\tilde{\xi} + \tfrac{1}{12}(N^2 - 1)a^2\zeta_{\perp}] \tag{18.4-45}$$

The effective Brownian force is given by Eq. 18.3-5. For this model this expression becomes

$$\mathscr{F}_s^{(b)} = -kT \frac{\partial}{\partial Q_s} \ln \frac{\Psi}{\sin\theta} \tag{18.4-46}$$

Thus one finds that the diffusion equation, Eq. 18.2-44, for this model is

$$\begin{aligned}\frac{\partial}{\partial t}\Psi = \frac{1}{6\lambda}\left\{\frac{\partial}{\partial\theta}\sin\theta\left[\frac{\partial}{\partial\theta}\left(\frac{\Psi}{\sin\theta}\right)\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi\right\} \\ - \frac{1}{2X_{\perp}}\frac{\partial}{\partial\theta}(\boldsymbol{u}\boldsymbol{c}_1:(\tilde{X}\dot{\boldsymbol{\gamma}} - X_{\perp}\boldsymbol{\omega})\Psi) - \frac{1}{2X_{\perp}}\frac{\partial}{\partial\phi}(\boldsymbol{u}\boldsymbol{c}_2:(\tilde{X}\dot{\boldsymbol{\gamma}} - X_{\perp}\boldsymbol{\omega})\Psi)\end{aligned} \tag{18.4-47}$$

where

$$\lambda = \frac{X_{\perp}}{6kT} \tag{18.4-48}$$

is the time constant. This result may also be written in the form

$$\frac{\partial}{\partial t} f = \frac{1}{6\lambda}\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}} f\right) - \frac{\tilde{X}}{X_{\perp}}\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}]f\right) + \frac{(X_{\perp} - \tilde{X})}{2X_{\perp}}\left(\boldsymbol{\omega}:\boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}} f\right) \tag{18.4-49}$$

where

$$f = \frac{\Psi}{n\sin\theta} \tag{18.4-50}$$

This equation is the principal result of this example; it may be compared with that for the multibead-rod with hydrodynamic interaction, Eq. 16.2-37. The two equations differ primarily in the term involving $\boldsymbol{\omega}$. In addition, the time constants in the two equations are defined differently. It may be shown from the diffusion equation, Eq. 18.4-47, that

$$\begin{aligned}\frac{\partial}{\partial t}\langle \boldsymbol{uu}\rangle &= \frac{1}{3\lambda}\boldsymbol{\delta} - \frac{1}{\lambda}\langle \boldsymbol{uu}\rangle - \frac{\tilde{X}}{X_\perp}\langle \boldsymbol{uuuu}\rangle:\dot{\boldsymbol{\gamma}} \\ &\quad + \frac{\tilde{X}}{2X_\perp}\{\langle \boldsymbol{uu}\rangle\cdot\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}\cdot\langle \boldsymbol{uu}\rangle\} \\ &\quad + \tfrac{1}{2}\{\langle \boldsymbol{uu}\rangle\cdot\boldsymbol{\omega} - \boldsymbol{\omega}\cdot\langle \boldsymbol{uu}\rangle\} \qquad (18.4\text{-}51)\end{aligned}$$

or

$$\begin{aligned}\lambda\langle \boldsymbol{uu}\rangle_{(1)} &= \tfrac{1}{3}\boldsymbol{\delta} - \langle \boldsymbol{uu}\rangle - \lambda\frac{\tilde{X}}{X_\perp}\langle \boldsymbol{uuuu}\rangle:\dot{\boldsymbol{\gamma}} \\ &\quad + \frac{\lambda}{2}\left(\frac{\tilde{X}}{X_\perp} - 1\right)\{\langle \boldsymbol{uu}\rangle\cdot\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}\cdot\langle \boldsymbol{uu}\rangle\} \qquad (18.4\text{-}52)\end{aligned}$$

where the subscript (1) on $\langle \boldsymbol{uu}\rangle$ indicates the convected derivative. It may also be shown by direct substitution that for steady flows the solution of the diffusion equation, Eq. 18.4-49, is given to first order in $\boldsymbol{\kappa}$ by

$$f = \frac{1}{4\pi}\left[1 + \frac{3\tilde{X}\lambda}{2X_\perp}(\dot{\boldsymbol{\gamma}}:\boldsymbol{uu}) + \cdots\right] \qquad (18.4\text{-}53)$$

From this it follows that

$$\langle \boldsymbol{uu}\rangle = \tfrac{1}{3}\boldsymbol{\delta} + \frac{\tilde{X}}{5X_\perp}\lambda\dot{\boldsymbol{\gamma}} + \cdots \qquad (18.4\text{-}54)$$

$$\langle \boldsymbol{uu}\rangle_{(1)} = -\tfrac{1}{3}\dot{\boldsymbol{\gamma}} + \frac{\lambda\tilde{X}}{10X_\perp}\{\boldsymbol{\omega}\cdot\dot{\boldsymbol{\gamma}} - \dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\omega}\} - \frac{\lambda\tilde{X}}{5X_\perp}\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\} + \cdots \qquad (18.4\text{-}55)$$

$$\langle \boldsymbol{uuuu}\rangle:\dot{\boldsymbol{\gamma}} = \tfrac{2}{15}\dot{\boldsymbol{\gamma}} + \frac{4\lambda\tilde{X}}{35X_\perp}[\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\} + \tfrac{1}{4}(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}})\boldsymbol{\delta}] + \cdots \qquad (18.4\text{-}56)$$

These results, which follow directly from Eq. 18.4-49, are used in the next example in the development of the expression for the stress tensor.

EXAMPLE 18.4-2 The Stress Tensor for the Multirod-Rod Model

Use Eq. 18.4-4 to develop an explicit expression for the polymer contribution, $\boldsymbol{\pi}_p$, to the stress tensor of a dilute solution using the multirod-rod model of Example 18.4-1.

SOLUTION The stress tensor of the solution is given by Eq. 18.4-4, in which the sum on the index α includes all solvent and solute species. Here we are dealing with only one solute species and find from Eqs. 18.4-1 and 18.4-4 that the contribution of this polymer species to the total stress tensor is:

$$\begin{aligned}\boldsymbol{\pi}_p &= \boldsymbol{\pi}_k + \frac{X}{X_\perp}\sum_s \int \boldsymbol{u}\boldsymbol{d}_s(\mathscr{F}_s^{(b)} + (\mathbf{M}_s:\boldsymbol{\kappa}))\Psi\, d\theta\, d\phi \\ &\quad - \tfrac{1}{12}N(N^2 - 1)a^2\int \boldsymbol{u}[\boldsymbol{\zeta}\cdot\boldsymbol{\kappa}\cdot\boldsymbol{u}]\Psi\, d\theta\, d\phi \qquad (18.4\text{-}57)\end{aligned}$$

where

$$X = \tfrac{1}{12} N(N^2 - 1)a^2\zeta_\perp \tag{18.4-58}$$

From this one finds that

$$\begin{aligned}\boldsymbol{\pi}_p = nkT\,\boldsymbol{\delta} + nkT\frac{X}{X_\perp}\Bigg\{\boldsymbol{\delta} - 3\langle\boldsymbol{uu}\rangle - 3\lambda\left(\frac{\tilde{X}}{X_\perp} + \frac{\zeta_\parallel}{\zeta_\perp} - 1\right)\langle\boldsymbol{uuuu}\rangle:\dot{\boldsymbol{\gamma}}\\ + 3\lambda\left(\frac{\tilde{X}}{X_\perp} - 1\right)\langle\boldsymbol{uu}\rangle\cdot\dot{\boldsymbol{\gamma}}\Bigg\}\end{aligned} \tag{18.4-59}$$

In the limiting case that the friction tensor is isotropic ($\zeta_\parallel = \zeta_\perp$) and the rotational friction coefficients are zero, this expression reduces to the Kramers expression for the stress tensor of a multibead rod as given by Eq. A, Table 14.3-1, with the time constant given by Eq. 14.3-1.

When one uses the relation developed from the diffusion equation and given by Eq. 18.4-52 one finds that the symmetric part of the stress tensor is

$$\boldsymbol{\pi}_p^{(s)} = nkT\,\boldsymbol{\delta} + 3nkT\lambda\frac{X}{X_\perp}\left\{\langle\boldsymbol{uu}\rangle_{(1)} + \left(1 - \frac{\zeta_\parallel}{\zeta_\perp}\right)\langle\boldsymbol{uuuu}\rangle:\dot{\boldsymbol{\gamma}}\right\} \tag{18.4-60}$$

and the antisymmetric part is

$$\boldsymbol{\pi}_p^{(a)} = nkT\left(\frac{3X\lambda}{2X_\perp}\right)\left(\frac{\tilde{X}}{X_\perp} - 1\right)\{\langle\boldsymbol{uu}\rangle\cdot\dot{\boldsymbol{\gamma}} - \dot{\boldsymbol{\gamma}}\cdot\langle\boldsymbol{uu}\rangle\} \tag{18.4-61}$$

The first of these relations is a generalization of the Giesekus expression given as Eq. D in Table 14.3-1.

When one uses the results developed from a perturbation solution of the diffusion equation, as given by Eqs. 18.4-54 to 56, in the expression for the full stress tensor one finds that to second order in $\boldsymbol{\kappa}$

$$\begin{aligned}\boldsymbol{\pi}_p = nkT\boldsymbol{\delta} - b_1\dot{\boldsymbol{\gamma}} + \tfrac{1}{2}b_2\{\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\omega} - \boldsymbol{\omega}\cdot\dot{\boldsymbol{\gamma}}\}\\ + (b_2 - b_{11})\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\} - \tfrac{1}{4}b_{11}(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}})\boldsymbol{\delta} + \cdots\end{aligned} \tag{18.4-62}$$

where

$$b_1 = \frac{nkT\lambda X}{5X_\perp\zeta_\perp}(3\zeta_\perp + 2\zeta_\parallel) \tag{18.4-63}$$

$$b_2 = -\frac{3\,nkT\lambda^2X\tilde{X}}{5X_\perp{}^2} \tag{18.4-64}$$

$$b_{11} = \frac{12nkT\lambda^2X\tilde{X}}{35X_\perp{}^2\zeta_\perp}(\zeta_\parallel - \zeta_\perp) \tag{18.4-65}$$

are the second-order fluid constants. Note that, to this order, the stress tensor is symmetric. The antisymmetric contribution does, however, enter at third order; to lowest order,

$$\begin{aligned}\boldsymbol{\pi}^{(a)} &= -\frac{3nkT\lambda^3X\tilde{X}}{20X_\perp{}^4}(\tilde{X} - X_\perp)^2\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\omega} - 2\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\omega}\cdot\dot{\boldsymbol{\gamma}} + \boldsymbol{\omega}\cdot\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\}\\ &= \frac{3nkT\lambda^3X\tilde{X}}{10X_\perp{}^4}(\tilde{X} - X_\perp)^2\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(2)} - \boldsymbol{\gamma}_{(2)}\cdot\boldsymbol{\gamma}_{(1)}\}\end{aligned} \tag{18.4-66}$$

where $\boldsymbol{\gamma}_{(1)} \equiv \dot{\boldsymbol{\gamma}}$ and $\boldsymbol{\gamma}_{(2)} = (\boldsymbol{\gamma}_{(1)})_{(1)}$ (see §D.3); note that $\tilde{X} - X_\perp$ is the same as $N(\tilde{\xi} - \xi_\perp)$.

It is interesting that this model leads to a stress tensor that is *not* symmetric. The antisymmetric contribution comes from the inclusion of the hydrodynamic torque terms in Eq. 18.1-13 associated with the finite structure of the beads. The antisymmetric behavior does not arise until the third order since $\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(2)} - \boldsymbol{\gamma}_{(2)}\cdot\boldsymbol{\gamma}_{(1)}\}$ is the lowest order antisymmetric combination of the $\boldsymbol{\gamma}_{(n)}$ tensors.

In order to obtain numerical evaluations of the quantities in Eqs. 18.4-63 to 66, it is necessary to have explicit expressions for the various friction coefficients. Brenner[5] has developed such expressions from "slender body" theory. From hydrodynamic considerations he finds that if a long slender body is modeled as a cylinder of length a and diameter b, then for $a \gg b$

$$\zeta_{\perp} = \frac{4\pi a\eta_s}{\ln(a/b)}, \qquad \zeta_{\parallel} = \tfrac{1}{2}\,\zeta_{\perp} \tag{18.4-67}$$

$$\xi_{\perp} = \frac{\pi a^3\eta_s}{3\ln(a/b)}, \qquad \tilde{\xi} = \tfrac{1}{2}\,\xi_{\perp} \tag{18.4-68}$$

With these values one finds from Eqs. 18.4-40, 45, and 58 that

$$X_{\perp} = \frac{N^3\pi a^3\eta_s}{3\ln(a/b)} \tag{18.4-69}$$

$$\tilde{X} = \frac{N(2N^2-1)\pi a^2\eta_s}{6\ln(a/b)} \tag{18.4-70}$$

$$X = \frac{N(N^2-1)\pi a^3\eta_s}{3\ln(a/b)} \tag{18.4-71}$$

and that the second-order fluid constants are

$$b_1 = \tfrac{4}{5}\,nkT\lambda\left(\frac{N^2-1}{N^2}\right) \tag{18.4-72}$$

$$b_2 = -\tfrac{3}{10}\,nkT\lambda^2\left[\frac{(N^2-1)(2N^2-1)}{N^4}\right] \tag{18.4-73}$$

$$b_{11} = \tfrac{2}{7}\,b_2 \tag{18.4-74}$$

From this last relation it follows that $\Psi_{2,0}/\Psi_{1,0} = -\frac{1}{7}$. In addition the third-order contribution to the antisymmetric part of the stress tensor is

$$\boldsymbol{\pi}^{(a)} = \frac{3nkT\lambda^3}{80\,N^8}(N^2-1)(2N^2-1)\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(2)} - \boldsymbol{\gamma}_{(2)}\cdot\boldsymbol{\gamma}_{(1)}\} \tag{18.4-75}$$

In Eqs. 18.4-72 through 18.4-75

$$\lambda = \frac{N^3\pi a^3\eta_s}{6kT\ln(a/b)} \tag{18.4-76}$$

is the time constant.

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[5] H. Brenner, *Int. J. Multiphase Flow*, **1**, 195–341 (1974).

PROBLEMS

18B.1 Dimensionless Mobility Tensors

Show that the dimensionless mobility tensors, $\mathbf{B}_{\nu\mu}$, defined by Eq. 18.2-5 may be written in the series form,

$$\begin{aligned}\mathbf{B}_{\nu\mu} &= \delta_{\nu\mu}\boldsymbol{\delta} - \{\boldsymbol{\zeta}_\nu \cdot \boldsymbol{\Omega}_{\nu\mu}\} \\ &\quad + \sum_\eta \{\boldsymbol{\zeta}_\nu \cdot \boldsymbol{\Omega}_{\nu\eta} \cdot \boldsymbol{\zeta}_\eta \cdot \boldsymbol{\Omega}_{\eta\mu}\} + \cdots \end{aligned} \tag{18B.1-1}$$

If it can be shown that this series converges then this result illustrates that the set of tensors $\mathbf{B}_{\nu\mu}$ exists.

18B.2 Drift of the Center of Resistance

Make use of Eq. 18.4-10 and the discussion following Eq. 18.2-18 to show that in the approximation of equilibrium-averaged hydrodynamic interaction

$$\frac{m_p}{\bar{N}} \int \mathbf{Z}^{-1} \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})\Psi_\alpha(\boldsymbol{r}, Q, t)dQ = m_p \int ([\![\dot{\boldsymbol{r}}_h]\!] - \boldsymbol{v}(\boldsymbol{r}_h))\Psi_\alpha(\boldsymbol{r}, Q, t)dQ \tag{18B.2-1}$$

where $\boldsymbol{r}_h$ is the hydrodynamic center of resistance.

18B.3 Translational Diffusion Coefficient for the Elastic Dumbbell Model

Show that, for a dilute solution of polymer molecules modeled as elastic dumbbells with Hookean springs, the expression for the diffusion coefficient given by Eq. 18.4-29 reduces to that given by Eq. 13.6-20.

18C.1 Simplification of the General Expression for the Stress Tensor for a Special Case

Prove directly from Eq. 18.4-4 that, if the model consists of structureless beads with no constraints, the stress tensor is given by Eq. 18.1-18. For this purpose, first note from Eq. 18.4-5 that

$$\sum_\mu [\![\dot{\boldsymbol{R}}_\mu]\!] \cdot \tilde{\boldsymbol{\zeta}}_{\mu\nu} = \sqrt{m_\nu} \sum_s \boldsymbol{a}_{\nu s} \left(\mathscr{F}_s^{(e)} + \mathscr{F}_s^{(\phi)} + \mathscr{F}_s^{(b)} + \mathscr{F}_s^{(b,e)} + \mathbf{M}_s : \boldsymbol{\kappa}\right) \tag{18C.1-1}$$

where the $\boldsymbol{a}_{\nu s}$ are the modified reciprocal base vectors defined by Eq. 16.3-6. Next, from the definition of the coupling tensors, $\boldsymbol{M}_s^{(1)}$, Eq. 18.2-26, show that

$$\sum_\nu \sqrt{m_\nu}\, \boldsymbol{R}_\nu \boldsymbol{a}_{\nu s} \mathbf{M}_s^{(1)} = \bar{N} \sum_{\nu\mu\eta} \sqrt{\frac{m_\nu}{m_\eta}}\, \boldsymbol{R}_\nu \boldsymbol{a}_{\nu s} \boldsymbol{R}_\mu \boldsymbol{b}_{\eta s} \cdot \tilde{\boldsymbol{\zeta}}_{\eta\mu} \tag{18C.1-2}$$

and therefore that

$$\begin{aligned}\sum_{\nu\mu} \boldsymbol{R}_\nu ([\![\dot{\boldsymbol{R}}_\mu]\!] - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu) \cdot \tilde{\boldsymbol{\zeta}}_{\mu\nu} &= \sum_{\nu s} \sqrt{m_\nu}\, \boldsymbol{R}_\nu \boldsymbol{a}_{\nu s} (\mathscr{F}_s^{(e)} + \mathscr{F}_s^{(\phi)} + \mathscr{F}_s^{(b)} + \mathscr{F}_s^{(b,e)} + \mathbf{M}_s^{(2)} : \boldsymbol{\kappa}) \\ &\quad + \sum_{\nu\mu\eta} \sqrt{\frac{m_\nu}{m_\eta}}\, \boldsymbol{R}_\nu \left(\bar{N} \sum_s \boldsymbol{a}_{\nu s} \boldsymbol{b}_{\eta s} - \delta_{\nu\eta}\boldsymbol{\delta}\right) \cdot \tilde{\boldsymbol{\zeta}}_{\eta\mu} \boldsymbol{R}_\mu : \boldsymbol{\kappa}^\dagger \end{aligned} \tag{18C.1-3}$$

Next show from the definition of the $\boldsymbol{a}_{\nu s}$, Eq. 16.3-6, and the definition of the elements of the metric matrix $\tilde{g}_{st}^{(1)}$, Eq. 18.2-25, that

$$\sum_{\nu} \boldsymbol{a}_{\nu s} \cdot \boldsymbol{b}_{\nu t} = \frac{1}{\tilde{N}} \left(\delta_{st} - \sum_{u} \tilde{G}_{su} \tilde{g}_{ut}^{(2)} \right) \tag{18C.1-4}$$

$$\sum_{\nu t u} \boldsymbol{a}_{\nu s} \cdot \boldsymbol{b}_{\nu t} \boldsymbol{b}_{\mu u} G_{tu} = \frac{1}{\tilde{N}} \sum_{u} G_{su} \boldsymbol{b}_{\mu u} - \frac{1}{\tilde{N}} \sum_{t u v} \tilde{G}_{su} \tilde{g}_{ut}^{(2)} G_{tv} \boldsymbol{b}_{\mu v} \tag{18C.1-5}$$

If the beads are structureless and there are no constraints in the model, show from Eqs. 12D.3-5 and 16.3-7 that

$$\boldsymbol{a}_{\nu s} = \frac{1}{\tilde{N}} \sum_{t} G_{st} \boldsymbol{b}_{\nu t} \tag{18C.1-6}$$

Now use Eq. 12D.3-5 again to verify that

$$\sum_{s} \boldsymbol{a}_{\nu s} \boldsymbol{b}_{\mu s} = \frac{1}{\tilde{N}} \left[\delta_{\nu\mu} - \frac{\sqrt{m_\nu m_\mu}}{m} \right] \boldsymbol{\delta} \tag{18C.1-7}$$

Then find from Eq. 18C.1-3 that for structureless beads and no constraints

$$\sum_{\nu\mu} \boldsymbol{R}_\nu ([\![\dot{\boldsymbol{R}}_\mu]\!] - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu) \cdot \boldsymbol{\zeta}_{\mu\nu} = \frac{1}{\tilde{N}} \sum_{\nu} \boldsymbol{R}_\nu (\mathscr{F}_\nu^{(e)} + \mathscr{F}_\nu^{(\phi)} + \mathscr{F}_\nu^{(b)} + \mathscr{F}_\nu^{(b,e)}) \tag{18C.1-8}$$

$$\mathscr{F}_\nu^{(b,e)} = \sqrt{m_\nu} \sum_{st} G_{st} \boldsymbol{b}_{\nu s} \mathscr{F}_t^{(b,e)} \tag{18C.1-9}$$

Verify that when this result is used in the expression for the stress tensor, Eq. 18.4-4, the latter reduces to that given by Eq. 18.1-18.

18C.2 Translational Diffusion Coefficient for the Multibead-Rod Model

a. Use the results developed in Examples 16.1-1 and 16.2-1 to show that for a dilute solution of molecules modeled as multibead rods Eq. 18.4-22 reduces to

$$\boldsymbol{\Lambda} = kT\mathbf{Z}^{-1} \tag{18C.2-1}$$

b. From this develop an expression for the translational diffusion coefficient of the system, and show that the result is identical to that given by Eq. 14.6-45.

18D.1 Proof of Tensor Identities Needed in Discussion of Mass Flux

Making use of Eqs. 18.2-6, 7, 11, and 12, prove that

$$\boldsymbol{\lambda}_\nu^\dagger = \sum_{\mu} \mathbf{B}_{\nu\mu} \cdot \boldsymbol{\zeta}_\mu \cdot \mathbf{Z}^{-1} \tag{18D.1-1}$$

Then make use of Eq. 18.2-5 to prove Eq. 18.4-8, and Eqs. 18.2-6, 20, and 21 to prove Eq. 18.4-9.

CHAPTER 19

PHASE-SPACE THEORY FOR CONCENTRATED SOLUTIONS AND MELTS

In the foregoing chapter it was shown how the main kinetic theory results of Chapter 17 can be used to develop theories for the rheological responses of dilute polymer solutions. In this chapter we show how to use the same results of Chapter 17 to develop a theory for the rheological behavior of undiluted polymers ("polymer melts"). A comparison of the block diagram in Fig. 19.0-1 with the analogous diagram in Fig. 18.0-1 emphasizes the formal similarity between the two kinetic theory developments.

Dilute polymer solutions and undiluted polymers do have some important differences at the molecular level as can be recognized if we consider the motion of one polymer molecule in the fluid. In Figure 19.0-2 we show the configurations of a polymer chain at time t and time $t + \Delta t$ in a fluid undergoing stress relaxation after cessation of flow. In a *dilute solution* each bead of the polymer chain is bombarded from all sides by the solvent molecules and as the beads go through the solvent, an isotropic Stokes' law appears to be a reasonable assumption for describing the hydrodynamic drag. After a time interval Δt the chain may have wandered off into quite a different configuration. In a *concentrated solution or melt*, however, the polymer chain finds it very difficult to move sideways and its principal motion is more or less in the direction of the chain backbone; that is, we expect the hydrodynamic drag and the Brownian motion to be highly anisotropic. As a consequence the major difference between the dilute solution kinetic theory and the theory for concentrated fluids is in the form of the mathematical expressions used for the hydrodynamic drag (§19.1) and the Brownian motion (§19.2). Two new parameters make their appearance here: ε, which specifies the anisotropy of the hydrodynamic drag force, and ε', which accounts for the anisotropy of the Brownian motion (these parameters correspond roughly to the parameters σ and β in §13.7).

Some polymer physicists[1,2] have chosen to describe the constraints on a polymer chain in a concentrated system by saying that the chain moves in a "tube." The "tube" concept seems to have been very useful for qualitative discussions and for interrelating a wide range of phenomena. Doi and Edwards[2] used the idea of "tube" constraints in setting up the first comprehensive kinetic theory for polymer melts based on the consideration of the motion of a typical polymer chain in a concentrated solution. In our presentation in this

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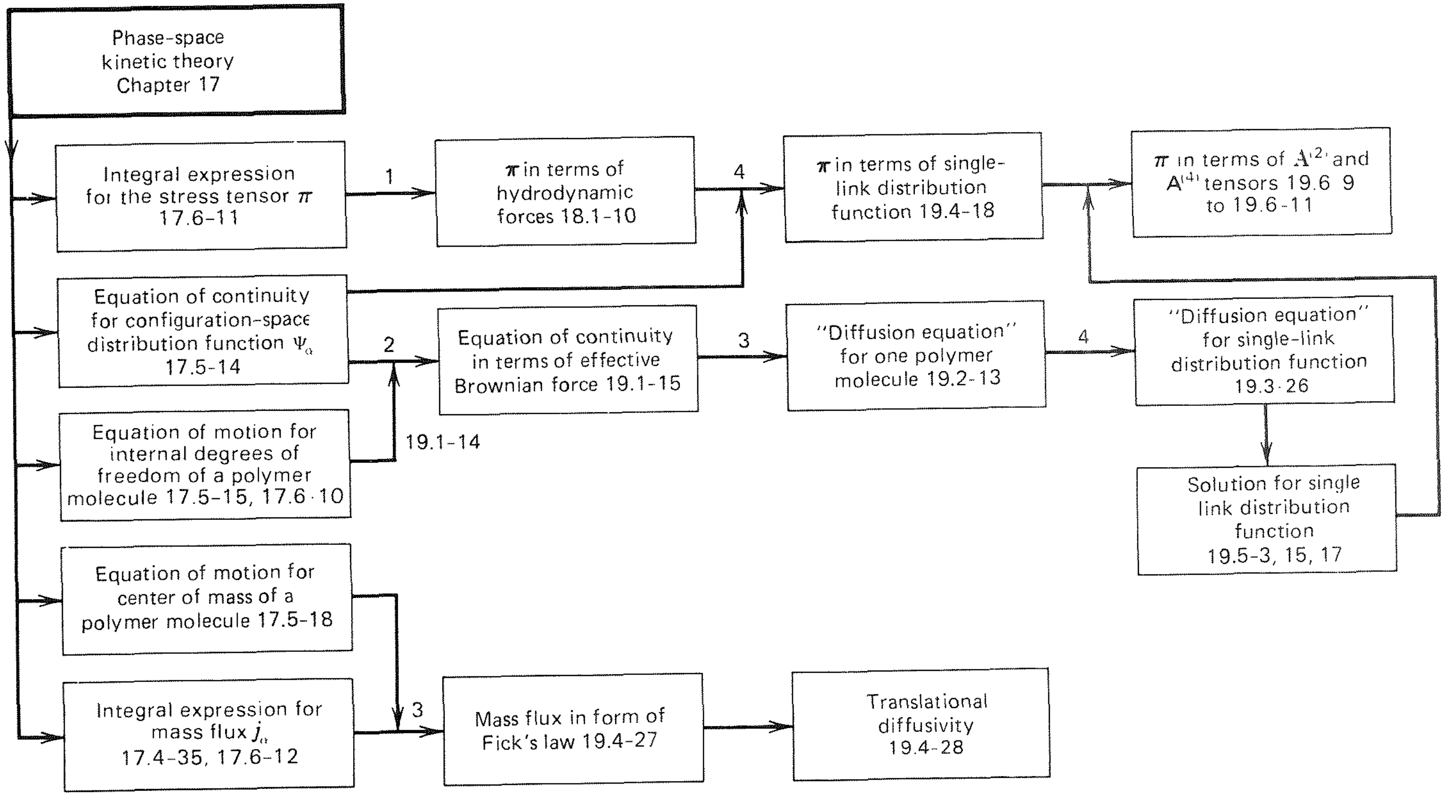
[1] See, for example, S. F. Edwards, *Proc. Phys. Soc.*, **92**, 9–16 (1967); P.-G. de Gennes, and L. Léger, *Ann. Rev. Phys. Chem.*, **33**, 49–61 (1982); P.-G. de Gennes, *Physics Today*, **36**, 33–39 (1983).

[2] M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789–1832 (1978); **75**, 38–54 (1979). See also M. Doi and S. F. Edwards, *Theory of Polymer Dynamics*, Oxford University Press (1986), Chapter 7.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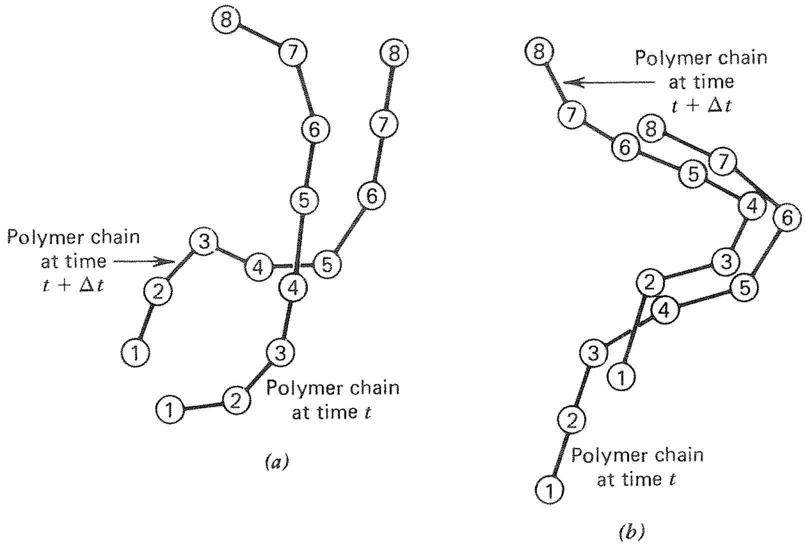

FIGURE 19.0-2. Comparison of the motion of one molecule in (*a*) a dilute polymer solution and in (*b*) a concentrated solution or polymer melt; in the latter the motion of a polymer molecule is severely constrained by the other polymer molecules in the fluid.

chapter we do not follow the Doi-Edwards theory, but rather a more systematic kinetic theory approach[3] that is closely patterned after the dilute solution theories. In spite of the totally different approaches used in these two theories for concentrated systems, many of the key results are closely related; as the story unfolds, we point out the similarities and the salient differences.

This chapter differs in two other respects from Chapter 18. Whereas in the foregoing chapter we worked with arbitrary bead-rod-spring models, the discussion in this chapter is restricted to the Kramers freely jointed bead-rod chain model illustrated in Fig. 11.3-1. In particular, we consider a system consisting of a mixture of molecules of various species α, as shown in Fig. 19.0-3. Each species is modeled as a chain of N_α identical beads, joined by $(N_\alpha - 1)$ links, each of length a, the molecules differing only in length. Some of the properties of the Kramers model have been discussed in §§11.3, 12.1, and 16.5. As pointed out in §16.5 it is convenient in discussing this model to label the generalized coordinates by two indices and take Q_{k1} and Q_{k2} to be the polar angles θ_k and ϕ_k that specify the

FIGURE 19.0-1. Kinetic theory for undiluted polymers (polymer melts).

MAJOR APPROXIMATIONS	MODEL
1. Short-range force approximation 18.1-5	
2. Modified Stokes law empiricism 19.1-1	
3. Approximations for momentum-space averages 19.2-4, 9, 10	Interacting Kramers bead-rod chains
4. Mild-curvature approximation 19.3-4, 19.4-12	

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[3] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016-2033 (1982); R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102-1106 (1982); *J. Chem. Phys.*, **77**, 4747-4757 (1982); H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758-4766 (1982); X. J. Fan and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **15**, 341-373 (1984); C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191-204 (1983); R. B. Bird and C. F. Curtiss, *Phys. Today*, **37**, 36-43 (1984).

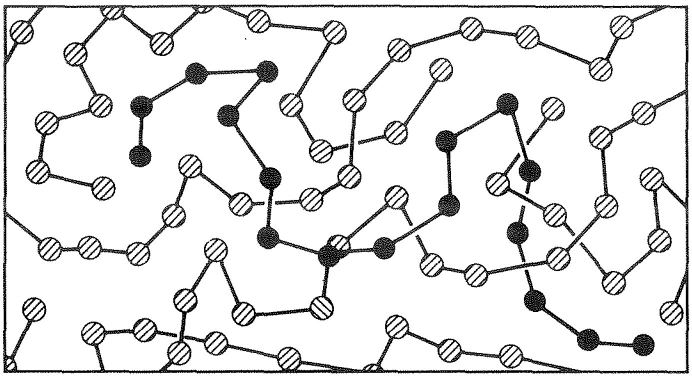

FIGURE 19.0-3. In the model of an undiluted polymer considered in this chapter, the fluid is modeled as a collection of interacting bead-rod chains. Polydispersity is accounted for by allowing a distribution of chain lengths corresponding to a distribution of molecular weights. A polymer molecule of molecular weight M_α is represented by N_α beads joined together with massless rods of length a. The number N_α is equal to M_α/M_0, where M_0 is the "molecular weight" of that segment of the polymer molecule represented by one bead. One chain, corresponding to a species with $N_\alpha = 17$, is shown with solid beads.

orientation of the unit vector, $\boldsymbol{u}_k$, of the link joining beads k and $k + 1$. Indices $i, j, k, \ldots$ (ranging from 1 to $N - 1$) are used to label the rods; $\nu, \mu, \ldots$ (ranging from 1 to N) are labels for beads; and $p, q, \ldots$ are 1 or 2 corresponding to θ and ϕ.

In this chapter we introduce an additional important approximation—the "mild-curvature approximation." This approximation permits us to follow Doi and Edwards and reduce the problem to one involving only the single-link distribution function $f(\boldsymbol{u}, \sigma, t)$, which gives the probability that a link located a fractional distance σ along the chain has the orientation given by the unit vector $\boldsymbol{u}$ at the time t. The mild curvature assumption is used in §19.3 to get the differential equation for the time evolution of $f(\boldsymbol{u}, \sigma, t)$ and in §19.4 to get an expression for the stress tensor in terms of $f(\boldsymbol{u}, \sigma, t)$. To summarize, then, in addition to the restriction to a specific model, four main approximations are inherent in the theory presented here:

1. The *short-range-force approximation* already discussed in §18.1.
2. The *anisotropic Stokes' law approximation*, discussed in §19.1, which replaces the approximation used in §18.2 for dilute solutions.
3. The *anisotropic Brownian motion* (or *"reptation"*) *approximation*, given in §19.2, which replaces the approximations used in §18.3 for dilute solutions.
4. The *mild-curvature approximation*, introduced in §§19.3 and 19.4, which was not used in dilute solution theories.

Thus, aside from the fourth approximation used here, the form of the theory for undiluted polymers is quite similar to that for dilute solutions. This emphasizes the advantage of a unified approach to the kinetic theory of polymeric liquids.

Once the differential equation for $f(\boldsymbol{u}, \sigma, t)$ has been solved (§19.5), then a constitutive equation for the melt may be obtained (§19.6). Finally, in §§19.7 and 19.8, we compare the theoretical material functions with experimental data.

§19.1 THE HYDRODYNAMIC FORCES

As discussed in the previous chapter, to reduce the development from one in the phase space of the entire system to one in the phase space of a single molecule, we introduce an approximation for the hydrodynamic force. In Eq. 18.2-1 a nonisotropic modification of Stokes' law was proposed for the hydrodynamic force acting on the νth bead of the bead-spring-rod model. In this chapter a different kind of modification of Stokes' law is used. We propose empiricisms for the *differences* between the hydrodynamic forces on adjacent pairs of beads[1] and for the *sum* of the hydrodynamic forces on all the beads of the Kramers bead-rod chain model. This is done so that tensor friction coefficients can be introduced that depend on the orientations of the rods. Thus we take (for $1 \leq k \leq N - 1$)

$$\boxed{\boldsymbol{F}^{(h)}_{k+1} - \boldsymbol{F}^{(h)}_{k} = -\bar{N}^{\beta}\boldsymbol{\zeta}_k \cdot \{[\![\dot{\boldsymbol{R}}_{k+1} - \dot{\boldsymbol{R}}_k]\!] - [\boldsymbol{v}(\boldsymbol{r} + \boldsymbol{R}_{k+1}) - \boldsymbol{v}(\boldsymbol{r} + \boldsymbol{R}_k)]\}} \tag{19.1-1}$$

where the friction tensors $\boldsymbol{\zeta}_k$ are:

$$\boldsymbol{\zeta}_k = \zeta[\boldsymbol{\delta} - (1 - \varepsilon)\boldsymbol{u}_k\boldsymbol{u}_k] \tag{19.1-2}$$

and $\bar{N} = \sum x_\alpha N_\alpha$ is the average number of beads per chain in the polydisperse fluid with mole fractions x_α. This expression for the differences of hydrodynamic forces is a generalization of that introduced in the elementary kinetic theory for dumbbells (see Eqs. 13.2-2 and 13.7-12). In this modified Stokes' law expression three empirical constants appear:[2] the scalar *friction coefficient* ζ, the *link tension coefficient* ε, and the *chain constraint exponent* β. The parameter ε, which determines the anisotropy of the friction tensor, is taken here to be a constant, although it could be taken to be a function of $\dot{\gamma} = (\frac{1}{2}\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})^{1/2}$; if $\varepsilon = 1$ the tensor is isotropic and if $\varepsilon = 0$ there is no component of the difference of the forces on two succeeding beads in the direction of the link joining them (i.e., in the direction of the backbone of the chain). From the viscosity and normal stress curves it has been found that ε is in the range from 0.3 to 0.5 for concentrated solutions and undiluted polymers, both monodisperse and polydisperse. For an explanation of the term "link tension coefficient" see Example 19.1-1. The parameter β is introduced because it appears reasonable that the magnitude of the hydrodynamic force should increase slowly with increasing average length in a polydisperse system. It is found from experimental data on the molecular weight dependence of the zero-shear-rate viscosity that β is about 0.3 to 0.5.

If one assumes homogeneous flow (that is $\boldsymbol{\kappa} = (\nabla\boldsymbol{v})^\dagger$ is independent of position), one may make use of Eq. 16.5-1 to rewrite Eq. 19.1-1, in the form

$$\boldsymbol{F}^{(h)}_{k+1} - \boldsymbol{F}^{(h)}_{k} = -\bar{N}^{\beta}a\boldsymbol{\zeta}_k \cdot ([\![\dot{\boldsymbol{u}}_k]\!] - [\boldsymbol{\kappa}\cdot\boldsymbol{u}_k]) \tag{19.1-3}$$

---

[1] Equation 19.1-1 for Kramers chains in monodisperse concentrated solutions or undiluted polymers was first proposed by C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016–2025, 2026–2033 (1981); the polydisperse expression given in Eq. 19.1-1 is new. Equation 19.1-7 is introduced here for the first time in order to discuss translational diffusion.

[2] In the Doi–Edwards development there is no explicit introduction of a Stokes' law type of expression. A chain friction coefficient is introduced via the Nernst–Einstein equation for a chain undergoing a one-dimensional Brownian motion. The Doi-Edwards constitutive equation results from taking $\varepsilon = 0$ and $\beta = 0$ in our development.

For the sake of comparing with Eq. 18.2-19, the above can be rewritten to show the hydrodynamic force on the νth bead

$$\boldsymbol{F}_\nu^{(h)} = -\sum_\mu \tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot (\llbracket \dot{\boldsymbol{R}}_\mu \rrbracket - [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu]) + \frac{1}{N} \boldsymbol{F}^{(h)} \tag{19.1-4}$$

where

$$\tilde{\boldsymbol{\zeta}}_{\nu\mu} = \bar{N}^\beta \sum_j B_{\nu j} \zeta_j \bar{B}_{j\mu} \tag{19.1-5}$$

and

$$\boldsymbol{F}^{(h)} = \sum_\nu \boldsymbol{F}_\nu^{(h)} \tag{19.1-6}$$

is the total hydrodynamic force on a molecule. It is to be noted that the tensors $\tilde{\boldsymbol{\zeta}}_{\nu\mu}$ defined here are not the same as those introduced in §18.2 and Table 16.1-2, but it is convenient to use the same symbol because of the resulting similarity of this equation with Eq. 18.2-19.

Since only the hydrodynamic force differences are introduced by Eq. 19.1-1, the total force $\boldsymbol{F}^{(h)}$ is not yet specified. In this development we take the total hydrodynamic force on a molecule of species α to be

$$\boxed{\boldsymbol{F}^{(h)\alpha} = -\zeta^\alpha(\llbracket \dot{\boldsymbol{r}}^\alpha \rrbracket - \boldsymbol{v}(\boldsymbol{r}^\alpha))} \tag{19.1-7}$$

where ζ^α is the (scalar) friction coefficient of the molecule as a whole. This expression is used in §19.4 to develop an expression for the translational diffusion coefficient.

The next step in the development is to obtain an expression for the average generalized velocities $\llbracket \dot{Q}_{ip} \rrbracket$, which when introduced into the equation of continuity leads to the diffusion equation for the distribution function. Because of the similarity of Eq. 19.1-4 to Eq. 18.2-19, much of this development follows closely that of §18.2. As in the previous development, we first note that Eq. 17.1-5 (the definition of the base vectors) can be used to rewrite the expression for $\boldsymbol{F}_\nu^{(h)}$ in Eq. 19.1-4 as

$$\boldsymbol{F}_\nu^{(h)} = \frac{1}{N} \boldsymbol{F}^{(h)} - \sum_{\mu i p} \frac{1}{\sqrt{m}} [\tilde{\boldsymbol{\zeta}}_{\mu\nu} \cdot \boldsymbol{b}_{\mu, ip}] \llbracket \dot{Q}_{ip} \rrbracket + \sum_\mu [\tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu] \tag{19.1-8}$$

From this we obtain a result (similar to Eq. 18.2-24) associated with each of the generalized coordinates Q_{ip}, that is, the polar angles θ_i and ϕ_i specifying the direction, $\boldsymbol{u}_i$, of link i,

$$\bar{N} \sum_\nu \frac{1}{\sqrt{m}} (\boldsymbol{b}_{\nu, ip} \cdot \boldsymbol{F}_\nu^{(h)}) = -\sum_j \sum_q \tilde{g}_{ip, jq} \llbracket \dot{Q}_{jq} \rrbracket + (\mathbf{M}_{ip} : \boldsymbol{\kappa}) \tag{19.1-9}$$

where the metric matrix elements are

$$\tilde{g}_{ip, jq} = \frac{\bar{N}}{m} \sum_\nu \sum_\mu (\boldsymbol{b}_{\nu, ip} \cdot \tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{b}_{\mu, jq}) \tag{19.1-10}$$

and the coupling tensors are

$$\mathbf{M}_{ip} = \frac{\bar{N}}{\sqrt{m}} \sum_{\nu} \sum_{\mu} \{\boldsymbol{R}_{\mu} \boldsymbol{b}_{\nu, ip} \cdot \tilde{\zeta}_{\nu\mu}\} \tag{19.1-11}$$

It follows from the definition of the $\tilde{g}_{ip, jq}$ (Eq. 19.1-10), the expressions for the base vectors (Eq. 16.5-4), and the definition of the $\tilde{\zeta}_{\nu\mu}$ (Eq. 19.1-5) that

$$\tilde{g}_{ip, jq} = \frac{\bar{N}^{1+\beta}\zeta}{m} g_{ip, jq} \tag{19.1-12}$$

The elements of the inverse matrix are then

$$\tilde{G}_{ip, jq} = \frac{m}{\bar{N}^{1+\beta}\zeta} G_{ip, jq} \tag{19.1-13}$$

where the $G_{ip, jq}$ are given by Eq. 16.5-8. Note that the $\tilde{g}_{ip, jq}$ and the $\tilde{G}_{ip, jq}$ introduced here are not the same as the quantities defined in §18.2 and Table 16.1-2 (see the comment regarding $\tilde{\zeta}_{\nu\mu}$ after Eq. 19.1-6). Thus paralleling the development of §18.2, we find

$$[\![\dot{Q}_{ip}]\!] = \frac{m}{\bar{N}^{1+\beta}\zeta} \sum_{j} \sum_{q} G_{ip, jq} (\mathscr{F}_{jq}^{(e)} + \mathscr{F}_{jq}^{(b)} + \mathbf{M}_{jq} : \boldsymbol{\kappa}) \tag{19.1-14}$$

as the analogue of Eq. 18.2-43.

The last result may be used in the equation of continuity (Eq. 17.5-14); if one neglects the external forces one then finds that

$$\boxed{\frac{\partial \Psi_{\alpha}}{\partial t} = -\frac{1}{\bar{N}^{1+\beta}\zeta a^2} \sum_{ijklpq} A_{ik} A_{jl} \frac{\partial}{\partial Q_{ip}} [(\mathbf{K}_{kl} : \boldsymbol{d}_{jq} \boldsymbol{d}_{ip})(\mathscr{F}_{jq}^{(b)} + \mathbf{M}_{jq} : \boldsymbol{\kappa})\Psi_{\alpha}]} \tag{19.1-15}$$

where the $\mathbf{K}_{kl}$ are the Kramers tensors defined by Eq. 16.5-9. When one introduces into this equation an approximation for the generalized Brownian forces, $\mathscr{F}_{jq}^{(b)}$, as functions in the configurational space, this equation becomes the diffusion equation for the configurational distribution functions Ψ_{α}.

EXAMPLE 19.1-1 The Link Tension Coefficient

Consider a polymer chain in a steady elongational flow $v_z = \dot{\varepsilon} z$, $v_x = -\frac{1}{2}\dot{\varepsilon} x$, $v_y = -\frac{1}{2}\dot{\varepsilon} y$, where $\dot{\varepsilon}$ is the (constant) elongational rate. Obtain an expression for the tension in a link aligned with the axis of stretching (link "A" in Fig. 19.1-1) and in a link perpendicular to it (link "B" in Fig. 19.1-1).

SOLUTION Equations 19.1-2 and 19.1-3 can be combined, and the resulting expression can be dotted into $\boldsymbol{u}_k$ to give

$$((\boldsymbol{F}_{k+1}^{(h)} - \boldsymbol{F}_{k}^{(h)}) \cdot \boldsymbol{u}_k) = \varepsilon \bar{N}^{\beta} a \zeta (\boldsymbol{\kappa} : \boldsymbol{u}_k \boldsymbol{u}_k) \tag{19.1-16}$$

In steady elongational flow $\boldsymbol{\kappa} = [-\frac{1}{2}(\boldsymbol{\delta}_x \boldsymbol{\delta}_x + \boldsymbol{\delta}_y \boldsymbol{\delta}_y) + \boldsymbol{\delta}_z \boldsymbol{\delta}_z]\dot{\varepsilon}$. For a link aligned with the axis of stretching, $\boldsymbol{u}_k = \boldsymbol{\delta}_z$, and

$$((\boldsymbol{F}_{k+1}^{(h)} - \boldsymbol{F}_{k}^{(h)}) \cdot \boldsymbol{u}_k) = \varepsilon \bar{N}^{\beta} a \zeta \dot{\varepsilon} \tag{19.1-17}$$

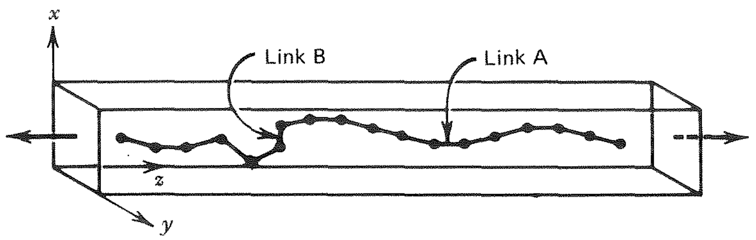

FIGURE 19.1-1. A Kramers chain, representing a macromolecule, in a steady elongational flow. The tension in link A, aligned with the z-axis, is $\varepsilon \bar{N}^{\beta} a \zeta \dot{\varepsilon}$, whereas the tension in link B, aligned with the x-axis, is $-\frac{1}{2}\varepsilon \bar{N}^{\beta} a \zeta \dot{\varepsilon}$. This shows why ε is called the "link tension coefficient."

is the tension in the link. Similarly for a link aligned with, say, the x-axis, the tension is given by

$$((\boldsymbol{F}^{(h)}_{k+1} - \boldsymbol{F}^{(h)}_{k}) \cdot \boldsymbol{u}_k) = -\tfrac{1}{2}\varepsilon \bar{N}^{\beta} a \zeta \dot{\varepsilon} \tag{19.1-18}$$

That is, in this case the link feels a compressive force. If one chooses ε to be zero, there is no tension in a link.[3]

§19.2 THE BROWNIAN FORCES

A general expression for the generalized Brownian force is given by Eq. 18.3-7. For the Kramers bead-rod-chain model, in which the beads are taken to be mass points without structure, the second and third terms are zero, and the remaining term can be written as

$$\begin{aligned} \mathscr{F}^{(b)}_{ip} &= -\frac{m}{\Psi_\alpha} \sum_{\nu\mu jq} B_{\nu i} \bar{B}_{j\mu} \boldsymbol{c}_{ip} \cdot \frac{\partial}{\partial Q_{jq}} [\boldsymbol{d}_{jq} \cdot \llbracket \dot{\boldsymbol{R}}_\mu \dot{\boldsymbol{R}}_\nu \rrbracket \Psi_\alpha] \\ &= -\frac{ma^2}{\Psi_\alpha} \sum_{jkq} C_{ik} \boldsymbol{c}_{ip} \cdot \frac{\partial}{\partial Q_{jq}} [\boldsymbol{d}_{jq} \cdot \llbracket \dot{\boldsymbol{u}}_j \dot{\boldsymbol{u}}_k \rrbracket \Psi_\alpha] \end{aligned} \tag{19.2-1}$$

To eliminate the momentum coordinates from the problem we introduce an approximation for the momentum-space averages, $\llbracket \dot{\boldsymbol{u}}_j \dot{\boldsymbol{u}}_k \rrbracket$, arising in the above equation. Then when this expression for $\mathscr{F}^{(b)}_{ip}$ is inserted into Eq. 19.1-14, the latter no longer requires information about the momentum-space distribution function.

a. Equilibration-in-Momentum-Space Approximation

The averages of the products of velocities can be rewritten in terms of products of generalized momenta by using Eqs. 17.1-14 and 16.5-4:

$$\begin{aligned} \llbracket \dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j \rrbracket &= \sum_p \sum_q \llbracket \dot{Q}_{ip} \dot{Q}_{jq} \rrbracket \boldsymbol{c}_{ip} \boldsymbol{c}_{jq} \\ &= \sum_{pqkrls} G_{ip,kr} G_{jq,ls} \llbracket P_{kr} P_{ls} \rrbracket \boldsymbol{c}_{ip} \boldsymbol{c}_{jq} \end{aligned} \tag{19.2-2}$$

---

[3] This lack of tension for $\varepsilon = 0$ seems to correspond to the assumption of Doi and Edwards, in their theory, that all springs in their "slip-link network" have a uniform tension (F_{eq}) regardless of the flow field.

If we assume equilibration in momentum space (cf. §18.3a), then we find by using Eq. 12.4-10 that

$$[\![\dot{u}_i\dot{u}_j]\!]_{\mathrm{eq}} = kT\sum_p\sum_q G_{ip,jq}c_{ip}c_{jq} \tag{19.2-3}$$

and by using the expression for the metric matrix elements, Eq. 16.5-8, that

$$\begin{aligned}[\![\dot{\boldsymbol{u}}_i\dot{\boldsymbol{u}}_j]\!]_{\mathrm{eq}} &= \frac{kT}{ma^2}\sum_{kl} A_{ik}A_{jl}(\boldsymbol{\delta} - \boldsymbol{u}_i\boldsymbol{u}_i)\cdot\mathbf{K}_{kl}\cdot(\boldsymbol{\delta} - \boldsymbol{u}_j\boldsymbol{u}_j) \\ &= \frac{kT}{ma^2}\sum_{kl} A_{ik}A_{jl}\mathbf{K}_{kl}\end{aligned} \tag{19.2-4}$$

If one uses this expression in Eq. 19.2-1, one obtains an expression for the effective Brownian forces in the approximation of equilibration in momentum space.

b. Reptation Approximation

On the other hand, as a different approximation, we may assume that

$$[\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}(\boldsymbol{r}_c))(\dot{\boldsymbol{r}}_\mu - \boldsymbol{v}(\boldsymbol{r}_c))]\!] = \frac{\alpha}{4}(\boldsymbol{u}_{\nu-1} + \boldsymbol{u}_\nu)(\boldsymbol{u}_{\mu-1} + \boldsymbol{u}_\mu) \tag{19.2-5}$$

where α is a scalar coefficient. The idea behind this approximation is the concept of *reptating*[1] motion, that is, that "on the average" the velocity of a bead relative to the macroscopic velocity, $\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}$, is in the direction of the chain, a direction which is the average of that of the two links associated with the bead. The end beads, of course, must be considered somewhat differently. This idea was introduced earlier in §13.7 in the discussion of encapsulated dumbbells. It should be pointed out, however, that since Eq. 19.2-5 evaluated at equilibrium is inconsistent with Eq. 19.2-4, the reptation approximation cannot be exact at equilibrium. Nevertheless, it appears to be a good approximation away from equilibrium.

To obtain a reasonable estimate of the coefficient α, we note that at equilibrium

$$\begin{aligned}\sum_\nu [\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})\cdot(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!] &= \frac{1}{m}\sum_{\nu ipjq}(\boldsymbol{b}_{\nu,ip}\cdot\boldsymbol{b}_{\nu,jq})[\![\dot{Q}_{ip}\dot{Q}_{jq}]\!] \\ &= \frac{1}{m}\sum_{ipjq} G_{ip,jq}[\![P_{ip}P_{jq}]\!] \\ &= \frac{2(N-1)kT}{m}\end{aligned} \tag{19.2-6}$$

---

[1] The notion of *reptation* ("snakelike motion") was first proposed by P. -G. de Gennes, *J. Chem. Phys.*, **55**, 572–579 (1971); see also P.-G. de Gennes, *Phys. Today*, **36**, 33–39 (1983). The first use of reptation in polymer kinetic theory and rheology was by M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789–1832 (1978); **75**, 38–154 (1979).

That is, the total kinetic energy in a coordinate system moving with the stream velocity, $\boldsymbol{v}$, is $(N - 1)kT$, which is $\frac{1}{2}kT$ for each degree of freedom. Introducing the approximation Eq. 19.2-5 into this result and neglecting the complications at the ends we find

$$\alpha = \frac{4(N - 1)kT/m}{N + \sum_\nu (\boldsymbol{u}_{\nu-1} \cdot \boldsymbol{u}_\nu)} \tag{19.2-7}$$

as the value of quantity α.

Making use of Eq. 16.5-1, we find that Eq. 19.2-5 implies that

$$[\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!]_{\text{rep}} = \frac{\alpha}{a^2} (\delta \boldsymbol{u}_i)(\delta \boldsymbol{u}_j) \tag{19.2-8}$$

where

$$\delta \boldsymbol{u}_i = \tfrac{1}{2}(\boldsymbol{u}_{i+1} - \boldsymbol{u}_{i-1}) \tag{19.2-9}$$

This expression is to be compared with that given by Eq. 19.2-4 which results from assuming equilibration in momentum space.

c. Superposition Approximation

The approximation for the momentum average, $[\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!]$, that we use in the present development is obtained by combining the two approximations just considered:

$$\begin{aligned}[\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!] &= (1 - \varepsilon')[\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!]_{\text{rep}} + \varepsilon'[\![\boldsymbol{u}_i \boldsymbol{u}_j]\!]_{\text{eq}} \\ &= \frac{(1 - \varepsilon')}{a^2} \alpha(\delta \boldsymbol{u}_i)(\delta \boldsymbol{u}_j) + \frac{\varepsilon' kT}{ma^2} \sum_{kl} A_{ik} A_{jl} \mathbf{K}_{kl}\end{aligned} \tag{19.2-10}$$

where ε' is the *reptation coefficient*. In the Doi–Edwards and Curtiss–Bird theories ε' is taken to be zero, but here we take ε' to be a function of $\dot{\gamma} = (\frac{1}{2}\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})^{1/2}$ such that $\varepsilon' = 1$ when $\dot{\gamma} = 0$ (that is, at equilibrium) and $0 \leq \varepsilon' \leq 1$ otherwise (that is, away from equilibrium). Except for these conditions the form of ε' is not specified.

When the superposition approximation is introduced into Eq. 19.2-1, we obtain

$$\boxed{\begin{aligned}\mathscr{F}_{ip}^{(b)} = &- \frac{kT}{\Psi_\alpha} \boldsymbol{c}_{ip} \cdot \sum_{jkq} C_{ik} \frac{\partial}{\partial \boldsymbol{Q}_{jq}} \\ &\times \left[\boldsymbol{d}_{jq} \cdot \left(\frac{m\alpha}{kT} (1 - \varepsilon')(\delta \boldsymbol{u}_j)(\delta \boldsymbol{u}_k) + \varepsilon' \sum_{lm} A_{jl} A_{km} \mathbf{K}_{lm} \right) \right] \Psi_a\end{aligned}} \tag{19.2-11}$$

as an approximation for the generalized Brownian force.

Next, we introduce the expressions for the generalized Brownian force and the coupling tensor $\mathbf{M}_{ip}$ (from Eq. 19.1-11) into the equation of continuity, Eq. 19.1-15. In doing this, however, we note that

$$\begin{aligned}\sum_{lq} A_{jl}\{\mathbf{K}_{kl}\cdot \boldsymbol{d}_{jq}\boldsymbol{c}_{jq}\} &= \sum_{l} A_{jl}\{\mathbf{K}_{kl}\cdot(\boldsymbol{\delta} - \boldsymbol{u}_j\boldsymbol{u}_j)\}\\ &= \sum_{l} A_{jl}\mathbf{K}_{kl} \end{aligned}\tag{19.2-12}$$

Thus, we obtain

$$\begin{aligned}\frac{\partial}{\partial t}\Psi_\alpha = {} & \frac{kT}{\bar{N}^{1+\beta}\zeta a^2}\sum_{ijklpq} A_{ik}\frac{\partial}{\partial Q_{ip}}\\ & \times\left(\boldsymbol{d}_{ip}\cdot\mathbf{K}_{kl}\cdot\left[\frac{\partial}{\partial Q_{jq}}\boldsymbol{d}_{jq}\cdot\left(\frac{m\alpha}{kT}(1-\varepsilon')(\delta\boldsymbol{u}_j)(\delta\boldsymbol{u}_l)\Psi_\alpha + \varepsilon'\sum_{mn} A_{jm}A_{ln}\mathbf{K}_{mn}\Psi_\alpha\right)\right]\right)\\ & - \frac{1}{\zeta}\sum_{iklp} A_{ik}\frac{\partial}{\partial Q_{ip}}(\boldsymbol{d}_{ip}\cdot\mathbf{K}_{kl}\cdot\boldsymbol{\zeta}_l\cdot\boldsymbol{\kappa}\cdot\boldsymbol{u}_l\Psi_\alpha)\\ & - \frac{1}{\bar{N}^{1+\beta}\zeta a^2}\sum_{ijklpq} A_{ik}A_{jl}\frac{\partial}{\partial Q_{ip}}(\boldsymbol{d}_{ip}\cdot\mathbf{K}_{kl}\cdot\boldsymbol{d}_{jq}\mathscr{F}_{jq}^{(e)}\Psi_\alpha)\end{aligned}\tag{19.2-13}$$

This is the diffusion equation in the configuration space of a single molecule of species α.

§19.3 THE SINGLE-LINK DISTRIBUTION FUNCTION

In the discussion of polymer melts we introduce the "mild-curvature" approximation which was not used in the theory for dilute solutions in Chapter 18. This approximation, which is discussed in more detail later, is the assumption that the configuration-space distribution function, $\Psi_\alpha(Q, t)$, has a significant value only for those configurations in which the chain approximates a curve with continuous derivatives (that is, with no "kinks"). This approximation, which is introduced at two points, reduces the problem to one which involves only the single-link distribution function $f_j^\alpha(\boldsymbol{u}, t)$. This function, which is a contraction of the full configuration-space distribution function, describes the probability that link j in the chain is oriented in the direction $\boldsymbol{u}$.

The single-link distribution function is defined as

$$f_j^\alpha(\boldsymbol{u}, t) = \frac{1}{n_\alpha}\int \delta(\boldsymbol{u}_j - \boldsymbol{u})\Psi_\alpha(Q, t)dQ \tag{19.3-1}$$

From this definition and the definition of Ψ_α, it follows that this function is normalized so that

$$\int f_j^\alpha(\boldsymbol{u}, t)d\boldsymbol{u} = 1 \tag{19.3-2}$$

An equation for the time evolution of the function $f_j^\alpha(\boldsymbol{u}, t)$ is obtained by multiplying the diffusion equation, Eq. 19.2-13, by the appropriate delta function and integrating over the configuration space. Thus one finds that, in the absence of external forces

$$\begin{aligned}\frac{\partial}{\partial t} f_j^\alpha = {} & \frac{kT}{n_\alpha \bar{N}^{1+\beta}\zeta a^2} \sum_{iklpq} A_{jk} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} \\ & \times \left(\boldsymbol{d}_{jp} \cdot \mathbf{K}_{kl} \cdot \left[\frac{\partial}{\partial Q_{iq}} \boldsymbol{d}_{iq} \cdot \left((1 - \varepsilon') \frac{m\alpha}{kT} (\delta \boldsymbol{u}_i)(\delta \boldsymbol{u}_l) \Psi_\alpha + \varepsilon' \sum_{mn} A_{im} A_{ln} \mathbf{K}_{mn} \Psi_\alpha \right) \right] \right) dQ \\ & - \frac{1}{n_\alpha \zeta} \sum_{klp} A_{jk} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \mathbf{K}_{kl} \cdot \boldsymbol{\zeta}_l \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_l \Psi_\alpha) dQ \end{aligned} \tag{19.3-3}$$

With the mild curvature approximation the right side of this equation may be expressed in terms of the single-link distribution function and thus one obtains an equation describing the time evolution of this function. In the next section the use of the same approximation leads to an expression for the stress tensor which involves only averages with respect to the single-link distribution function.

The integrations on the right side of the last equation are over the entire configuration space of the polymer molecule and thus include all possible configurations of the chain. We will, however, assume that the distribution function, $\Psi_\alpha(Q, t)$, is such that only those configurations in which the chain approximates a curve with continuous derivatives contribute significantly to the integrals. That is, we will assume in these integrals that the orientations of adjacent links do not vary significantly. Thus, since the A_{ij} are zero unless $j = i$ or $j = i \pm 1$, we may use Eq. 16.5-9 and make the approximations that

$$\begin{aligned}\sum_k A_{jk} \mathbf{K}_{kl} &= \delta_{jl} \boldsymbol{\delta} - \sum_k A_{jk} \hat{C}_{kl} \boldsymbol{u}_k \boldsymbol{u}_l \\ &\doteq \delta_{jl} \boldsymbol{\delta} - \sum_k \hat{A}_{jk} \hat{C}_{kl} \boldsymbol{u}_j \boldsymbol{u}_l \\ &= \delta_{jl} (\boldsymbol{\delta} - \boldsymbol{u}_j \boldsymbol{u}_l) \end{aligned} \tag{19.3-4}$$

and from Eq. 19.2-7, that for large N

$$\alpha = \frac{2kT}{m} \tag{19.3-5}$$

With these approximations, the equation for the single-link distribution function, Eq. 19.3-3, becomes

$$\begin{aligned}\frac{\partial}{\partial t} f_j^\alpha = {} & \frac{2(1 - \varepsilon')kT}{n_\alpha \bar{N}^{1+\beta}\zeta a^2} \sum_{pq} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} \left\{ \boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{jq}} [\boldsymbol{d}_{jq} \cdot (\delta \boldsymbol{u}_j)(\delta \boldsymbol{u}_j) \Psi_\alpha] \right\} dQ \\ & + \frac{\varepsilon' kT}{n_\alpha \bar{N}^{1+\beta}\zeta a^2} \sum_{ipq} A_{ji} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} \left[\boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{iq}} \boldsymbol{d}_{iq} \Psi_\alpha \right] dQ \\ & - \frac{1}{n_\alpha} \sum_p \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j \Psi_\alpha) dQ \end{aligned} \tag{19.3-6}$$

It is noted in passing that if one introduces the approximation Eq. 19.3-4 into the expression for the generalized Brownian force, Eq. 19.2-11, and sets $\varepsilon' = 1$, (that is, assumes equilibration in momentum space) one finds that

$$\begin{aligned}\mathscr{F}_{ip}^{(b)} &= -\frac{kT}{\Psi_\alpha} c_{ip}\cdot\sum_q \frac{\partial}{\partial Q_{iq}} d_{iq}\Psi_\alpha \\ &= -kT\frac{\partial}{\partial Q_{ip}}\ln\left(\frac{\Psi_\alpha}{\sin\theta_i}\right)\end{aligned} \tag{19.3-7}$$

This result is identical with that given by Eq. 18.3-5, if in the latter the determinant of the metric tensor, g, is approximated by the value obtained in the random-walk approximation (see §12.3(a)).

With some manipulation the terms on the right of Eq. 19.3-6 may be expressed in terms of the single-link distribution function, and thus one obtains a diffusion equation for this function. We consider, first, the second term on the right. The terms in the sum with $i \neq j$ become zero when the integration over the coordinate Q_{iq} is carried out. Thus, this term becomes

$$\frac{2\varepsilon' kT}{\bar{N}^{1+\beta}\zeta a^2}\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}} f_j^\alpha \tag{19.3-8}$$

The transformation of the first term on the right of Eq. 19.3-6 is somewhat more lengthy. From the definition of the single-link distribution function, Eq. 19.3-1, one finds that for integer k,

$$f_{j+k}^\alpha(\boldsymbol{u}, t) = \frac{1}{n_\alpha}\int \delta(\boldsymbol{u}_j + \boldsymbol{u}_{kj} - \boldsymbol{u})\Psi_\alpha(Q, t)dQ \tag{19.3-9}$$

where

$$\boldsymbol{u}_{kj} = \boldsymbol{u}_{j+k} - \boldsymbol{u}_j \tag{19.3-10}$$

For sufficiently long chains, one may take the index j, appearing as a subscript on $f_j(\boldsymbol{u}, t)$, to be an argument taking on an essentially continuous range of values. Then the left side of Eq. 19.3-9 may be written as a Taylor series,

$$f_j^\alpha(\boldsymbol{u}, t) + k\frac{\partial}{\partial j}f_j^\alpha(\boldsymbol{u}, t) + \tfrac{1}{2}k^2\frac{\partial^2}{\partial j^2}f_j^\alpha(\boldsymbol{u}, t) + \cdots \tag{19.3-11}$$

In a similar manner one replaces the delta function in the integral on the right of Eq. 19.3-9 by a Taylor series in $\boldsymbol{u}_{kj}$ to obtain as an expression for the right side of the equation

$$\begin{aligned}&\frac{1}{n_\alpha}\int\Psi_\alpha(Q, t)\left\{1 + \sum_p(\Delta Q_{jp})\frac{\partial}{\partial Q_{jp}} + \frac{1}{2}\sum_p\sum_q(\Delta Q_{jp})(\Delta Q_{jq})\frac{\partial}{\partial Q_{jq}}\frac{\partial}{\partial Q_{jq}} + \cdots\right\}\delta(\boldsymbol{u}_j - \boldsymbol{u})dQ \\ &\quad = \frac{1}{n_\alpha}\int\delta(\boldsymbol{u}_j - \boldsymbol{u})\left\{\Psi_\alpha - \sum_p\frac{\partial}{\partial Q_{jp}}[(\Delta Q_{jp})\Psi_\alpha] + \frac{1}{2}\sum_p\sum_q\frac{\partial}{\partial Q_{jp}}\frac{\partial}{\partial Q_{jq}}\right. \\ &\quad\quad \left.\times[(\Delta Q_{jq})(\Delta Q_{jp})\Psi_\alpha] + \cdots\right\}dQ\end{aligned} \tag{19.3-12}$$

where ΔQ_{jp} is the change in the coordinate of $\boldsymbol{u}_j$ associated with the increment $\boldsymbol{u}_{kj}$; that is,

$$\boldsymbol{u}_{kj} = \sum_p \Delta Q_{jp} \cdot \frac{\partial}{\partial Q_{jp}} \boldsymbol{u}_j + \frac{1}{2} \sum_p \sum_q (\Delta Q_{jp})(\Delta Q_{jq}) \frac{\partial}{\partial Q_{jq}} \frac{\partial}{\partial Q_{jp}} \boldsymbol{u}_j + \cdots \tag{19.3-13}$$

The next step is to invert this series and obtain an expression for ΔQ_{jr} as a series in the incremental vector, $\boldsymbol{u}_{kj}$. We first note that the three components of $\boldsymbol{u}_{kj}$ are given as series in ΔQ_{jr} of the form ($r = 1, 2$),

$$(\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) = \Delta Q_{jr} + \frac{1}{2} \sum_p \sum_q (\Delta Q_{jp})(\Delta Q_{jq}) \left(\boldsymbol{d}_{jr} \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{c}_{jp} \right) + \cdots \tag{19.3-14}$$

$$(\boldsymbol{u}_j \cdot \boldsymbol{u}_{kj}) = \frac{1}{2} \sum_p \sum_q (\Delta Q_{jp})(\Delta Q_{jq}) \left(\boldsymbol{u}_j \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{c}_{jp} \right) + \cdots \tag{19.3-15}$$

From the first of these relations one finds that

$$\begin{aligned} \Delta Q_{jr} &= (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) - \frac{1}{2} \sum_p \sum_q (\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jp}\boldsymbol{d}_{jq}) \left(\boldsymbol{d}_{jr} \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{c}_{jp} \right) + \cdots \\ &= (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) + \frac{1}{2} \sum_p \sum_q (\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jq}\boldsymbol{d}_{jp}) \left(\boldsymbol{c}_{jp} \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{d}_{jr} \right) + \cdots \\ &= (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) + \frac{1}{2} \sum_q \left(\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jq}(\boldsymbol{\delta} - \boldsymbol{u}_j\boldsymbol{u}_j) \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{d}_{jr} \right) + \cdots \end{aligned} \tag{19.3-16}$$

It follows, however, from Eq. 19.3-15 that the second part of the second term in the last form of this series (the term involving $\boldsymbol{u}_j\boldsymbol{u}_j$) is of higher order in the incremental vector $\boldsymbol{u}_{kj}$, and thus one finds that to second order in $\boldsymbol{u}_{kj}$,

$$\Delta Q_{jr} = (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) + \frac{1}{2} \sum_q \left(\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jq} \frac{\partial}{\partial Q_{jq}} \boldsymbol{d}_{jr} \right) + \cdots \tag{19.3-17}$$

When this relation is used in the expression given by Eq. 19.3-13 one finds that the right side of Eq. 19.3-9 is

$$\frac{1}{n_\alpha} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \left[\Psi_\alpha - \sum_p \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \boldsymbol{u}_{kj} \Psi_\alpha) + \frac{1}{2} \sum_p \sum_q \frac{\partial}{\partial Q_{jp}} \left(\boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{jq}} (\boldsymbol{d}_{jq} \cdot \boldsymbol{u}_{kj}\boldsymbol{u}_{kj} \Psi_\alpha) \right) \right] dQ \tag{19.3-18}$$

The third term in this expression is similar in form to the first term on the right of Eq. 19.3-6.

If we again assume that the distribution function $\Psi_\alpha(Q, t)$ is such that only those configurations in which the chain approximates a continuous curve contribute significantly to the integral of the last expression, we may for small values of k replace $\boldsymbol{u}_{kj}$, defined by Eq. 19.3-10, by

$$\boldsymbol{u}_{kj} = k \delta \boldsymbol{u}_j \tag{19.3-19}$$

where $\delta \boldsymbol{u}_j$ is defined by Eq. 19.2-9. One may then equate termwise the two sides of Eq. 19.3-9 as given by Eqs. 19.3-11 and 19.3-18 to find that

$$\frac{1}{n_\alpha} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \sum_p \sum_q \frac{\partial}{\partial Q_{jp}} \left[\boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \delta \boldsymbol{u}_j \delta \boldsymbol{u}_j \Psi_\alpha) \right] dQ = \frac{\partial^2}{\partial j^2} f_j^\alpha(\boldsymbol{u}, t) \qquad (19.3\text{-}20)$$

We have thus expressed the first term on the right of Eq. 19.3-6 in terms of the single-link distribution function.

In the transformation of the third term on the right of Eq. 19.3-6 we use the fact that $\delta(\boldsymbol{u}_j - \boldsymbol{u}) = \delta(\theta_j - \theta)\, \delta(\phi_j - \phi) \sin\theta$.

$$\begin{aligned} \frac{1}{n_\alpha} \sum_p \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j \Psi_\alpha) dQ &= -\frac{1}{n_\alpha} \sum_p \int (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j) \Psi_\alpha \frac{\partial}{\partial Q_{jp}} \delta(\boldsymbol{u}_j - \boldsymbol{u}) dQ \\ &= \frac{1}{n_\alpha} \sum_p \frac{\partial}{\partial Q_p} \int (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j) \Psi_\alpha \delta(\boldsymbol{u}_j - \boldsymbol{u}) dQ \\ &\quad + \frac{1}{n_\alpha} \cot\theta \int (\boldsymbol{d}_{j1} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j) \Psi_\alpha \delta(\boldsymbol{u}_j - \boldsymbol{u}) dQ \\ &= \sum_p \left(\boldsymbol{d}_p \cdot \frac{\partial}{\partial Q_p} \boldsymbol{\kappa} \cdot \boldsymbol{u} f_j^\alpha \right) - 2(\boldsymbol{u} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}) f_j^\alpha \\ &= \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{u}\boldsymbol{u}\boldsymbol{u}] f_j^\alpha \right) \qquad (19.3\text{-}21) \end{aligned}$$

One may now combine the results of the previous paragraphs to write Eq. 19.3-6 in the form

$$\frac{\partial}{\partial t} f_j^\alpha = \frac{2(1 - \varepsilon')kT}{\bar{N}^{1+\beta} \zeta a^2} \frac{\partial^2}{\partial j^2} f_j^\alpha + \frac{2\varepsilon' kT}{\bar{N}^{1+\beta} \zeta a^2} \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} f_j^\alpha \right) - \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{u}\boldsymbol{u}\boldsymbol{u}] f_j^\alpha \right) \qquad (19.3\text{-}22)$$

It is convenient to rewrite this equation in a somewhat modified form after introducing several definitions. First, we let

$$\sigma = \frac{j}{N_\alpha} \qquad (19.3\text{-}23)$$

be the fractional distance along a chain and define

$$f_\alpha(\boldsymbol{u}, \sigma, t) = f_j^\alpha(\boldsymbol{u}, t) \qquad (19.3\text{-}24)$$

Then, we let

$$\boxed{\lambda_\alpha = \frac{N_\alpha^2 \bar{N}^{1+\beta} \zeta a^2}{2kT}} \qquad (19.3\text{-}25)$$

be a *characteristic time*[1] associated with chains of length N_α. In terms of these quantities the single-link diffusion equation of species α is

$$\boxed{\frac{\partial f_\alpha}{\partial t} = \frac{(1-\varepsilon')}{\lambda_\alpha}\frac{\partial^2}{\partial\sigma^2}f_\alpha + \frac{\varepsilon' N_\alpha^2}{\lambda_\alpha}\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}}f_\alpha\right) - \left(\frac{\partial}{\partial \boldsymbol{u}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}]f_\alpha\right)} \tag{19.3-26}$$

If $\varepsilon' = 1$ this equation is identical to the diffusion equation for the distribution function of rigid dumbbells, Eq. 14.2-8, except that the rigid dumbbell time constant λ is replaced by $\lambda_\alpha/6N_\alpha^2$, and if $\varepsilon' = 0$ the equation reduces to the corresponding equation developed by Doi and Edwards[1]. In either case the third term on the right describes the perturbation of the single-link distribution function caused by a velocity gradient. The first two terms on the right describe "diffusion" effects associated with the Brownian motion. If one assumes equilibration in momentum space, $\varepsilon' = 1$, and the diffusion term involves the two dimensional gradient operator, $\partial/\partial\boldsymbol{u}$, that is, changes in orientation of the link. If one takes $\varepsilon' = 0$ the Brownian motion described by the first term is reptating motion. It is interesting to note that the parameter ε, which describes the anisotropy of the friction tensor, does not appear in this equation.

§19.4 THE STRESS TENSOR AND THE MASS FLUX

Most of this section deals with the development of an expression for the stress tensor using the general formula given in §18.1. However, at the end of the section we develop an expression for the mass-flux vector and the translational diffusivity starting with the general formula given in §17.6.

a. The Stress Tensor

To obtain an expression for the stress tensor for a polymeric melt consisting of a mixture of molecules of various lengths we return to the general expression given by Eq. 18.1-10 in terms of the hydrodynamic forces, $\boldsymbol{F}_\nu^{(h)\alpha}$, and make use of the expression for these forces given by Eq. 19.1-4. Combining these relations and using Eqs. 16.5-2 and 3, we find that

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k + a^2\bar{N}^{1+\beta}\sum_{\alpha jk} C_{jk}\int \boldsymbol{u}_k\zeta_j\cdot([\![\dot{\boldsymbol{u}}_j]\!] - [\boldsymbol{\kappa}\cdot\boldsymbol{u}_j])\Psi_\alpha\, dQ \tag{19.4-1}$$

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[1] For a *monodisperse* fluid Eq. 19.3-25 becomes $\lambda = N^{3+\beta}\zeta a^2/2kT$. (In their analogous equation M. Doi and S. F. Edwards [*J. Chem. Soc., Faraday Trans. II*, **74**, 1818–1832 (1978)] have $\lambda = \pi^2 T_d$, where $T_d = N^3\zeta a^2/\pi^2 kT$ is the "disengagement time"; that is, there is a difference of a factor of $N^\beta/2$ between the two time constants.) The proportionality $\lambda \propto N^3$ has been obtained by some simple arguments using the "tube model" [see P. G. de Gennes and L. Léger, *Ann. Rev. Phys. Chem.*, **33**, 49–61 (1982) and P. G. De Gennes, *Physics Today*, **36**, 33–39 (1983)]. For *polydisperse* fluids Eq. 19.3-25 contains $\bar{N} = \sum_\alpha x_\alpha N_\alpha$, which is a mole fraction averge of the N_α. Whereas we have $\lambda_\alpha \propto N_\alpha^2\bar{N}^{1+\beta}$, Doi and Edwards recommend $\lambda_\alpha \propto N_\alpha^3$ for species α in a mixture. Example 19.6-1 explores the consequences of this difference in the expression for time constants.

where $\boldsymbol{\pi}_k$ is the contribution of the Brownian motion of the centers of mass of the polymer molecules defined by Eq. 17.6-6. Use of the explicit expression for the friction tensor, Eq. 19.1-2, in this relation then gives

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k + 2kT\sum_{\alpha jk} \frac{\lambda_\alpha C_{jk}}{N_\alpha^2} \int \{\boldsymbol{u}_k [\![\dot{\boldsymbol{u}}_j]\!] - \boldsymbol{u}_k \boldsymbol{u}_j \cdot \boldsymbol{\kappa}^\dagger + (1 - \varepsilon)\boldsymbol{u}_k \boldsymbol{u}_j \boldsymbol{u}_j \boldsymbol{u}_j : \boldsymbol{\kappa}\}\Psi_\alpha \, dQ \qquad (19.4\text{-}2)$$

where λ_α is the time constant associated with molecules of species α as defined by Eq. 19.3-25. To eliminate the momentum average $[\![\dot{\boldsymbol{u}}_j]\!]$ from this expression we make use of the general equation of continuity as given by Eq. 17.5-14; multiplication of the latter by $\boldsymbol{u}_j \boldsymbol{u}_k$ and integration over all configurations gives

$$\begin{aligned}
\frac{\partial}{\partial t} \int \boldsymbol{u}_j \boldsymbol{u}_k \Psi_\alpha \, dQ &= -\sum_i \sum_q \int \boldsymbol{u}_j \boldsymbol{u}_k \frac{\partial}{\partial Q_{iq}} ([\![\dot{Q}_{iq}]\!]\Psi_\alpha) dQ \\
&= \sum_q \int \Psi_\alpha([\![\dot{Q}_{jq}]\!] \boldsymbol{c}_{jq} \boldsymbol{u}_k + [\![\dot{Q}_{kq}]\!] \boldsymbol{u}_j \boldsymbol{c}_{kq}) dQ \\
&= \int \Psi_\alpha([\![\dot{\boldsymbol{u}}_j]\!] \boldsymbol{u}_k + \boldsymbol{u}_j [\![\dot{\boldsymbol{u}}_k]\!]) dQ \qquad (19.4\text{-}3)
\end{aligned}$$

From this relation and the expression for the stress tensor given by Eq. 19.4-2, one finds that the symmetric part of the stress tensor is

$$\begin{aligned}
\boldsymbol{\pi}^{(s)} &= \tfrac{1}{2}(\boldsymbol{\pi} + \boldsymbol{\pi}^\dagger) \\
&= \boldsymbol{\pi}_k + kT \sum_{\alpha jk} \frac{\lambda_\alpha}{N_\alpha^2} C_{jk} \left\{ \frac{\partial}{\partial t} \int \boldsymbol{u}_j \boldsymbol{u}_k \Psi_\alpha \, dQ \right. \\
&\quad - \int \boldsymbol{u}_k \boldsymbol{u}_j \Psi_\alpha \, dQ \cdot \boldsymbol{\kappa}^\dagger - \boldsymbol{\kappa} \cdot \int \boldsymbol{u}_j \boldsymbol{u}_k \Psi_\alpha \, dQ \\
&\quad \left. + (1 - \varepsilon) \int (\boldsymbol{u}_k \boldsymbol{u}_j + \boldsymbol{u}_j \boldsymbol{u}_k) \boldsymbol{u}_j \boldsymbol{u}_j \Psi_\alpha \, dQ : \boldsymbol{\kappa} \right\} \qquad (19.4\text{-}4)
\end{aligned}$$

The contribution to the stress tensor of the Brownian motion of the centers of mass of the molecules as given by Eq. 17.6-6 is

$$\boldsymbol{\pi}_k = m \sum_\alpha N_\alpha \int [\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!]^\alpha \Psi_\alpha(Q, t) dQ \qquad (19.4\text{-}5)$$

If one assumes equilibration in momentum space this expression leads to an isotropic term

$$\boldsymbol{\pi}_k = kT\boldsymbol{\delta} \sum_\alpha n_\alpha \qquad (19.4\text{-}6)$$

On the other hand if one uses the reptation approximation one finds from Eq. 19.2-5 that

$$[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!] = \frac{\alpha}{4N_\alpha^2} \sum_j \sum_k (\boldsymbol{u}_{j-1} + \boldsymbol{u}_j)(\boldsymbol{u}_{k-1} + \boldsymbol{u}_k) \tag{19.4-7}$$

Then introducing the mild curvature approximation, we use Eq. 19.3-5 for α and replace $\boldsymbol{u}_{j-1}$ by $\boldsymbol{u}_j$ to find that

$$[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!] = \frac{2kT}{N_\alpha^2 m} \sum_j \sum_k \boldsymbol{u}_j \boldsymbol{u}_k \tag{19.4-8}$$

One then finds from Eq. 19.4-5 that in this reptation approximation

$$\boldsymbol{\pi}_k = 2kT \sum_{\alpha jk} \frac{1}{N_\alpha} \int \boldsymbol{u}_j \boldsymbol{u}_k \Psi_\alpha(Q, t)\, dQ \tag{19.4-9}$$

Next, in analogy with the treatment of the Brownian force in §19.2, we take $\boldsymbol{\pi}_k$ to be a linear combination of this expression and the equilibrium expression given by Eq. 19.4-6,

$$\boldsymbol{\pi}_k = kT \sum_\alpha \left[\varepsilon' n_\alpha \boldsymbol{\delta} + \frac{2(1-\varepsilon')}{N_\alpha} \sum_{jk} \int \boldsymbol{u}_j \boldsymbol{u}_k \Psi_\alpha(Q, t)\, dQ \right] \tag{19.4-10}$$

determined by the same empirical function, ε', of the invariant $\dot{\gamma}$.

The Kramers matrix C_{jk} is a symmetric matrix with elements given by

$$C_{j,j+k} = \frac{j(N-j)}{N} - \frac{jk}{N} \qquad (0 \le k \le N - j - 1)$$

$$C_{j,j-k} = \frac{j(N-j)}{N} - \frac{(N-j)k}{N} \qquad (0 \le k \le j - 1) \tag{19.4-11}$$

(See Eqs. 11.6-7 and the following for more information on the Kramers matrix.) Thus, along any row or column a maximum occurs on the diagonal. To obtain an expression for the stress tensor in terms of the single-link distribution function we again make the mild-curvature approximation. We assume the distribution function Ψ_α is such that in the integrals of those terms in the expression for the symmetric part of the stress tensor, Eq. 19.4-4, which are multiplied by C_{jk} we may approximate $\boldsymbol{u}_k$ by $\boldsymbol{u}_j$. Furthermore, it may be shown[1] that the antisymmetric part of the stress tensor is negligible. Then since $\sum_k C_{jk} = \frac{1}{2} j(N-j)$ we find that

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k + \frac{1}{2} kT \sum_{\alpha j} n_\alpha \lambda_\alpha \frac{j(N_\alpha - j)}{N_\alpha^2} \left\{ \frac{\partial}{\partial t} \langle \boldsymbol{uu} \rangle_j - \langle \boldsymbol{uu} \rangle_j \cdot \boldsymbol{\kappa}^\dagger - \boldsymbol{\kappa} \cdot \langle \boldsymbol{uu} \rangle_j + 2(1-\varepsilon) \langle \boldsymbol{uuuu} \rangle_j : \boldsymbol{\kappa} \right\} \tag{19.4-12}$$

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[1] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, 74, 2016–2033 (1981); see page 2021.

where the angular brackets indicate an average with respect to the single-link distribution function, that is,

$$\langle \boldsymbol{uu} \rangle_j = \int \boldsymbol{uu} f_j(\boldsymbol{u}, t) d\boldsymbol{u} \tag{19.4-13}$$

$$\langle \boldsymbol{uuuu} \rangle_j = \int \boldsymbol{uuuu} f_j(\boldsymbol{u}, t) d\boldsymbol{u} \tag{19.4-14}$$

It is now convenient to introduce again the scaled distance along the chain $\sigma = j/N_\alpha$. One may then rewrite the stress tensor expression as

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k + \frac{1}{2} kT \sum_\alpha n_\alpha N_\alpha \lambda_\alpha \int_0^1 \sigma(1 - \sigma)\{\langle \boldsymbol{uu} \rangle_{(1)} + 2(1 - \varepsilon)\langle \boldsymbol{uuuu} \rangle : \boldsymbol{\kappa}\} d\sigma \tag{19.4-15}$$

where the subscript on $\langle \boldsymbol{uu} \rangle_{(1)}$ indicates the convected derivative of $\langle \boldsymbol{uu} \rangle$, defined in Eq. D.2-4.

It may be shown from the diffusion equation for the single-link distribution function, Eq. 19.3-26, that the convected derivative is

$$\langle \boldsymbol{uu} \rangle_{(1)} = \frac{(1 - \varepsilon')}{\lambda} \frac{\partial^2}{\partial \sigma^2} \langle \boldsymbol{uu} \rangle + \frac{2\varepsilon' N_\alpha^2}{\lambda} \boldsymbol{\delta} - \frac{6\varepsilon' N_\alpha^2}{\lambda} \langle \boldsymbol{uu} \rangle - 2\langle \boldsymbol{uuuu} \rangle : \boldsymbol{\kappa} \tag{19.4-16}$$

With this result the last expression for the stress tensor, Eq. 19.4-15, may be written in an alternative form. In developing this expression we integrate the term involving $(\partial^2/\partial\sigma^2)$ $\langle \boldsymbol{uu} \rangle$ twice by parts assuming that the ends of the chains are oriented at random, that is,

$$f_\alpha(\boldsymbol{u}, 0, t) = f_\alpha(\boldsymbol{u}, 1, t) = \frac{1}{4\pi} \tag{19.4-17}$$

Thus one finds that

$$\boxed{\begin{aligned} \boldsymbol{\pi} = \boldsymbol{\pi}_k + kT \sum_\alpha n_\alpha N_\alpha \Big\{ &(1 - \varepsilon')\left[\frac{1}{3}\boldsymbol{\delta} - \int \langle \boldsymbol{uu} \rangle \, d\sigma\right] \\ &+ \varepsilon' N_\alpha^2 \left[\frac{1}{6}\boldsymbol{\delta} - 3 \int \sigma(1 - \sigma)\langle \boldsymbol{uu} \rangle d\sigma\right] \\ &- \varepsilon \lambda_\alpha \boldsymbol{\kappa} : \int \sigma(1 - \sigma) \langle \boldsymbol{uuuu} \rangle d\sigma \Big\} \end{aligned}} \tag{19.4-18}$$

where λ_α is the time constant of molecules of species α defined by Eq. 19.3-25.

Let us now return to the expression for $\boldsymbol{\pi}_k$, the contribution to the stress tensor of the Brownian motion of the centers of mass of the molecules as given by Eq. 19.4-10. First, we note that isotropic contributions to the stress tensor are of no rheological interest. Next we note that the diagonal terms in the double sum on j and k lead to a contribution to the stress tensor which is of the same form as the integral term at the end of the first line of Eq. 19.4-18 but smaller by a factor of $N_\alpha/2$. It appears reasonable to assume that the correlation between the orientations of successive links falls off sufficiently rapidly with the difference $(j - k)$ that the off-diagonal terms do not contribute enough to overcome this factor. Thus in the subsequent development we neglect[2] π_k; when we do this $\tau = \pi - \pi_k$.

b. The Mass Flux Vector

The mass flux of species α is given by Eq. 17.6-12. If one uses the expression for the total hydrodynamic force on a molecule of this species, Eq. 19.1-7, in this expression one finds

$$\boldsymbol{j}_\alpha = -\frac{m^\alpha}{\zeta^\alpha}\int \boldsymbol{F}^{(h)\alpha}\Psi_\alpha\, dQ - \nabla\cdot\sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!]\Psi_\alpha\, dQ \tag{19.4-19}$$

as the expression for the mass flux. Since the momentum average $[\![\dot{\boldsymbol{R}}_\nu]\!]$ is zero at equilibrium, the term in Eq. 19.4-19 containing this factor is second and higher order in the gradients of the macroscopic variables n_α and $\boldsymbol{v}$; therefore this is a "nonlinear" term. In the present discussion we neglect this term, as well as higher order terms which were already neglected in developing Eq. 17.6-12 from Eq. 17.4-35.

The mass fluxes are defined so that the sum over all α is zero (see Eq. 17.2-15). Thus, if we neglect the last term in Eq. 19.4-19, this equation may be rewritten in the form

$$\boldsymbol{j}_\alpha = -\frac{\rho_\alpha}{\zeta^\alpha}\left[\langle \boldsymbol{F}^{(h)\alpha}\rangle^\alpha - \sum_\beta \frac{\zeta^\alpha \rho_\beta}{\zeta^\beta \rho}\langle \boldsymbol{F}^{(h)\beta}\rangle^\beta\right] \tag{19.4-20}$$

where the angular brackets, $\langle\cdots\rangle^\alpha$, indicate an average over the configuration space with respect to the distribution function Ψ_α. From the force balance, Eq. 17.5-18, one finds that the total hydrodynamic force is simply related to the sum of the total external and Brownian forces. Thus,

$$\bar{N}\langle \boldsymbol{F}^{(h)\alpha}\rangle = -\langle \boldsymbol{F}^{(b)\alpha}\rangle - \langle \boldsymbol{F}^{(e)\alpha}\rangle \tag{19.4-21}$$

The contribution to the mass flux arising from the external forces $\boldsymbol{F}^{(e)\alpha}$ is associated with the concept of mobility, and that arising from the Brownian forces $\boldsymbol{F}^{(b)\alpha}$ will be shown to be associated with the effects of concentration gradients.

An expression for the total Brownian force on the center of mass of a molecule is given by Eq. 17.5-17. The first term in this expression involves the momentum average, $[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!]$, appearing on the left of Eq. 19.4-7, and which arose in the term π_k in the stress tensor (Eq. 19.4-5) describing the effect of this Brownian motion. As discussed in connection with π_k, the evaluation of this term using the reptation concept of Brownian motion requires a knowledge of the correlation among the directions of the links in the Kramers chain. Thus in the evaluation of this term we will assume equilibration in momentum space and use the expression for the Brownian force, $\boldsymbol{F}^{(b)\alpha}$, given by Eq. 18.3-6. With this expression, we find from Eq. 19.4-21 that

$$\bar{N}\langle \boldsymbol{F}^{(h)\alpha}\rangle = \frac{kT}{\rho_\alpha}\nabla\rho_\alpha - \langle \boldsymbol{F}^{(e)\alpha}\rangle^\alpha \tag{19.4-22}$$

---

[2] The center-of-mass motion was considered for the elastic dumbbell model by R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983), Eqs. 3.8 and 3.9.

and thus

$$\boldsymbol{j}_\alpha = -\frac{kT}{\bar{N}\zeta^\alpha}\left[\nabla\rho_\alpha - \frac{\rho_\alpha}{kT}\langle\boldsymbol{F}^{(e)\alpha}\rangle^\alpha - \sum_\beta \frac{\zeta^\alpha\rho_\alpha}{\zeta^\beta\rho}\left(\nabla\rho_\beta - \frac{\rho_\beta}{kT}\langle\boldsymbol{F}^{(e)\beta}\rangle^\beta\right)\right] \tag{19.4-23}$$

This expression may be rewritten as

$$\boldsymbol{j}_\alpha = -\sum_\beta D_{\text{tr}}^{\alpha\beta}\left[\nabla\rho_\beta - \frac{\rho_\beta}{kT}\langle\boldsymbol{F}^{(e)\beta}\rangle^\beta\right] \tag{19.4-24}$$

where the quantities

$$D_{\text{tr}}^{\alpha\beta} = \frac{kT}{\bar{N}\zeta^\beta}\left(\delta_{\alpha\beta} - \frac{\rho_\alpha}{\rho}\right) \tag{19.4-25}$$

form a matrix of translational diffusion coefficients.

We now turn our attention to the mass flux of a species α which is present only in a trace amount, so that $\rho_\alpha/\rho \ll 1$. Then it follows from Eq. 19.4-25 that $D_{\text{tr}}^{\alpha\beta}$ is diagonal ($D_{\text{tr}}^{\alpha\beta} = D_{\text{tr}}^\alpha\delta_{\alpha\beta}$) and

$$D_{\text{tr}}^\alpha = \frac{kT}{\bar{N}\zeta^\alpha} \tag{19.4-26}$$

For this situation the mass flux becomes

$$\boxed{\boldsymbol{j}_\alpha = -D_{\text{tr}}^\alpha\left(\nabla\rho_\alpha - \frac{\rho_\alpha}{kT}\langle\boldsymbol{F}^{(e)\alpha}\rangle^\alpha\right)} \tag{19.4-27}$$

This equation has the same form as Eq. 18.4-32, although the averaging of $\boldsymbol{F}^{(e)\alpha}$ is different. If we now let $\zeta^\alpha = (N_\alpha^2/\bar{N})\zeta$, where ζ is the single-bead friction coefficient, then one finds from Eq. 19.4-26 that

$$\boxed{D_{\text{tr}}^\alpha = \frac{kT}{N_\alpha^2\zeta}} \tag{19.4-28}$$

The above empiricism for ζ^α leads to an M_α^{-2} dependence for the self-diffusion of species α and also for a trace of polymer α diffusing in polymer β; this appears to describe the limited experimental data available[3]. A similar result has been obtained by "scaling arguments."[4]

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[3] M. Tirrell, *Rubber Chem. and Tech.*, **57**, 523-556 (1984).

[4] P.-G. de Gennes and L. Léger, *Ann. Rev. Phys. Chem.*, **33**, 49-61 (1982); P.-G. de Gennes, *Phys. Today*, **36**, 33-39 (1983).

§19.5 SOLUTION OF THE DIFFUSION EQUATION FOR THE SINGLE-LINK DISTRIBUTION FUNCTION

In this section we discuss the solution of the diffusion equation for the single link distribution function, Eq. 19.3-26, which is consistent with the assumption that the end links are oriented randomly as described by Eqs. 19.4-17. For this purpose we first define a function $F(\boldsymbol{u}, t, t')$ as the solution of the equation

$$\frac{\partial}{\partial t} F = \frac{\varepsilon' N^2}{\lambda}\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} F\right) - \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{u}\boldsymbol{u}\boldsymbol{u}]F\right) \tag{19.5-1}$$

subject to the "initial" condition that at $t = t'$

$$F(\boldsymbol{u}, t', t') = \frac{1}{4\pi} \tag{19.5-2}$$

It is to be noted that this equation is identical to that which determines the distribution function of rigid rods, Eq. 14.2-8, except that the time constant λ is replaced by $\lambda/6\varepsilon' N^2$. However, in this discussion the normalization condition, Eq. 14.1-3, is replaced by the initial condition, Eq. 19.5-2.

Next we will show that the required solution of the diffusion equation, Eq. 19.3-26, may be written as a time average of the function, $F(\boldsymbol{u}, t, t')$,

$$f(\boldsymbol{u}, \sigma, t) = \int_{-\infty}^{t} P(\varepsilon', \sigma, t - t')F(\boldsymbol{u}, t, t')dt' \tag{19.5-3}$$

involving the probability per unit time

$$P(\varepsilon', \sigma, s) = \frac{4(1 - \varepsilon')}{\pi} \sum_{n,\,\mathrm{odd}} \frac{1}{n\lambda_n^{(r)}} (\sin n\pi\sigma) e^{-(1-\varepsilon')s/\lambda_n^{(r)}} \tag{19.5-4}$$

and a series of time constants associated with the purely reptational motion

$$\lambda_n^{(r)} = \frac{\lambda}{\pi^2 n^2} \tag{19.5-5}$$

It may be shown from properties of Fourier series that

$$\int_0^{\infty} P(\varepsilon', \sigma, s)ds = \frac{4}{\pi} \sum_{n,\,\mathrm{odd}} \frac{1}{n} (\sin n\pi\sigma) = 1 \tag{19.5-6}$$

We will next show that the expression on the right of Eq. 19.5-3 is (1) a solution of the diffusion equation, (2) properly normalized, and (3) consistent with the conditions that the ends of the chain are oriented randomly (as described by Eq. 19.4-17).

To show that the expression on the right of 19.5-3 is a solution of the diffusion equation we differentiate with respect to t to find that

$$\begin{aligned}\frac{\partial}{\partial t} f = &\frac{(1-\varepsilon')}{\lambda} \sum_{n,\,\mathrm{odd}} n(\sin n\pi\sigma) \\ &- \frac{4(1-\varepsilon')^2}{\pi} \sum_{n,\,\mathrm{odd}} \frac{1}{n\lambda_n^{(r)2}} (\sin n\pi\sigma) \int_{-\infty}^{t} e^{-(1-\varepsilon')(t-t')/\lambda_n^{(r)}} F(\boldsymbol{u}, t, t')\, dt' \\ &+ \int_{-\infty}^{t} P(\varepsilon', \sigma, t-t') \left[\frac{\varepsilon' N^2}{\lambda} \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} F(\boldsymbol{u}, t, t') \right) \right. \\ &\left. - \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] F(\boldsymbol{u}, t, t') \right) \right] dt' \end{aligned} \qquad (19.5\text{-}7)$$

The first term on the right arises from differentiating the upper limit of the integral and making use of the initial condition, Eq. 19.5-2; the second term arises from differentiating $P(\varepsilon', \sigma, t - t')$, and the third term from differentiating $F(\boldsymbol{u}, t, t')$ and using the defining equation, Eq. 19.5-1. The first term may be shown to be zero and the remaining terms lead to the terms on the right of the diffusion equation.

Next we show that the solution, Eq. 19.5-3, is properly normalized. For this purpose we first integrate Eq. 19.5-1 over $\boldsymbol{u}$ and make use of Eqs. E.7-1 and E.7-2 to find that

$$\frac{\partial}{\partial t} \int F(\boldsymbol{u}, t, t') d\boldsymbol{u} = 0 \qquad (19.5\text{-}8)$$

that is, the normalization of the function is independent of time, and thus from the initial condition, Eq. 19.5-2

$$\int F(\boldsymbol{u}, t, t') d\boldsymbol{u} = 1 \qquad (19.5\text{-}9)$$

Then on integrating the expression for $f(\boldsymbol{u}, \sigma, t)$, Eq. 19.5-3, and making use of the normalization of $P(\varepsilon', \sigma, s)$, Eq. 19.5-6, one finds that

$$\int f(\boldsymbol{u}, \sigma, t) d\boldsymbol{u} = 1 \qquad (19.5\text{-}10)$$

and thus the solution is normalized.

Finally, we consider the form of the solution, Eq. 19.5-3, near $\sigma = 0$ and $\sigma = 1$. Since at these points, $\sin n\pi\sigma = 0$, near these points only those terms with very large n contribute to the sum. In these terms if $\varepsilon' < 1$ the only contribution to the integrals arises from values of t' near t, where $F(\boldsymbol{u}, t, t') \doteq 1/4\pi$. Thus, for these values of σ,

$$f(\boldsymbol{u}, \sigma, t) \rightarrow \frac{1}{4\pi} \int_{-\infty}^{t} P(\varepsilon', \sigma, t - t') dt' = \frac{1}{4\pi} \qquad (19.5\text{-}11)$$

That is, if ε' is not exactly unity, the end links are oriented randomly;[1] it is clear from the form of the diffusion equation that for $\varepsilon' = 1$, the solution is independent of σ.

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[1] The form of the distribution function near $\sigma = 0$ and 1 for steady flows to first order in $\dot{\gamma}$ is discussed in more detail near the end of this section (see Eqs. 19.5-21 and 24).

a. Exact Solution in the Pure Reptation Limit ($\varepsilon' = 0$)

Next we consider the solution of the equation for $F(\boldsymbol{u}, t, t')$ Eq. 19.5-1, in the pure reptation limit in which $\varepsilon' = 0$. For this purpose, we first consider the properties of the finite strain tensor, $\boldsymbol{\gamma}^{[0]}(t, t')$, which are discussed briefly in Appendix D. From Eq. D.3-3 it may be shown that

$$\frac{\partial}{\partial t}\boldsymbol{\gamma}^{[0]}(t, t') = -(\boldsymbol{\kappa} + \boldsymbol{\kappa}^{\dagger}) - \{\boldsymbol{\gamma}^{[0]}\cdot\boldsymbol{\kappa} + \boldsymbol{\kappa}^{\dagger}\cdot\boldsymbol{\gamma}^{[0]}\} \tag{19.5-12}$$

in which $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa}^{\dagger}$ may be functions of t. From this it follows that

$$\frac{\partial}{\partial t}[1 + (\boldsymbol{\gamma}^{[0]}:\boldsymbol{uu})]^{-3/2} = -\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}](1 + \boldsymbol{\gamma}^{[0]}:\boldsymbol{uu})^{-3/2}\right) \tag{19.5-13}$$

On comparing this equation with Eq. 19.5-1 one finds that in the limit that $\varepsilon' = 0$,

$$F(\boldsymbol{u}, t, t') = \frac{1}{4\pi(1 + \boldsymbol{\gamma}^{[0]}:\boldsymbol{uu})^{3/2}} \tag{19.5-14)^{2} \quad (}$$

When this expression is used in Eq. 19.5-3, with $\varepsilon' = 0$, one obtains the solution of the diffusion equation, in the "reptating" limit,

$$\boxed{f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\int_{-\infty}^{t}\frac{P(\sigma, t - t')}{(1 + \boldsymbol{\gamma}^{[0]}:\boldsymbol{uu})^{3/2}}\,dt'} \tag{19.5-15}$$

where

$$\begin{aligned} P(\sigma, s) &= P(0, \sigma, s) \\ &= \frac{4\pi}{\lambda}\sum_{n,\text{odd}} n(\sin \pi n\sigma)\exp(-s/\lambda_n^{(r)}) \end{aligned} \tag{19.5-16}$$

---

[2] Equation 19.5-14 was first obtained by C. F. Curtiss and R. B. Bird [*J. Chem. Phys.*, 74, 2016–2033 (1981)] by transforming the expression of M. Doi and S. F. Edwards [*J. Chem. Soc., Faraday Trans. II*, 74, 1818–1832 (1978)]:

$$F(\boldsymbol{u}, t, t') = \frac{1}{4\pi}\int \delta(\boldsymbol{u} - \hat{\boldsymbol{u}})d\bar{\boldsymbol{u}} \tag{19.5-14a}$$

where

$$\hat{\boldsymbol{u}}(\bar{\boldsymbol{u}}, t, t') = \frac{[\mathbf{E}(t, t')\cdot\bar{\boldsymbol{u}}]}{|[\mathbf{E}(t, t')\cdot\bar{\boldsymbol{u}}]|} \tag{19.5-14b}$$

Here $\mathbf{E}(t, t')$ is the displacement-gradient tensor. See Example 8.3-2 for the transformation of coordinates needed to interrelate the two expressions for $F(\boldsymbol{u}, t, t')$. It is interesting that in the differential equation (Eq. 19.5-1) the flow field is described by the kinematic tensor $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^{\dagger}$, but that in the solution (Eq. 19.5-14 or 19.5-14a) the kinematic tensor $\boldsymbol{\gamma}^{[0]} = \{\boldsymbol{\Delta}^{\dagger}\cdot\boldsymbol{\Delta} - \boldsymbol{\delta}\}$ or $\mathbf{E}$ appears. The relations between $\boldsymbol{\Delta}$ or $\mathbf{E}$ and $\boldsymbol{\kappa}$ are quite complicated (see problem 8D.1).

A retarded-motion expansion for $f(\boldsymbol{u}, \sigma, t)$ can be obtained by expanding the denominator of the integral in Eq. 19.5-15 in a Taylor series and then expanding $\gamma^{[0]}(t, t')$ about $t' = t$ (see Problem 9B.2). Then the time integrals can be performed and one finally obtains

$$f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\Bigg[1 + \tfrac{3}{4}\lambda(\gamma^{(1)}:\boldsymbol{uu})(\sigma - \sigma^2) + \frac{1}{32}\lambda^2(5\gamma^{(1)}\gamma^{(1)}\vdots\,\boldsymbol{uuuu} - 2\gamma^{(2)}:\boldsymbol{uu})(\sigma - 2\sigma^3 + \sigma^4) + \cdots\Bigg] \tag{19.5-17}$$

The λ^3-term has also been worked out but is not included here.[3]

b. Perturbation Solution for $\varepsilon' \neq 0$

As was pointed out earlier, if $\varepsilon' \neq 0$ Eq. 19.5-1 is essentially the rigid rod equation discussed in Chapter 14. Although no completely general solution of this equation is known some results in Chapter 14 may be used in the present discussion.

As an example of the use of the rigid rod results we consider the perturbation solution for arbitrary, irrotational, time-dependent flows discussed in §14.5. From Eqs. 14.5-4, 14, and 21 it follows that

$$\begin{aligned} F(\boldsymbol{u}, t, t') = \frac{1}{4\pi}\Bigg\{1 &+ \frac{3}{2}\int_{t'}^{t} e^{-6\varepsilon' N^2(t-t'')/\lambda}(\dot{\gamma}(t''):\boldsymbol{uu})dt'' \\ &- \frac{3}{14}\int_{t'}^{t}\int_{t'}^{t''}(\dot{\gamma}(t''):\dot{\gamma}(t''') - 3\{\dot{\gamma}(t'')\cdot\dot{\gamma}(t''')\}:\boldsymbol{uu})e^{-6\varepsilon' N^2(t-t')/\lambda}\,dt'''dt'' \\ &+ \frac{3}{14}\int_{t'}^{t}\int_{t'}^{t''}\Bigg((\dot{\gamma}(t''):\dot{\gamma}(t''') - 10\{\dot{\gamma}(t'')\cdot\dot{\gamma}(t''')\}:\boldsymbol{uu} \\ &+ \frac{35}{2}(\dot{\gamma}(t''):\boldsymbol{uu})(\dot{\gamma}(t'''):\boldsymbol{uu})\Bigg)e^{-2\varepsilon' N^2(10t-7t''-3t''')/\lambda}\,dt'''\,dt'' + \cdots\Bigg\} \end{aligned} \tag{19.5-18}$$

This solution is consistent with the initial condition, Eq. 19.5-2, and becomes the solution discussed in §14.5 in the limit that $t' \to -\infty$. In a similar manner higher terms in the series may be obtained from the expressions given in §14.5. When this result is used in the expression for the distribution function, Eq. 19.5-3, one finds that

$$f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\left\{1 + \frac{6}{\pi}\sum_{n,\,\mathrm{odd}}\frac{1}{n}(\sin \pi n\sigma)\int_{-\infty}^{t} e^{-(t-t')/\lambda_n}(\dot{\gamma}(t'):\boldsymbol{uu})dt' + \cdots\right\} \tag{19.5-19}$$

where the λ_n are a set of effective time constants

$$\lambda_n = \left[\frac{(1-\varepsilon')}{\lambda_n^{(r)}} + \frac{6\varepsilon' N^2}{\lambda}\right]^{-1} = \frac{\lambda}{(1-\varepsilon')\pi^2 n^2 + 6\varepsilon' N^2} \tag{19.5-20}$$

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[3] C. F. Curtiss and R. B. Bird, *J. Chem Phys.*, 74, p. 2024 (1981).

For steady flows $\dot{\gamma}$ is independent of time and

$$f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\{1 + \lambda(\dot{\boldsymbol{\gamma}}:\boldsymbol{uu})g(\sigma) + \cdots\} \tag{19.5-21}$$

where

$$g(\sigma) = \frac{6}{\pi}\sum_{n,\text{odd}} \frac{\sin n\pi\sigma}{n[(1-\varepsilon')n^2\pi^2 + 6\varepsilon' N^2]} \tag{19.5-22}$$

This series may be written in the alternate form

$$g(\sigma) = -\frac{3}{2(1-\varepsilon')x^2}\sum_{n=1}^{\infty}\frac{x^{2n}}{(2n)!}E_{2n}(\sigma) \tag{19.5-23}$$

where $x = [6\varepsilon' N^2/(1-\varepsilon')]^{1/2}$ and the $E_{2n}(\sigma)$ are the[4] "Euler polynomials." Using the definition of these polynomials one may sum this series to find that

$$g(\sigma) = \frac{3[\sinh \frac{1}{2}x\sigma][\sinh \frac{1}{2}x(1-\sigma)]}{(1-\varepsilon')x^2 \cosh \frac{1}{2}x} \tag{19.5-24}$$

One then gets for small values of x (or ε')

$$g(\sigma) = \frac{3\sigma(1-\sigma)}{4(1-\varepsilon')}\left[1 - \frac{x^2}{12}(1 + \sigma - \sigma^2) + \cdots\right] \tag{19.5-25}$$

and for large x (or $\varepsilon' \to 1$)

$$g(\sigma) \to \frac{3}{2(1-\varepsilon')x^2} = \frac{1}{4N^2} \tag{19.5-26}$$

except at $\sigma = 0$ or 1. On the other hand, if ε' is not unity, $g(\sigma)$ as given by Eq. 19.5-24 is zero at $\sigma = 0$ and 1.

Thus one sees explicitly that for steady state flows to first order in $\dot{\gamma}$, the solution of the equation for the single-link distribution function, $f(\boldsymbol{u}, \sigma, t)$, as given by Eq. 19.5-3, is $1/(4\pi)$ at $\sigma = 0$ and 1, except in the limit that $\varepsilon' \to 1$, and that in this limit the function is discontinuous at these points.

§19.6 THE CONSTITUTIVE EQUATION

One may combine the formal solution of the diffusion equation for the single-link distribution function developed in the previous section with the expression for the stress tensor developed in §19.4 to obtain a constitutive equation in terms of the solution, $F(\boldsymbol{u}, t, t')$, of the rigid rod equation, Eq. 19.5-1.

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[4] M. Abramowitz and I. A. Stegun (Eds.), *Handbook of Mathematical Functions*, National Bureau of Standards, Washington D. C. (1964), pp. 803 *et seq.*

First, we define a second-order tensor $\mathbf{A}^{(2)}$ and a fourth-order tensor $\mathbf{A}^{(4)}$ by

$$\mathbf{A}^{(2)}(t, t') = \int F(\boldsymbol{u}, t, t')\boldsymbol{uu}\, d\boldsymbol{u} \tag{19.6-1}$$

$$\mathbf{A}^{(4)}(t, t') = \int F(\boldsymbol{u}, t, t')\boldsymbol{uuuu}\, d\boldsymbol{u} \tag{19.6-2}$$

With these definitions it follows from the expression for the single-link distribution function, Eq. 19.5-3, that

$$\int_0^1 \langle \boldsymbol{uu} \rangle d\sigma = \int_{-\infty}^t \mu(t, t')\mathbf{A}^{(2)}(t, t')dt' \tag{19.6-3}$$

$$\int_0^1 \sigma(1 - \sigma)\langle \boldsymbol{uu} \rangle d\sigma = \int_{-\infty}^t \nu(t, t')\mathbf{A}^{(2)}(t, t')dt' \tag{19.6-4}$$

$$\int_0^1 \sigma(1 - \sigma)\langle \boldsymbol{uuuu} \rangle d\sigma = \int_{-\infty}^t \nu(t, t')\mathbf{A}^{(4)}(t, t')dt' \tag{19.6-5}$$

where

$$\mu(s) = \int_0^1 P(\varepsilon', \sigma, s)d\sigma = \frac{8(1 - \varepsilon')}{\lambda} \sum_{n,\,\mathrm{odd}} e^{-(1-\varepsilon')s/\lambda_n^{(r)}} \tag{19.6-6}$$

$$\nu(s) = \frac{2(1 - \varepsilon')}{\lambda} \int_s^\infty \mu(s')ds' = \frac{16(1 - \varepsilon')}{\pi^2 \lambda} \sum_{n,\,\mathrm{odd}} \frac{1}{n^2} e^{-(1-\varepsilon')s/\lambda_n^{(r)}} \tag{19.6-7}$$

When these expressions are used in Eq. 19.4-18 for the stress tensor, one finds that

$$\boxed{\begin{aligned} \boldsymbol{\tau} = kT \sum_\alpha n_\alpha N_\alpha \Big[& \tfrac{1}{3}(1 - \varepsilon')\boldsymbol{\delta} + \tfrac{1}{6}\varepsilon' N_\alpha^2 \boldsymbol{\delta} - (1 - \varepsilon') \int_{-\infty}^t \mu_\alpha(t - t')\mathbf{A}_\alpha^{(2)}(t, t')dt' \\ & - 3\varepsilon' N_\alpha^2 \int_{-\infty}^t \nu_\alpha(t - t')\mathbf{A}_\alpha^{(2)}(t, t')dt' - \varepsilon\lambda_\alpha \boldsymbol{\kappa}(t) : \int_{-\infty}^t \nu_\alpha(t - t')\mathbf{A}_\alpha^{(4)}(t, t')dt' \Big] \end{aligned}} \tag{19.6-8}$$

where the sum over α is the sum over the various species of molecules. In the polydisperse liquid being considered here the molecules differ only in length, that is, in the value of N_α; there is a time constant λ_α associated with each species. In general, the functions $\mu(s)$ and $\nu(s)$, as well as the tensors $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$, depend on the value of λ_α.

a. Complete Constitutive Equation in the Pure Reptation Limit ($\varepsilon' = 0$)

In the limit that $\varepsilon' = 0$, the function $F(\boldsymbol{u}, t, t')$ is independent of λ_α, and as a consequence $\mathsf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ are also independent of λ_α. The stress tensor is then[1]

$$\boxed{\begin{aligned}\boldsymbol{\tau} = \left(\sum_\alpha n_\alpha N_\alpha\right)kT\bigg[\tfrac{1}{3}\boldsymbol{\delta} - \int_{-\infty}^{t}\left(\sum_\alpha w_\alpha \mu_\alpha(t-t')\right)\mathsf{A}^{(2)}(t, t')dt' \\ - \tfrac{1}{2}\varepsilon\dot{\boldsymbol{\gamma}}(t)\mathbf{:}\int_{-\infty}^{t}\left(\sum_\alpha w_\alpha \lambda_\alpha \nu_\alpha(t-t')\right)\mathbf{A}^{(4)}(t, t')dt'\bigg]\end{aligned}} \qquad (19.6\text{-}9)$$

in which $w_\alpha = n_\alpha N_\alpha / \sum_\beta n_\beta N_\beta$ is the mass fraction of species α, and[2]

$$\mathsf{A}^{(2)} = \frac{1}{4\pi}\int \frac{\boldsymbol{uu}\,d\boldsymbol{u}}{(1 + \boldsymbol{\gamma}^{[0]}\mathbf{:}\boldsymbol{uu})^{3/2}} = \frac{1}{4\pi}\int \hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\,d\boldsymbol{u} \qquad (19.6\text{-}10)$$

$$\mathbf{A}^{(4)} = \frac{1}{4\pi}\int \frac{\boldsymbol{uuuu}\,d\boldsymbol{u}}{(1 + \boldsymbol{\gamma}^{[0]}\mathbf{:}\boldsymbol{uu})^{3/2}} = \frac{1}{4\pi}\int \hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\,d\boldsymbol{u} \qquad (19.6\text{-}11)$$

with $\hat{\boldsymbol{u}}(\boldsymbol{u}, t, t')$ being defined in Eq. 19.5-14b. The two forms of $\mathsf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ result from the use of the alternative forms for $F(\boldsymbol{u}, t, t')$ given in Eqs. 19.5-14 and 14a (see Example 8.3-3 for the relation between the two forms).

In Eq. 19.6-9 we have then arrived at the complete constitutive equation[3] for the polydisperse polymer melt, modeled as a collection of interacting Kramers chains. Given the kinematics of the flow field one can obtain $\boldsymbol{\gamma}^{[0]}(t, t')$ and then $\mathsf{A}^{(2)}$ and $\mathbf{A}^{(4)}$. Substitution of these kinematic tensors into Eq. 19.6-9 then gives the stress in the fluid, provided that the time constants λ_α for the chain are known.

The stress-tensor expression in Eq. 19.6-9 may be put into the form of a *retarded motion expansion* (see Eq. 6.2-1) by performing the following manipulations: expand the expressions for $\mathsf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ as Taylor series in $\boldsymbol{\gamma}^{[0]}(t, t')$; expand $\boldsymbol{\gamma}^{[0]}$ about $t' = t$ using Eq. 9B.2-1; use Problem 9B.1 to replace all $\boldsymbol{\gamma}^{(n)}$ by combinations of $\boldsymbol{\gamma}_{(n)}$; finally, do the

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[1] The Doi Edwards constitutive equation [M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789 1832 (1978); see Eq. 3.15 on p. 1822] can be obtained from Eq. 19.6-9 by specializing to a monodisperse fluid, setting $\varepsilon = 0$, and replacing kT by $3kT$. As noted earlier, in connection with Eq. 19.3-25, there is also a difference in the time constants in the two theories. For polydisperse fluids the mixing rules given by Doi and Edwards [*J. Chem. Soc., Faraday Trans. II*, **74**, pp. 1828 1829 (1978)] are the same as those implied by Eq. 19.6-9, except that the λ_α needed for calculating $\mu_\alpha(t - t')$ and $\nu_\alpha(t - t')$ are defined differently: in the Doi Edwards theory $\lambda_\alpha \propto N_\alpha^3$, whereas Eq. 19.3-25 gives $\lambda_\alpha \propto N_\alpha^2 \bar{N}^{1+\beta}$ with $\bar{N} = \sum_\alpha x_c N_\alpha$.

[2] The tensors $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ used here are simply related to the two second-order tensors $\boldsymbol{A}$ and $\boldsymbol{B}$ used by C. F. Curtiss and R. B. Bird [*J. Chem. Phys.*, **74**, 2016 2033 (1981)] as follows $\boldsymbol{A} = \mathsf{A}^{(2)}$, and $\boldsymbol{B} = \frac{1}{2}\lambda\{\dot{\boldsymbol{\gamma}}\mathbf{:}\mathbf{A}^{(4)}\}$. P. K. Currie [*J. Non-Newtonian Fluid Mech.*, **11**, 53 68 (1982)] has shown that $\boldsymbol{A}$ and $\boldsymbol{B}$ are both derivable from a "potential function" (see Table 8.3-2 and Example 8.3-3).

[3] This constitutive equation has been used along with the equations of continuity and motion for making flow calculations [D. S. Malkus and B. Bernstein, *J. Non-Newtonian Fluid Mech.*, **16**, 77 116 (1984)].

integrations over t'. The result is

$$\boldsymbol{\tau} = -\left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\left(\frac{1}{60}+\frac{\varepsilon}{90}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha\right)\boldsymbol{\gamma}_{(1)} - \left(\frac{1-\varepsilon}{1050}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right)\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(1)}\}\right.$$
$$\left.-\left(\frac{1}{600}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right)\boldsymbol{\gamma}_{(2)}+\cdots\right] \qquad (19.6\text{-}12)$$

From this expansion, including the third-order terms which are also available,[4] we can get the following results (cf. Example 6.2-1 and Problem 6B.2):

Viscometric Functions:

$$\eta = \left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\frac{1}{60}\left(1+\frac{2}{3}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha\right) - \frac{17}{70560}\left(1-\frac{2}{5}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^3\right)\dot{\gamma}^2+\cdots\right] \qquad (19.6\text{-}13)$$

$$\Psi_1 = \left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\frac{1}{300}\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right) - \frac{341}{3492720}\left(1-\frac{1}{2}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^4\right)\dot{\gamma}^2+\cdots\right] \qquad (19.6\text{-}14)^5$$

$$\Psi_2 = -\left(\sum_\alpha n_\alpha N_\alpha\right)kT(1-\varepsilon)\left[\frac{1}{1050}\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right) - \frac{341}{9604980}\left(\sum_\alpha w_\alpha\lambda_\alpha^4\right)\dot{\gamma}^2+\cdots\right] \qquad (19.6\text{-}15)^5$$

Elongational Viscosity:

$$\bar{\eta} = 3\left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\frac{1}{60}\left(1+\frac{2}{3}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha\right)+\left(\frac{1}{1400}+\frac{\varepsilon}{1050}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right)\dot{\varepsilon}\right.$$
$$\left.+\left(-\frac{17}{78400}+\frac{17\varepsilon}{58800}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^3\right)\dot{\varepsilon}^2+\cdots\right] \qquad (19.6\text{-}16)$$

In these expressions the time constants λ_α are given by $\lambda_\alpha = N_\alpha^2\bar{N}^{1+\beta}\zeta a^2/2kT$ and $\bar{N} = \sum_\alpha x_\alpha N_\alpha$; the x_α are mole fractions, the w_α are mass fractions, and the n_α are number densities. Note that the normal-stress ratio at $\dot{\gamma} = 0$ is given by

$$\frac{\Psi_{2,0}}{\Psi_{1,0}} = -\tfrac{2}{7}(1-\varepsilon) \qquad (19.6\text{-}17)$$

for monodisperse and polydisperse fluids.[6] It is interesting to note that the "rod climbing" phenomenon occurs for small deformation rates only if $\Psi_{2,0}/\Psi_{1,0} > -\frac{1}{4}$ or $\varepsilon > \frac{1}{8}$; this means that the Doi–Edwards theory ($\varepsilon = 0$) does not predict rod climbing at the

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[4] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, p. 2029 (1981).

[5] The $\dot{\gamma}^2$-terms in the expression for Ψ_1 and Ψ_2 were not obtained from the fourth-order terms in Eq. 19.6-12, but rather by expanding the integrals in Eqs. 19.7-10 and 11.

[6] The quantity $\Psi_{2,0}/\Psi_{1,0}$ has been measured for linear polybutadienes and polystyrenes in normal butylbenzene and found to be about -0.29 [see S. Ramachandran, Ph.D. Thesis, University of Utah, Salt Lake City (1983), as cited in S. Ramachandran and E. B. Christiansen, *J. Non-Newtonian Fluid Mech.*, **13**, 21–32 (1983)]; the same authors reported $\Psi_{2,0}/\Psi_{1,0} \doteq -0.214$ for star polymers.

second-order fluid level, in conflict with known experimental facts (see Problem 6B.6), even if polydispersity is accounted for.[7]

b. Retarded-Motion Expansion and Linear Viscoelastic Reponse for $\varepsilon' \neq 0$

From the series expression for $F(\boldsymbol{u}, t, t')$ given by Eq. 19.5-18 one finds that for irrotational flows

$$\begin{aligned} \mathbf{A}^{(2)}(t, t') = {} & \frac{1}{3}\boldsymbol{\delta} + \frac{1}{5}\int_{t'}^{t} e^{-6\varepsilon' N^2(t-t')/\lambda}\dot{\boldsymbol{\gamma}}(t'')dt'' \\ & - \frac{1}{70}\int_{t'}^{t}\int_{t'}^{t''} e^{-6\varepsilon' N^2(t-t'')/\lambda}[2(\dot{\boldsymbol{\gamma}}(t''):\dot{\boldsymbol{\gamma}}(t'''))\boldsymbol{\delta} \\ & - 3\{\dot{\boldsymbol{\gamma}}(t'')\cdot\dot{\boldsymbol{\gamma}}(t''')\} - 3\{\dot{\boldsymbol{\gamma}}(t''')\cdot\dot{\boldsymbol{\gamma}}(t'')\}]dt'''dt'' + \cdots \end{aligned} \tag{19.6-18}$$

$$\begin{aligned} \mathbf{A}^{(4)}(t, t') = {} & \frac{1}{15}(\boldsymbol{\delta\delta} + \mathbf{I} + \mathbf{I}^{\dagger}) \\ & - \frac{1}{35}\int_{t'}^{t} e^{-6\varepsilon' N^2(t-t'')/\lambda}\{[\boldsymbol{\delta\delta} + \mathbf{I} + \mathbf{I}^{\dagger}]\cdot\dot{\boldsymbol{\gamma}}(t'') \\ & + \dot{\boldsymbol{\gamma}}(t'')\cdot[\boldsymbol{\delta\delta} + \mathbf{I} + \mathbf{I}^{\dagger}]\}dt'' + \cdots \end{aligned} \tag{19.6-19}$$

where $\mathbf{I}$ is the isotropic fourth rank tensor defined in §E.9. When these series are used in the expression for the stress tensor, Eq. 19.6-8, one finds that

$$\begin{aligned} \boldsymbol{\tau} = {} & -\frac{8kT}{5\pi^4}\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\mathrm{odd}} \frac{1}{n^4\lambda_n}\int_{-\infty}^{t}\Bigg[e^{-(t-t')/\lambda_n}\dot{\boldsymbol{\gamma}}(t') \\ & - \frac{1}{14}\int_{-\infty}^{t''} e^{-(t-t'')/\lambda_n}\{2(\dot{\boldsymbol{\gamma}}(t'):\dot{\boldsymbol{\gamma}}(t''))\boldsymbol{\delta} \\ & - 3\dot{\boldsymbol{\gamma}}(t')\cdot\dot{\boldsymbol{\gamma}}(t'') - 3\dot{\boldsymbol{\gamma}}(t'')\cdot\dot{\boldsymbol{\gamma}}(t')\}dt'' + \cdots\Bigg]dt' \\ & - \frac{16\varepsilon kT}{15\pi^4}\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\mathrm{odd}} \frac{1}{n^4}\Bigg[\dot{\boldsymbol{\gamma}}(t) + \frac{3}{14}\int_{-\infty}^{t} e^{-(t-t')/\lambda_n}\{(\dot{\boldsymbol{\gamma}}(t):\dot{\boldsymbol{\gamma}}(t'))\boldsymbol{\delta} \\ & + 2\dot{\boldsymbol{\gamma}}(t)\cdot\dot{\boldsymbol{\gamma}}(t') + 2\dot{\boldsymbol{\gamma}}(t')\cdot\dot{\boldsymbol{\gamma}}(t)\}dt' + \cdots\Bigg] \end{aligned} \tag{19.6-20}$$

where the λ_n are the time constants defined by Eq. 19.5-20. From this it may be shown that the coefficients in the retarded motion expansion are

$$b_1 = \eta_0 = \frac{8kT}{5\pi^4}(1 + \tfrac{2}{3}\varepsilon)\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\mathrm{odd}} \frac{1}{n^4} \tag{19.6-21}$$

$$b_2 = -\tfrac{1}{2}\Psi_{1,0} = -\frac{8kT}{5\pi^4}\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\mathrm{odd}} \frac{\lambda_n}{n^4} \tag{19.6-22}$$

$$b_{11} = \Psi_{2,0} = \tfrac{4}{7}(1 - \varepsilon)b_2 \tag{19.6-23}$$

In the limit that $\varepsilon' \to 0$ these results are equivalent to the first terms in the series given by Eqs. 19.6-13 to 15. It is interesting to note that η_0 and the ratio $\Psi_{1,0}/\Psi_{2,0}$ are independent of ε'. For a monodisperse system, the value of $\Psi_{1,0}$ (or $\Psi_{2,0}$) when $\varepsilon' = 1$ differs from the value when $\varepsilon' = 0$ by a factor of $5/(3N^2)$. The explicit form of the dependence of these quantities on ε' is examined in Problem 19D.1.

It may also be shown from Eq. 19.6-20 that the relaxation modulus is

$$G(t) = kT \sum_{\alpha} n_\alpha N_\alpha \left[\frac{\varepsilon}{45} \lambda \delta(t) + \frac{8\lambda}{5\pi^4} \sum_{n,\text{odd}} \frac{e^{-t/\lambda_{\alpha,n}}}{n^4 \lambda_{\alpha,n}} \right] \tag{19.6-24}$$

From this it follows that the complex viscosity is

$$\eta^* = kT \sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \left[\frac{\varepsilon}{90} + \frac{8}{5\pi^4} \sum_{n,\text{odd}} \frac{1}{n^4(1 + i\omega\lambda_{\alpha,n})} \right] \tag{19.6-25}$$

and that

$$\lim_{\omega \to \infty} \frac{\eta'(\omega)}{\eta'(0)} = \frac{(2\varepsilon/3)}{1 + (2\varepsilon/3)} \tag{19.6-26}$$

$$\lim_{\omega \to \infty} \omega\eta''(\omega) = \tfrac{1}{5} kT \left(1 - \frac{\varepsilon'}{2}\right) \sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \tag{19.6-27}$$

Experimental data on $\eta'(\omega)$ for polymer melts at high ω when compared with Eq. 19.6-26 suggest that ε should be very small or zero.[8] However, we feel that it is inappropriate to draw this conclusion, since the Kramers bead-rod model is too crude to account for the very small-scale motions that are probed by high frequencies in the oscillatory-flow experiment.

EXAMPLE 19.6-1 Effect of Polydispersity on Rheological Properties

Use Eqs. 19.6-13 and 19.6-14 to obtain the zero-shear-rate viscosity and first normal-stress coefficient for a polydisperse polymer melt. Then obtain the steady-state compliance J_e^0 in terms of appropriate molecular weight averages. Finally as an illustration of using a two-parameter empiricism for the molecular weight distribution, use the logarithmic-normal distribution[9] to compare the theoretical result with the experimentally determined molecular-weight distribution dependence

$$J_e^0 \propto \left(\frac{\bar{M}_z}{\bar{M}_w}\right)^{3.7} \tag{19.6-28}$$

deduced from data on polydimethylsiloxane and polystyrene in the range $1 < \bar{M}_z/\bar{M}_w < 3$ by Mills.[10]

SOLUTION We approximate the molecular weight distribution by a continuous function $w(M)$, such that $w(M)\,dM$ is the weight fraction of polymer with molecular weight between M and $M + dM$. We define molecular weight averages as follows:

$$\bar{M}_{z+j} = \frac{\int_0^\infty M^{2+j} w(M)\,dM}{\int_0^\infty M^{1+j} w(M)\,dM} \tag{19.6-29}$$

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[8] D. A. Bernard and J. Noolandi, *Macromolecules*, **16**, 1358–1366 (1983).

[9] H. Wesslau, *Makromolecule Chemie*, **20**, 111-142 (1956).

[10] N. J. Mills, *Nature* (London), **219**, 1249–1250 (1968); see also H. J. M. A. Mieras and C. F. H. van Rijn, *Nature*, **218**, 865–866 (1968).

For $j = -2, -1$, and 0 these quantities are generally called, respectively, the number-average molecular weight $\bar{M}_n$, the weight-average molecular weight $\bar{M}_w$, and the z-average molecular weight $\bar{M}_z$. Keep in mind that $\int_0^\infty w(M)\,dM = 1$.

Now we note that the sum $\sum_\alpha n_\alpha N_\alpha$ appearing in Eqs. 19.6-13 and 14 may be written as follows:

$$\sum_\alpha n_\alpha N_\alpha = \frac{\tilde{N}}{M_0} \sum_\alpha c_\alpha M_\alpha = \frac{\tilde{N}}{M_0} \rho \tag{19.6-30}$$

in which c_α is the molar concentration of species α, M_0 is the molecular weight of that part of the chain corresponding to one "bead", ρ is the mass density of the mixture, and $\tilde{N}$ is the Avogadro number. Next we note that the time constant λ_α, given in Eq. 19.3-25, can be rewritten in terms of molecular weights using $M_\alpha = N_\alpha M_0$, as follows:

$$\lambda_\alpha = \frac{\bar{N}^{1+\beta} N_\alpha^2 \zeta a^2}{2kT} = \frac{\bar{M}_n^{1+\beta} M_\alpha^2}{M_0^{3+\beta}} \left(\frac{\zeta a^2}{2kT}\right) \tag{19.6-31}$$

The sums, involving weight fractions w_α, appearing in Eqs. 19.6-13 and 14, may now be written as follows:

$$\begin{aligned} \sum_\alpha w_\alpha \lambda_\alpha &= \frac{\bar{M}_n^{1+\beta}}{M_0^{3+\beta}} \left(\frac{\zeta a^2}{2kT}\right) \int_0^\infty M^2 w(M) dM \\ &= \frac{\bar{M}_n^{1+\beta} \bar{M}_w \bar{M}_z}{M_0^{3+\beta}} \left(\frac{\zeta a^2}{2kT}\right) \end{aligned} \tag{19.6-32}$$

$$\begin{aligned} \sum_\alpha w_\alpha \lambda_\alpha^2 &= \left(\frac{\bar{M}_n^{1+\beta}}{M_0^{3+\beta}}\right)^2 \left(\frac{\zeta a^2}{2kT}\right)^2 \int_0^\infty M^4 w(M) dM \\ &= \frac{\bar{M}_n^{2+2\beta} \bar{M}_w \bar{M}_z \bar{M}_{z+1} \bar{M}_{z+2}}{M_0^{6+2\beta}} \left(\frac{\zeta a^2}{2kT}\right)^2 \end{aligned} \tag{19.6-33}$$

Therefore, the zero-shear-rate viscometric functions become

$$\eta_0 = \frac{\rho \tilde{N} kT}{60 M_0^{4+\beta}} (1 + \tfrac{2}{3}\varepsilon) \left(\frac{\zeta a^2}{2kT}\right) \bar{M}_n^{1+\beta} \bar{M}_w \bar{M}_z \tag{19.6-34}$$

$$\Psi_{1,0} = \frac{\rho \tilde{N} kT}{300 M_0^{7+2\beta}} \left(\frac{\zeta a^2}{2kT}\right)^2 \bar{M}_n^{2+2\beta} \bar{M}_w \bar{M}_z \bar{M}_{z+1} \bar{M}_{z+2} \tag{19.6-35}$$

and also

$$J_e^0 = \frac{\Psi_{1,0}}{2\eta_0^2} \propto \frac{\bar{M}_{z+1} \bar{M}_{z+2}}{\bar{M}_w \bar{M}_z} \tag{19.6-36}$$

Thus J_e^0 is predicted to be independent of molecular weight in a monodisperse system, but strongly dependent on molecular weight distribution in a polydisperse liquid, which is in qualitative agreement with experiment.

To go further one has to assume a form for the molecular-weight distribution $w(M)$. One two-parameter equation is the logarithmic-normal distribution

$$w(M) = \frac{\exp[-(\ln M - \ln \bar{M}_m)^2 / 2\sigma^2]}{\sqrt{2\pi}\, \sigma M} \tag{19.6-37}$$

in which σ and $\bar{M}_m$ are constants. It can be shown that for this distribution $\bar{M}_{z+j}/\bar{M}_{z+j-1} = \exp \sigma^2$. Using this result we then get[11]

$$J_e^0 \propto \left(\frac{\bar{M}_z}{\bar{M}_w}\right)^4 \tag{19.6-38}$$

which should be compared with the experimental result in Eq. 19.6-28.

Extensive comparisons[12] between experimental data and the mixture-theory results of Eqs. 19.6-36, 19.7-9, 19.7-10, and other equations for material functions suggest that the time constant λ_α of Eq. 19.3-25 is reasonable. This formula is, in turn, a consequence of the definition of $F^{(h)\alpha}$ in Eqs. 17.5-10 through 12. The generally satisfactory agreement between theory and experiment provides some additional support for the method of incorporation of concentration and molecular weight dependence in Eq. 17.5-10 (see footnote 1 in §17.5).

§19.7 SHEAR-FLOW RHEOLOGICAL PROPERTIES[1,2]

In this section we use Eq. 19.6-9 to obtain some of the material functions for monodisperse fluids for shear flows of the form $v_x = 0$, $v_y = \dot{\gamma}_{yz}(t)z$, $v_z = 0$ in the pure reptation limit, $\varepsilon' = 0$. For such flows the kinematic tensors $\dot{\boldsymbol{\gamma}}(t)$ and $\mathbf{E}(t, t')$ are (see Appendix C)

$$\dot{\boldsymbol{\gamma}}(t) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \dot{\gamma}_{yz}(t), \qquad \mathbf{E}(t, t') = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \Gamma \\ 0 & 0 & 1 \end{pmatrix} \tag{19.7-1}$$

in which $\Gamma(t, t') = -\gamma_{yz}(t, t') = \int_{t'}^{t} \dot{\gamma}_{yz}(t'')dt''$ is the negative of the shear strain from t to t'. Then the unit vector $\hat{\boldsymbol{u}}(t, t')$ appearing in Eqs. 19.6-10 and 11 is:

$$\hat{\boldsymbol{u}} = \frac{[\mathbf{E} \cdot \boldsymbol{u}]}{|\mathbf{E} \cdot \boldsymbol{u}|} = \frac{1}{\sqrt{1 + 2\Gamma u_y u_z + \Gamma^2 u_z^2}} \begin{pmatrix} u_x \\ u_y + \Gamma u_z \\ u_z \end{pmatrix} \tag{19.7-2}$$

Here $u_x = \sin \theta \cos \phi$, $u_y = \sin \theta \sin \phi$, and $u_z = \cos \theta$, where θ and ϕ are the polar angles describing $\boldsymbol{u}$; this expression for $\hat{\boldsymbol{u}}$ then has to be inserted into Eqs. 19.6-10 and 11. From the latter we get the yz-components of $\mathbf{A}^{(2)}$ and $\mathbf{B}^{(2)} = \frac{1}{2}\{\lambda\dot{\boldsymbol{\gamma}} : \mathbf{A}^{(4)}\}$, needed to get the shear stress

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[11] The importance of polydispersity in polymer-melt kinetic theory was emphasized by M. Doi and S. F. Edwards [*J. Chem. Soc., Faraday Trans II*, **74**, 1818–1832 (1978), Eqs. 7.2-7.4]. Their recommended averaging procedure is different from ours and leads to

$$J_e \propto \frac{\bar{M}_{z+2}\bar{M}_{z+3}\bar{M}_{z+4}}{\bar{M}_w\bar{M}_z\bar{M}_{z+1}} \xrightarrow[\text{distribution}]{\text{logarithmic normal}} \left(\frac{\bar{M}_z}{\bar{M}_w}\right)^9 \tag{19.6-38a}$$

For more on this subject see M. Kurata, *Macromolecules*, **17**, 895–898 (1984) and W. W. Graessley, *J. Polymer Sci., Polymer Phys. Ed.*, **18**, 27–34 (1980).

[12] J. D. Schieber, C. F. Curtiss, and R. B. Bird, *Ind. Eng. Chem. Fundam.*, **25**, 471–475 (1986); J. D. Schieber *J. Chem. Phys.*, *87*, 4917–4936 (1987).

[1] R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4747–4757 (1982) and H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982); errata in this paper have been pointed out X.-J. Fan and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **15**, 341–373 (1984).

[2] H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

τ_{yz}, by doing the ϕ-integrations and changing the θ-integrations to integrations over $x = \cos\theta$

$$A^{(2)}_{yz} = \frac{1}{2\Gamma}\int_0^1 [1 + g^{-1}(\Gamma^2 x^2 - 1)]dx \tag{19.7-3}$$

$$B^{(2)}_{yz} = \frac{\lambda\dot{\gamma}_{yz}}{4\Gamma^2}\int_0^1 \{1 + g^{-3}[(3\Gamma^6 + 8\Gamma^4)x^6 - (7\Gamma^4 + 8\Gamma^2)x^4 + 5\Gamma^2 x^2 - 1]\}dx \tag{19.7-4}$$

in which $g = [(\Gamma^4 + 4\Gamma^2)x^4 - 2\Gamma^2 x^2 + 1]^{1/2}$. Next we give the corresponding quantities needed to get the first and second normal-stress differences:

$$A^{(2)}_{yy} - A^{(2)}_{zz} = \Gamma A^{(2)}_{yz} \tag{19.7-5}$$

$$A^{(2)}_{zz} - A^{(2)}_{xx} = -\frac{1}{2}\int_0^1 \{1 - g^{-1}[(\Gamma^2 + 6)x^2 - 1]\}dx \tag{19.7-6}$$

$$\begin{aligned} B^{(2)}_{yy} - B^{(2)}_{zz} = \frac{\lambda\dot{\gamma}_{yz}}{4\Gamma}\int_0^1 \Bigg\{\frac{3 + 2\Gamma^2}{1 + \Gamma^2} &+ g^{-3}[(2\Gamma^6 + 2\Gamma^4 - 8\Gamma^2)x^6 \\ &- (7\Gamma^4 + 8\Gamma^2)x^4 + (6\Gamma^2 - 6)x^2 - 1]\Bigg\}dx \end{aligned} \tag{19.7-7}$$

$$B^{(2)}_{zz} - B^{(2)}_{xx} = -\frac{1}{2}\lambda\dot{\gamma}_{yz}\frac{d}{d\Gamma}(A^{(2)}_{zz} - A^{(2)}_{xx}) \tag{19.7-8}$$

The derivation of these equations is outlined in the original reference,[1] and tables of these quantities as functions of Γ are given.

When the components of $\mathbf{A}^{(2)}$ and $\mathbf{B}^{(2)}$ are substituted into Eq. 19.6-9 and the integration variable is changed to the dimensionless variable $s' = (t - t')/\lambda$, we get for the *steady shear flow* of monodisperse fluids:

$$\frac{\eta(\dot{\gamma})}{NnkT\lambda} = \frac{1}{\lambda\dot{\gamma}}\left[\int_0^\infty \lambda\mu(\lambda s')(A^{(2)}_{yz})_\Gamma\, ds' + \varepsilon\int_0^\infty \lambda\nu(\lambda s')(B^{(2)}_{yz})_\Gamma\, ds'\right] \tag{19.7-9}$$

$$\frac{\Psi_1(\dot{\gamma})}{NnkT\lambda^2} = \frac{1}{(\lambda\dot{\gamma})^2}\left[\int_0^\infty \lambda\mu(\lambda s')(A^{(2)}_{yy} - A^{(2)}_{zz})_\Gamma\, ds' + \varepsilon\int_0^\infty \lambda\nu(\lambda s')(B^{(2)}_{yy} - B^{(2)}_{zz})_\Gamma\, ds'\right] \tag{19.7-10}$$

$$\frac{\Psi_2(\dot{\gamma})}{NnkT\lambda^2} = \frac{1 - \varepsilon}{(\lambda\dot{\gamma})^2}\int_0^\infty \lambda\mu(\lambda s')(A^{(2)}_{zz} - A^{(2)}_{xx})_\Gamma\, ds' \tag{19.7-11}$$

In these equations the subscript Γ serves as a reminder that the components of $A^{(2)}$ and $B^{(2)}$ are functions of Γ, which is related to s' by $\Gamma = \dot{\gamma}(t - t') = \lambda\dot{\gamma}s'$; for steady shear flow we drop the subscripts yz on $\dot\gamma_{yz}$. For very small $\lambda\dot\gamma$ the viscometric functions η, Ψ_1, and Ψ_2 may be expanded to give Eqs. 19.6-13 to 15 appropriately simplified for a monodisperse fluid. For very large $\lambda\dot\gamma$ it has been found[1] that

$$\frac{\eta}{NnkT\lambda} \sim \frac{\varepsilon}{\lambda\dot\gamma} \qquad (\varepsilon \neq 0) \tag{19.7-12}$$

$$\frac{\Psi_1}{NnkT\lambda^2} \sim \frac{2\varepsilon \ln \lambda\dot\gamma}{(\lambda\dot\gamma)^2} \qquad (\varepsilon \neq 0) \tag{19.7-13}$$

$$\frac{\Psi_2}{NnkT\lambda^2} \sim -\frac{1.1619(1-\varepsilon)}{(\lambda\dot\gamma)^{5/2}} \tag{19.7-14}$$

When $\varepsilon = 0$ (Doi–Edwards theory) at very large $\dot\gamma$ it is found[3] that $\eta \propto \dot\gamma^{-3/2}$ and $\Psi_1 \propto \dot\gamma^{-2}$. The calculated curves of η, Ψ_1, and Ψ_2 are shown in Figs. 19.7-1 and 2.

Experimental data on η and Ψ_1 for well-fractionated melts and concentrated solutions can be reasonably well fit by the theoretical curves, as may be seen in Figs. 19.7-3 (polystyrene melts), 19.7-5 (poly-α-methylstyrene solutions), and 19.7-8 (polystyrene solutions). Values of ε in the range 0.3–0.5 seem to provide the best curve fits; the $\varepsilon = 0$ curve cannot describe the $\eta(\dot\gamma)$ and $\Psi_1(\dot\gamma)$ curves over a wide range of shear rates. In Figs. 19.7-4 and 6 we show how the values of η_0 and λ vary with the weight-averaged molecular weight. According to Eq. 19.6-13, η_0 and λ should have the same molecular weight dependence for monodisperse fluids ($\eta_0 \propto \lambda \propto M^{3+\beta}$) and the figures bear this out moderately well. In Fig. 19.7-7 we show how N increases with the molecular weight; note that N is not particularly large.

Finally in Fig. 19.7-9 we show the transient behavior at the inception of steady shear flow. For very small times the theory does not fit the data particularly well. This may in part

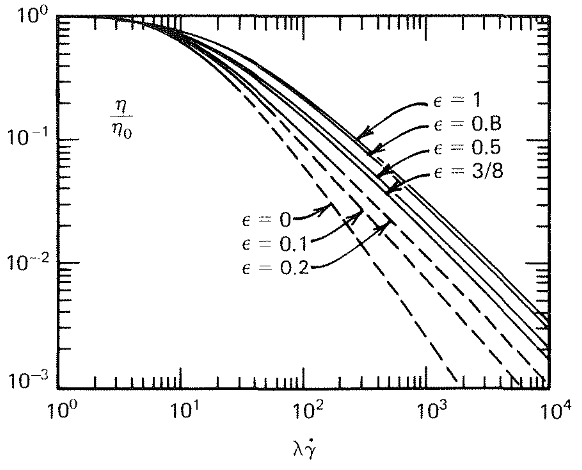

FIGURE 19.7-1. Viscosity as a function of shear rate $\dot\gamma$ for various values of the link tension coefficient ε. The time constant λ is $N^{3+\beta}\,\zeta a^2/2kT$ and the zero-shear-rate viscosity η_0 is $\frac{1}{60}(1 + \frac{2}{3}\varepsilon)\,NnkT\lambda$. The curves are dashed in the region where the slope is steeper than -1. The $\varepsilon = 0$ curve corresponds to the Doi–Edwards theory. Reproduced from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4747–4757 (1982).

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[3] M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789–1832 (1978); **75**, 38–54 (1979).

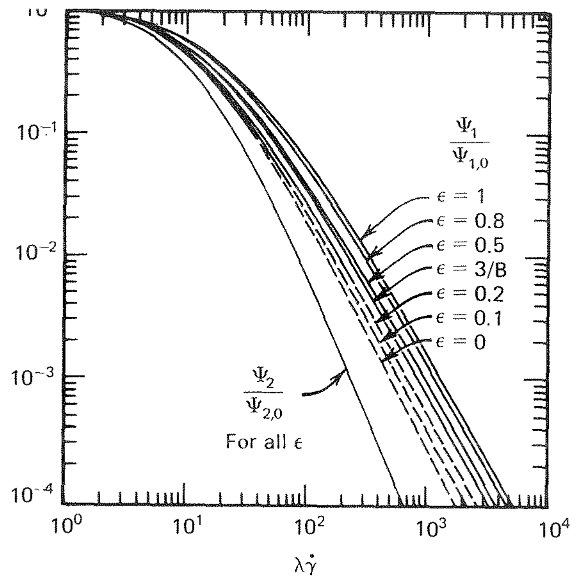

FIGURE 19.7-2. The normal-stress coefficients versus the dimensionless shear rate. The zero-shear-rate normal stress coefficients are $\Psi_{1,0} = (1/300)NnkT\lambda^2$ and $\Psi_{2,0} = -[(1-\varepsilon)/1050)]NnkT\lambda^2$. The dashed curves correspond to the region where the η/η_0 versus $\lambda\dot{\gamma}$ curves have a slope steeper than -1. The $\varepsilon = 0$ curve corresponds to the Doi-Edwards theory. Reproduced from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4747-4757 (1982).

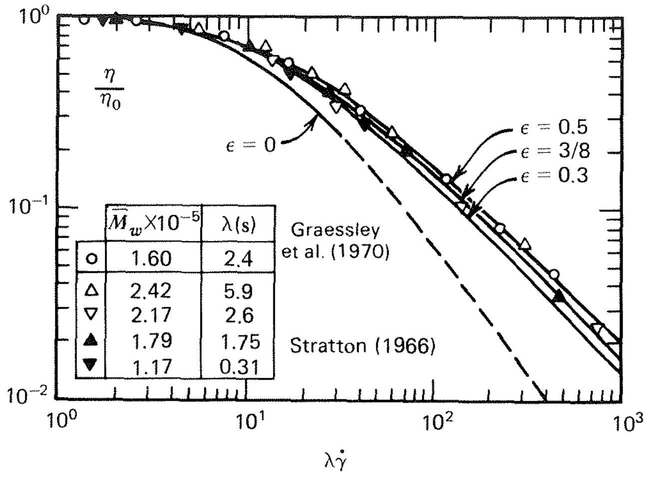

FIGURE 19.7-3. Comparison of the steady-state viscosity calculated from Eq. 19.7-9 with data on nearly monodisperse polystyrene melts of various molecular weights. The data of W. W. Graessley, S. D. Glasscock, and R. L. Crawley [*Trans. Soc. Rheol.*, **14**, 519-544 (1970)] are at 180°C, and those of R. A. Stratton [*J. Coll. Interf. Sci.*, **22**, 517-530 (1966)] are at 183°C. All the data are for samples with $\bar{M}_w/\bar{M}_n < 1.1$. The dashed part of the $\varepsilon = 0$ curve, corresponding to the Doi-Edwards theory, is unattainable, since the slope is steeper that -1. The experimental data extend well below the critical value of $\eta/\eta_0 \doteq 0.25$ of the $\varepsilon = 0$ curve. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4758-4766 (1982).

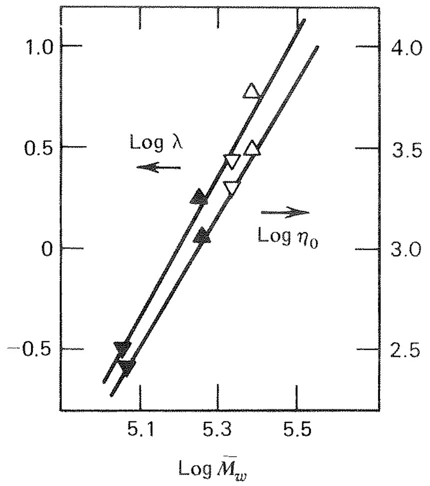

FIGURE 19.7-4. Plots of log η_0 and log λ versus log $\bar{M}_w$ from the data comparison of Fig. 19.7-3 for the data of Stratton. The quantities η_0(Pa · s) and λ(s) were determined by the best fit of the data with the theoretical curves in Fig. 19.7-1. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4758–4766 (1982).

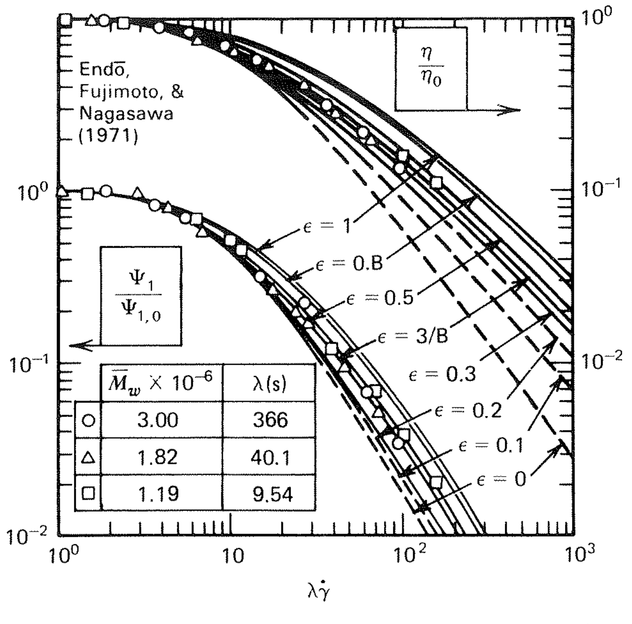

FIGURE 19.7-5. Data of H. Endō, T. Fujimoto, and M. Nagasawa, [*J. Polym. Sci.*, **A2**, **9**, 345–362 (1971)] on viscosity η and first normal stress coefficient Ψ_1 compared with curves of Figs. 19.7-1 and 2. The data are for 7% (by weight) solutions of poly-α-methylstrene of various molecular weights in Kanechlor at 25°C. All the polymer samples have $\bar{M}_w/\bar{M}_n < 1.01$. The same combinations of λ and ε fit both the η and Ψ_1 data. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4758–4766 (1982).

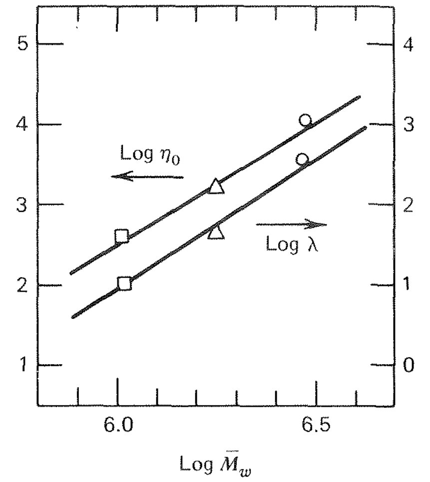

FIGURE 19.7-6. Plots of log η_0 and log λ vs. log $\bar{M}_w$ from the data comparison of Fig. 19.7-5 for the poly-α-methylstyrene solutions of Endō, Fujimoto and Nagasawa. The values of η_0(Pa·s) are the measured values and the values of λ(s) are those that give the best fit with the theoretical viscosity and normal-stress coefficient curves. Both lines have a slope of about 3.5, which corresponds to a value of 0.5 for β. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtis, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

be a result of the fact that the theoretical calculations do not account for the fluid inertia effects as the flow profiles are beginning to be established at the beginning of the experiment. On the other hand, it is more likely that the Kramers bead-spring chain model, with N not very large, is not capable of describing the rapid small-scale motions of the polymer molecules. This deficiency in the Kramers chain was also discussed in connection with the poor description of $\eta^*(\omega)$ at very high frequencies.

It must be borne in mind that the data comparisons given here are for monodisperse systems only. Even a small amount of polydispersity can have an appreciable effect. In Fig. 19.7-8, where the polymer being tested has $\bar{M}_w/\bar{M}_n = 1.25$, it was found that it was not

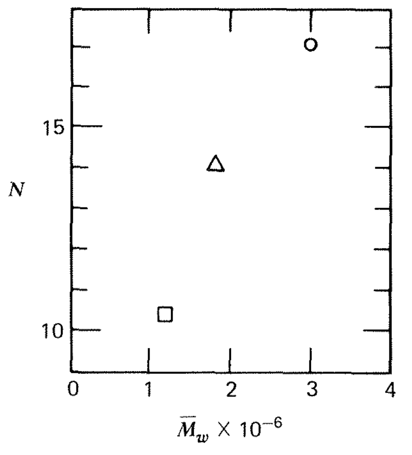

FIGURE 19.7-7. The number of beads per chain, N, versus the molecular weight from the data comparison in Fig. 19.7-6. The quantity N was determined from $\eta_0 = \frac{1}{60}(1 + \frac{2}{3}\varepsilon)N(\rho/\bar{M}_w)\tilde{N}kT\lambda$ of the solutions. $\rho = 1.3630$ g/cm^3 was given by M. Nagasawa (private communication (1982)). Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

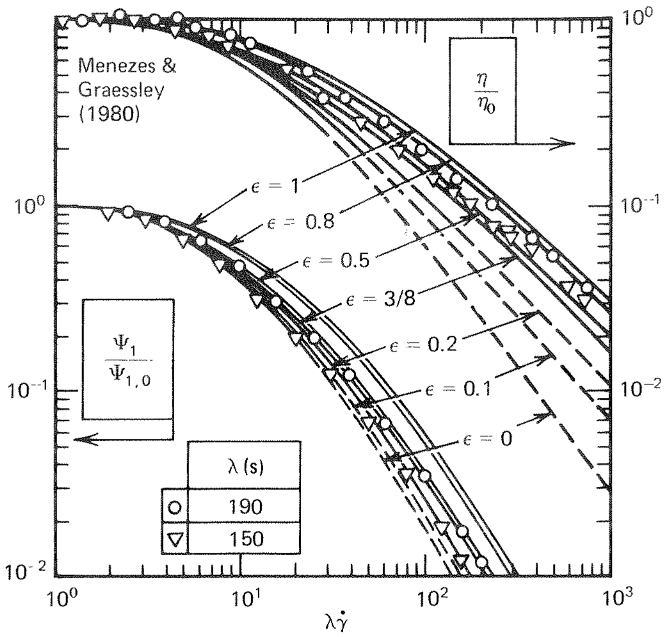

FIGURE 19.7-8. Data of E. V. Menezes and W. W. Graessley [*Rheol. Acta*, **19**, 38–50 (1980)] for viscosity η and first normal stress coefficient Ψ_1 compared with theoretical curves of Figs. 19.7-1 and 2. The data are for 12% (by weight) solutions of polystyrene ($\bar{M}_w = 1.8 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.25$) in tricresyl phosphate at 25°C. Because of polydispersity, it is not possible to fit both properties with a single combination of λ and ε: $\lambda = 150$s fits the η-data to the $\varepsilon = 0.5$ curve, whereas $\lambda = 190$s fits the Ψ_1-data to the $\varepsilon = 0.5$ curve. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

possible to fit two material functions, namely η and Ψ_1, with a single value of the time constant λ. It is necessary to use the mixture formula in Eq. 19.6-9 to account for polydispersity.[4]

§19.8 ELONGATIONAL-FLOW RHEOLOGICAL PROPERTIES[1]

We conclude this chapter with a brief discussion of the theoretical predictions for elongational flow, using Eq. 19.6-9 as a starting point. The flow pattern under consideration is $v_x = -\frac{1}{2}\dot{\varepsilon}(t)x$, $v_y = -\frac{1}{2}\dot{\varepsilon}(t)y$, $v_z = \dot{\varepsilon}(t)z$, for which

$$\dot{\boldsymbol{\gamma}}(t) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \dot{\varepsilon}(t), \qquad \boldsymbol{\gamma}^{[0]} = \begin{pmatrix} \Lambda - 1 & 0 & 0 \\ 0 & \Lambda - 1 & 0 \\ 0 & 0 & \Lambda^{-2} - 1 \end{pmatrix} \quad (19.8\text{-}1)$$

where $\Lambda(t, t') = \lambda_z(t, t') = \exp \int_{t'}^{t} \dot{\varepsilon}(t'')dt''$ is the "elongation ratio" (see Appendix C). Then the components of the tensors $\mathbf{A}^{(2)}$ and $\mathbf{B}^{(2)} = \frac{1}{2}\{\dot{\boldsymbol{\gamma}} : \mathsf{A}^{(4)}\}$ needed for getting the elongational

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[4] One attempt to do this was that of Y.-H. Lin, *J. Rheol.*, **28**, 1–22 (1984), who used the Doi–Edwards theory ($\varepsilon = 0$). For $\varepsilon \neq 0$ more satisfactory results are obtained, as may be seen in J. D. Schieber, C. F. Curtiss, and R. B. Bird, *Ind. Eng. Chem. Fundam.*, **25**, 471–475 (1986), J. D. Schieber, Univ. of Wisc. Rheology Research Center Reports Nos. 107 and 108 (1986).

[1] R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982).

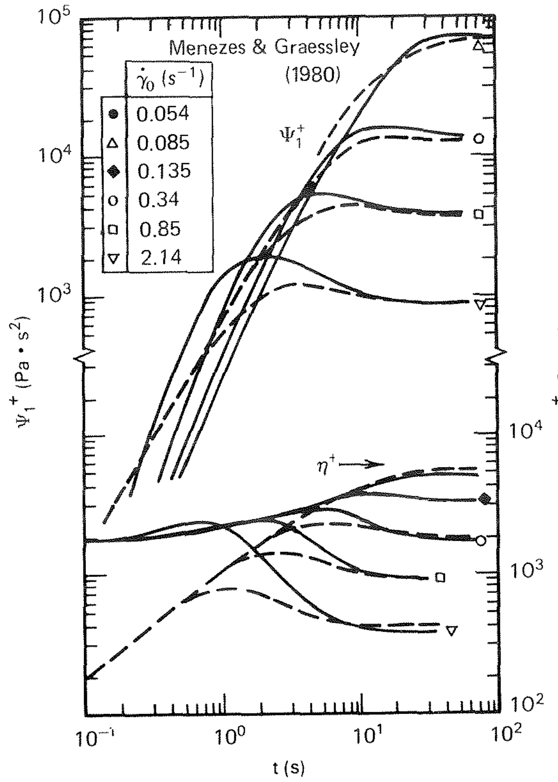

FIGURE 19.7-9. Data of E. V. Menezes and W. W. Graessley [*Rheol. Acta*, **19**, 38–50 (1980)] for η^+ and Ψ_1^+ at inception of steady shear flow (dashed lines) with the theoretical curves obtained from the kinetic theory (solid lines). The liquid used is the same as that described in the caption to Fig. 19.7-8. The theoretical curves for η^+ were calculated for $\lambda = 150$s, $\varepsilon = 0.5$, and for Ψ_1^+ with $\lambda = 190$s, $\varepsilon = 0.5$. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

viscosity may be found from Eqs. 19.6-10 and 11 to be

$$A_{zz}^{(2)} - A_{xx}^{(2)} = \frac{3}{2}\frac{\Lambda^3}{\Lambda^3 - 1}\left(1 - \frac{\arctan\sqrt{\Lambda^3 - 1}}{\sqrt{\Lambda^3 - 1}}\right) - \frac{1}{2}, \qquad \Lambda > 1 \qquad (19.8\text{-}2)$$

$$A_{zz}^{(2)} - A_{xx}^{(2)} = \frac{3}{2}\frac{\Lambda^3}{1 - \Lambda^3}\left(\frac{\operatorname{arctanh}\sqrt{1 - \Lambda^3}}{\sqrt{1 - \Lambda^3}} - 1\right) - \frac{1}{2}, \qquad \Lambda < 1 \qquad (19.8\text{-}3)$$

$$\frac{B_{zz}^{(2)} - B_{xx}^{(2)}}{\lambda\dot{\varepsilon}} = \frac{1}{8(\Lambda^3 - 1)^2}\left[8\Lambda^6 + 17\Lambda^3 + 2 - (15\Lambda^6 + 12\Lambda^3)\frac{\arctan\sqrt{\Lambda^3 - 1}}{\sqrt{\Lambda^3 - 1}}\right], \qquad \Lambda > 1 \qquad (19.8\text{-}4)$$

$$\frac{B_{zz}^{(2)} - B_{xx}^{(2)}}{\lambda\dot{\varepsilon}} = \frac{1}{8(1 - \Lambda^3)^2}\left[8\Lambda^6 + 17\Lambda^3 + 2 - (15\Lambda^6 + 12\Lambda^3)\frac{\operatorname{arctanh}\sqrt{1 - \Lambda^3}}{\sqrt{1 - \Lambda^3}}\right], \qquad \Lambda < 1 \qquad (19.8\text{-}5)$$

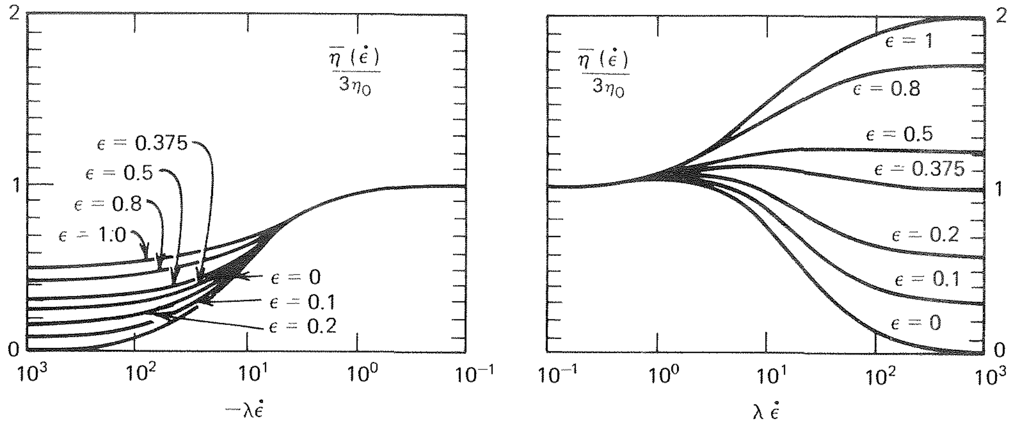

FIGURE 19.8-1. Elongational viscosity as a function of elongation rate $\dot{\varepsilon}$ for various values of the link tension coefficient ε. The time constant λ is $N^{3+\beta}\zeta a^2/2kT$. For small values of $|\lambda\dot{\varepsilon}|$, Eq. 19.6-16 can be used. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982). Copyright (1982) American Chemical Society.

With these quantities Eq. 19.6-9 may be used to get the normal stress differences in any time-dependent elongational flow.

Specifically for *steady elongational flow* Eq. 19.6-9 (written for a monodisperse fluid) can be integrated numerically. Then $\tau_{zz} - \tau_{xx}$, and hence $\bar{\eta}(\dot{\varepsilon})$, can be found. Figure 19.8-1 shows the behavior of $\bar{\eta}(\dot{\varepsilon})$ both for $\dot{\varepsilon} > 0$ (fiber stretching) and $\dot{\varepsilon} < 0$ (sheet stretching). Note that there is a nonzero slope at $\dot{\varepsilon} = 0$ and that the link tension coefficient ε has a substantial effect on the curves. For $\varepsilon = 3/8$ the elongational viscosity is very nearly constant for $\dot{\varepsilon} > 0$.

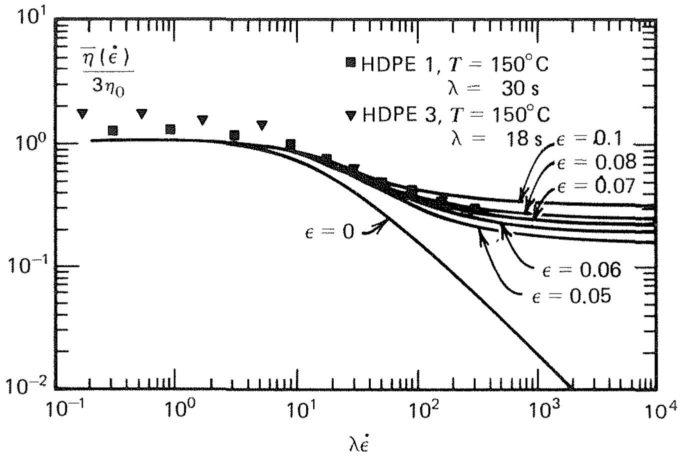

FIGURE 19.8-2. Comparison of experimental steady elongational viscosity data for high-density polyethylene melts with the calculated curves in Fig. 19.8-1; $\varepsilon = 0$ corresponds to the Doi–Edwards theory: (■) data of H. M. Laun [in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Vol. 2, Plenum, New York (1980), pp. 419–424]; (▼) data of H. Münstedt and H. M. Laun [*Rheol. Acta*, **20**, 211–221 (1981)]. Note that in plotting the experimental values of $\bar{\eta}(\dot{\varepsilon})/3\eta_0$, the quantity η_0 is the zero-shear-rate viscosity, determined experimentally. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982). Copyright (1982) American Chemical Society.

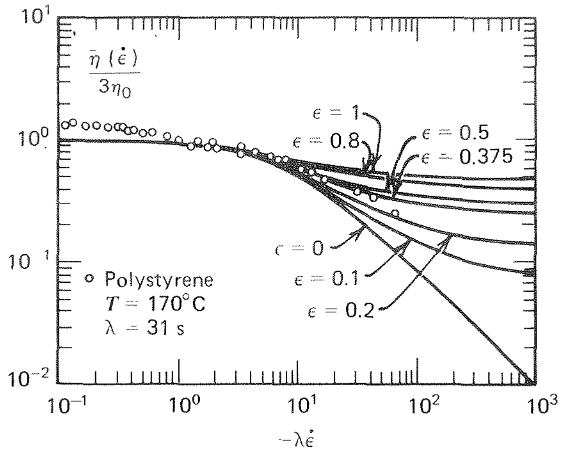

FIGURE 19.8-3. Comparison of the biaxial extension data for a polystyrene melt (Hostyren *N* 4000 V) of J. A. van Aken and H. Janeschitz-Kriegl [*Rheol. Acta*, **19**, 744-754 (1980); **21**, 388-393 (1982)] with the $\dot{\varepsilon} < 0$ part of the $\bar{\eta}(\dot{\varepsilon})$ curves in Fig. 19.8-1. The data have been temperature shifted to 170°C. In plotting the experimental values of $\bar{\eta}(\dot{\varepsilon})/3\eta_0$, the quantity η_0 is the zero-shear-rate viscosity, determined experimentally. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102-1106 (1982). Copyright (1982) American Chemical Society.

In Fig. 19.8-2 experimental data for $\bar{\eta}(\dot{\varepsilon})$ with $\dot{\varepsilon} > 0$ for polyethylene melts are shown. These are linear polyethylenes; unfortunately they are highly polydisperse, and this fact makes the data comparison of questionable value. Values of λ and ε ($= 0.08$) were chosen by fitting the experimental data. In Fig. 19.8-3 values of $\bar{\eta}(\dot{\varepsilon})$ for $\dot{\varepsilon} < 0$ inferred from birefringence data on polystyrene melts in biaxial extension are shown. Figures 19.8-2 and 3 by no means constitute a complete experimental test of the theory; however it can at least be seen that the theoretical curves exhibit the correct trends (except for $\varepsilon = 0$).

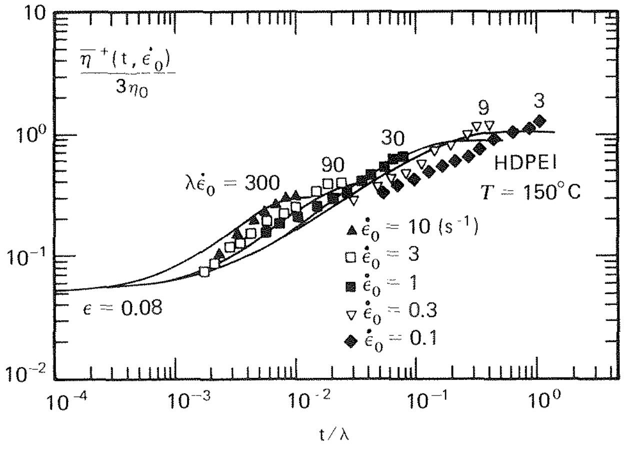

FIGURE 19.8-4. Comparison of experimental elongational growth viscosity with calculated curves based on Eqs. 19.6-9, and 19.8-2 to 5. The experimental data are those of H. M. Laun [in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Plenum, New York (1980), Vol. 2, pp. 419-424]. The combination of λ and ε (30 s, 0.08) that gives the best fit with the steady elongational viscosity is used. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102-1106 (1982). Copyright (1982) American Chemical Society.

One additional test, also incomplete, is the comparison of elongational stress growth data with the theoretical curves shown in Fig. 19.8-4. Here the parameters $\lambda = 30$ s and $\varepsilon = 0.08$ were determined from steady elongational data, and no additional parameters were used in making the data comparison in the figure.

We conclude this section by reminding the reader that the experiments for measuring $\bar{\eta}$ and $\bar{\eta}^+$ are exceedingly difficult to perform. For testing the theory, data on monodisperse systems would be highly desirable; also more theoretical calculations taking into account the polydispersity effects, with Eq. 19.6-9, should be performed.[2]

PROBLEMS

19C.1 The Single-Link Distribution Function and the Constitutive Equation for $\varepsilon' = 0$.

a. Obtain the expansion in Eq. 19.5-17 from the expression for $f(\boldsymbol{u}, \sigma, t)$ in Eq. 19.5-15.

b. Verify that Eq. 19.5-21 simplifies to the lowest order terms in Eq. 19.5-17 when ε' is set equal to zero.

c. Substitute Eq. 19.5-17 for $f(\boldsymbol{u}, \sigma, t)$ into Eq. 19.4-18 and obtain the retarded motion expansion in Eq. 19.6-12.

19D.1 Retarded Motion Expansion

Show that the sums over n in Eqs. 19.6-21 and 22 are given by

$$\sum_{n,\,\mathrm{odd}} \frac{1}{n^4} = \frac{\pi^4}{96} \tag{19D.1-1}$$

$$\sum_{n,\,\mathrm{odd}} \frac{\lambda_n}{n^4} = \frac{\pi^4 \lambda_\alpha}{4(1-\varepsilon')x^5}\left[\frac{\sinh x}{1+\cosh x} - \frac{1}{2}x + \frac{1}{24}x^3\right] \tag{19D.1-2}$$

where $x = [6\varepsilon' N_\alpha^2/(1-\varepsilon')]^{1/2}$.

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[2] J. D. Schieber, Univ. of Wisconsin Rheology Research Center Report No. 108 (1986).