CHAPTER 11
MECHANICAL MODELS FOR POLYMER MOLECULES

"The time has come," the penguin said,
"To speak of many things:
Of flowing macromolecules,
And little beads and springs
That join together into 'chains'
Or even 'stars' or 'rings'."

—With apologies to Lewis Carroll

Even in the kinetic theory of gases it is necessary to use simplified models to represent molecules in order to minimize the mathematical complications. In the earliest theories the rigid sphere model was used, and this accounted roughly for the strong repulsive forces between molecules, but completely neglected the weak attractive forces. Later kinetic theorists used point masses that interact according to a Lennard–Jones potential; this two-constant empirical model accounts semi-quantitatively for both attractive and repulsive forces. As the kinetic theories became more and more refined and as more powerful computers were developed, more elaborate molecular models were developed to take into account the molecular shape and the charge distribution within the molecules. Since the statistical mechanical calculation of equilibrium properties (thermodynamic properties and virial coefficients) is far easier than that of nonequilibrium properties (viscosity, thermal conductivity, and diffusivity) it is not surprising that the molecular modeling in equilibrium statistical mechanics has reached a higher level of realism and complexity than in the nonequilibrium part of the field.

In polymer kinetic theory we find a similar development: in the 1930s, when the subject was just beginning, the crude "dumbbell" models were introduced; in the ensuing years bead-rod and bead-spring chains were used for representing chainlike macromolecules; still more complex models accounting for steric hindrance, excluded volume, chain branching, and other effects were developed much later. If one is interested only in the equilibrium configurations and properties derived therefrom, one can afford to use rather realistic and complex modeling. However, if the object is to describe macromolecular configurations in nonequilibrium systems and the associated rheological properties—a far more difficult problem—then it becomes necessary to use considerably simpler models in order to do the mathematics and the numerical work. Inasmuch as this volume is primarily dedicated to the latter problem, the emphasis here will be on the simpler models, which have contributed greatly to our understanding of polymer rheology and fluid dynamics.

This chapter is devoted to a brief discussion of some of the mechanical models that are used in this book and in the research literature. We give some of the physical arguments that have led to these models and present the nomenclature that is used in the description of their configurations. In each of these models a few parameters are introduced. Ultimately numerical values must be given for these parameters, either by relating them to fundamental constants describing the true molecule or by choosing them in such a way that certain rheological data (viscosity, normal stresses, complex viscosity, etc.) are described. The use of empirical mechanical contrivances in lieu of the true molecule inevitably introduces parameters that have some degree of fuzziness; this is simply the price that one pays for the mathematical and numerical simplification achieved by the use of a mechanical model.

§11.1 MACROMOLECULAR STRUCTURE

Polymer molecules differ from the small molecules treated in the usual kinetic theory of gases and liquids in several important ways:

a. *Great diversity in structure.* Organic chemists have succeeded in synthesizing straight chain polymers, branched polymers, block copolymers, closed-ring polymers, ionomers, and rigid polymers. Ultimately it will be desirable to have kinetic theory calculations for models representing each of these (and still other) classes of polymers. To date most of the research has been done in linear flexible polymers, and this book reflects that emphasis.

b. *Molecular weight distributions.* When polymers are synthesized, the molecules in the sample do not all have the same length (i.e., they are not "monodisperse") but instead they are of varying length (i.e., they are "polydisperse"). Polydispersity has an enormous effect on the macroscopic properties; small amounts of very high molecular-weight components can alter the rheological properties significantly. Consequently, kinetic theories must be able to account for molecular weight distributions.

c. *Large number of internal degrees of freedom.* Since many polymeric materials contain molecules with molecular weights in the millions, each molecule in the material is capable of existing in a huge number of configurations. A kinetic theory of polymeric materials must therefore be able to account for the stretching, rotation, and deformation of the constituent molecules. The force transmitted along the chain backbones of the molecules in these various configurations is a key factor in obtaining an expression for the stress tensor, the central object of study in rheology.

Because of these three features of polymeric liquids, the molecular modeling and the kinetic theory development will be considerably different from the analogous topics in the kinetic theory of gases and simple liquids. For those interested in the development of molecular models and the history of kinetic theory, the two volumes of collected reprints assembled by Hermans will be valuable.[1]

To get some idea about the nature of the true systems that are the object of our study in this volume, let us look at the photographs of Fisher-Hirschfelder-Taylor models in Fig. 11.1-1. In (*a*) and (*b*) we show portions of polyethyleneoxide and polyethylene chains in several different configurations; this is a reminder of the complexity of polymer motions. In (*c*) we show portions of polystyrene and polyisobutylene chains; these photographs emphasize the importance of side-group substituents on the dynamics of chains. Finally, in

[1] J. J. Hermans, Ed., *Polymer Solution Properties: Part I, Statistics and Thermodynamics; Part II, Hydrodynamics and Light Scattering*, Dowden, Hutchinson, and Ross, Inc., Stroudsburg, PA (1978).

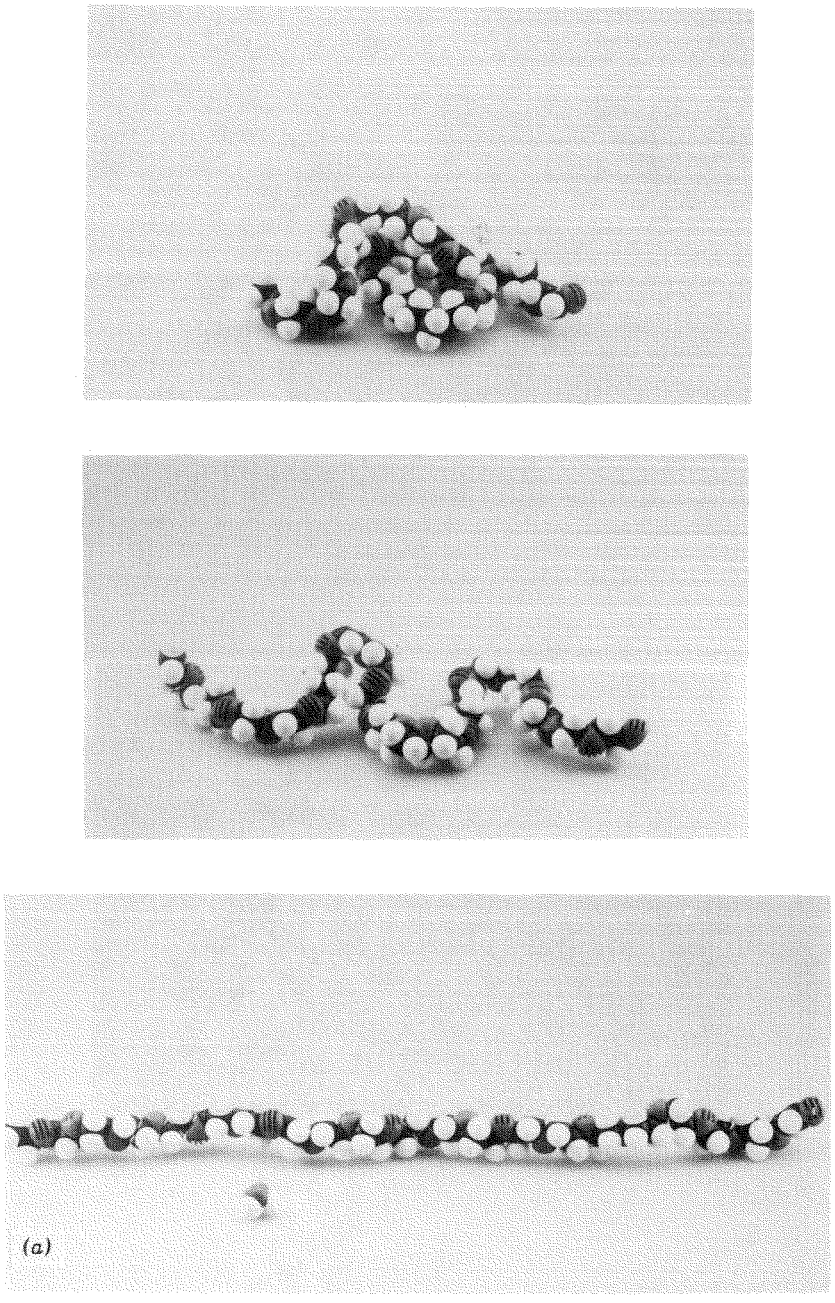
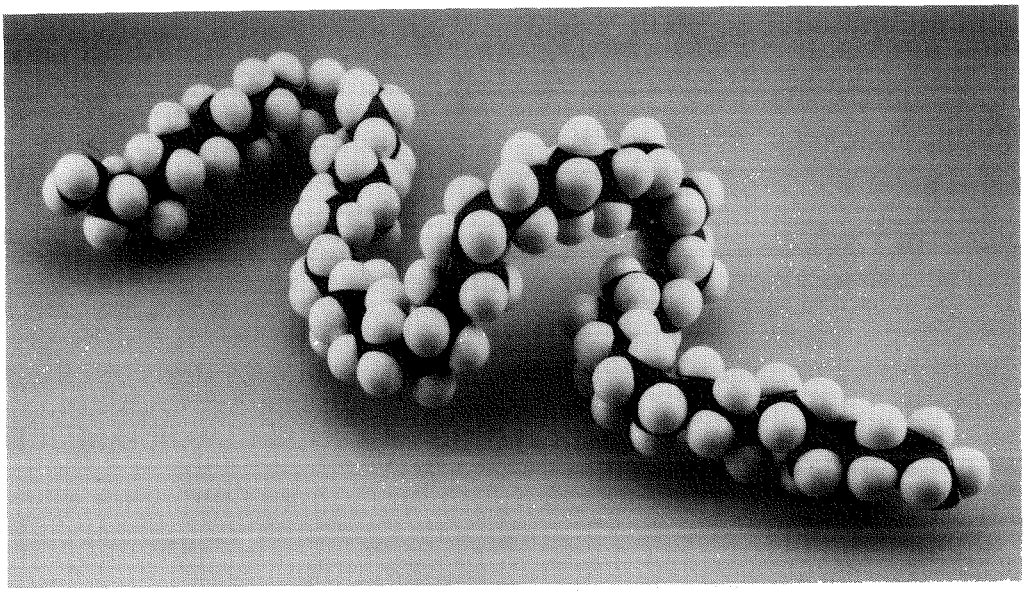


FIGURE 11.1-1. Photographs of molecular models: (*a*) 20 monomer units of a polyethyleneoxide chain, in three different conformations; under the fully stretched-out conformation is shown a water molecule for comparison. In (*a*), (*b*), and (*c*) only short portions of the chain are shown; in most polymeric fluids of interest, chains with 10^3–10^6 monomer units are typically encountered. Photographs prepared by J. D. Schieber and T. W. Liu, Chemical Engineering Department, University of Wisconsin-Madison (1984).



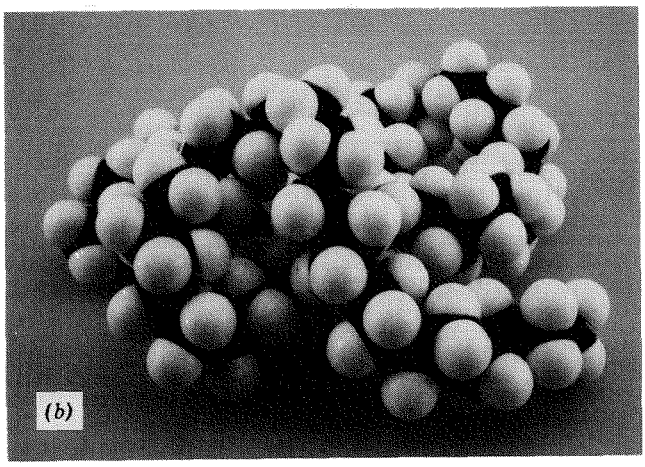
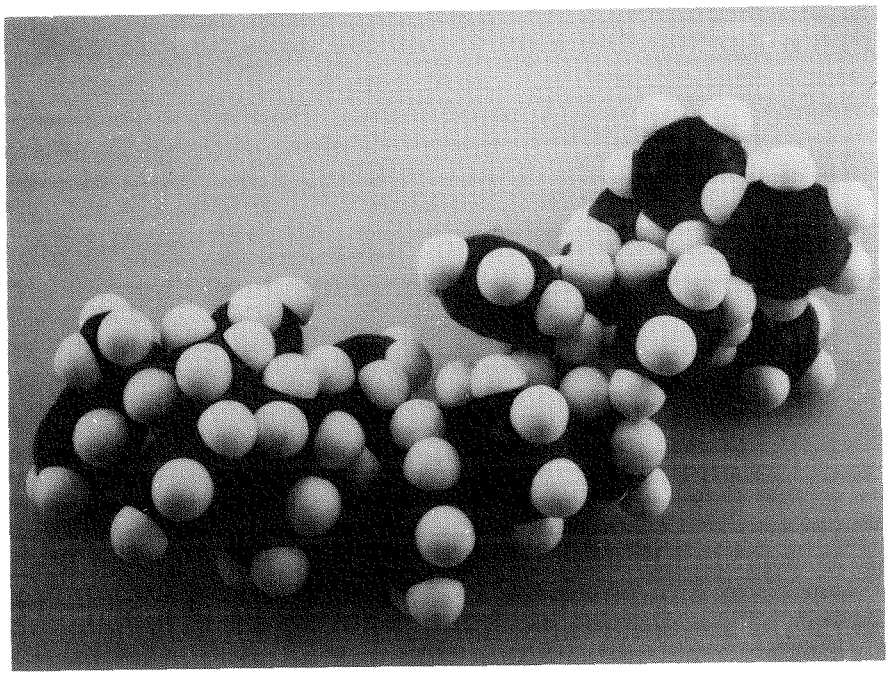
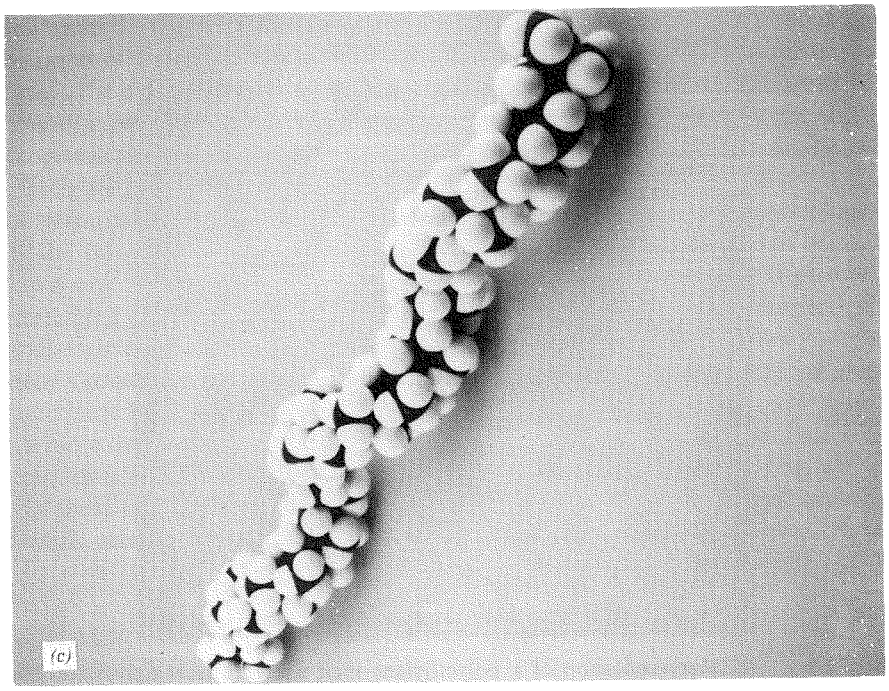
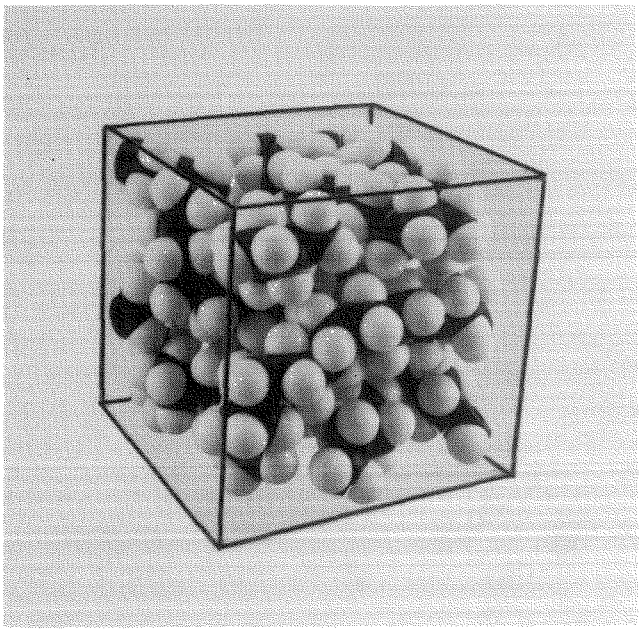


FIGURE 11.1-1. (*b*) 34 monomer units of a polyethylene chain, in two different conformations.





JRE 11.1-1. (*c*) 14 monomer units of a polystyrene chain showing the large side groups; and 22 ɔmer units of a polyisobutylene chain, which cannot move easily into other configurations ɪse of the steric hindrance of the side groups.



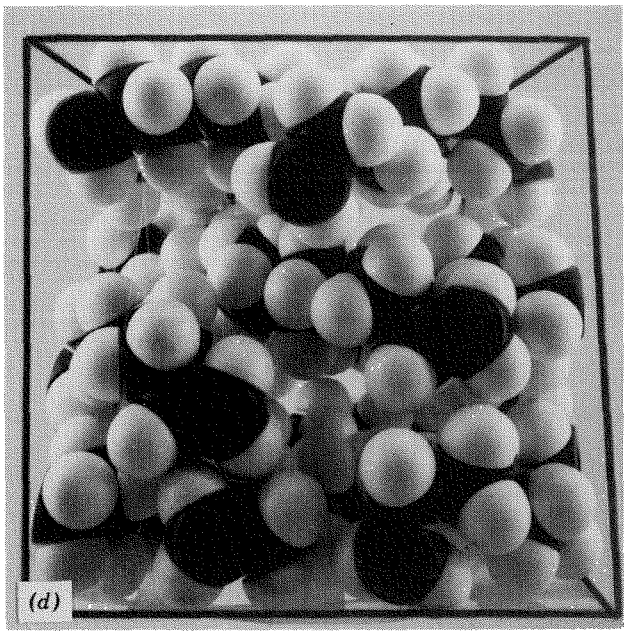


FIGURE 11.1-1. (*d*) Representation of a polyethylene melt showing how tightly the chains are packed; the cube, 15 Å on a side, contains 118 carbon atoms, or 58 monomer units.

(*d*) we show a region of an undiluted sample of polyethylene; this gives some idea as to the amount of empty space that a molecule has to move about in as well as the sort of environment that a portion of a macromolecule "sees" in an undiluted system. These photographs should be kept in mind as we discuss mechanical models in this chapter and as we develop kinetic theories in the ensuing chapters.

Of course, the photographs in Fig. 11.1-1 show only what the molecules look like at one instant of time. In the true system all of the molecules will be in a continual state of motion. The thermal energy of the system gives rise to the frenetic motion of the solvent molecules, which in turn bang into the polymer molecule and cause it to writhe around in a very complicated way. There will be large-scale motions of the polymer chain as a whole, and superimposed on this there will be more rapid wiggly motions of portions of the chain. This latter kind of motion is generally referred to as Brownian motion. Of course there will also be vibration of the bonds and torsional vibrations of the pendant groups as they oscillate back and forth within the constraints of steric hindrance. Since quantum mechanical phenomena are not important in systems such as this, the motion of the entire assembly of molecules can be described satisfactorily by classical mechanics.

In most of the theories developed to date, two major simplifications are made: (a) the Brownian motion is described by the gradient of a distribution function, which serves as a driving force; and (b) the intermolecular forces are accounted for by the use of some kind of Stokes' law expression that accounts approximately for the forces exerted on portions of the macromolecule. Later, in Chapter 17, we adopt a more fundamental viewpoint and obtain much more general expressions for both of these effects in terms of appropriate averages involving the intermolecular forces.

It should be evident that the system we are studying is extraordinarily complicated. From the point of view of the rheologist and the fluid dynamicist, the question is: Just how detailed does the modeling need to be in order to obtain useful results? The word "useful" has a different meaning to the fluid dynamicist who wants to describe flow behavior than to the rheologist interested in accurate description of material functions, or to the polymer chemist fascinated by differences in structure and molecular architecture. Even within one group of researchers the needs may be different. For example, for the rheologist it is primarily the slow bending and expanding motions of the chain that have to be described accurately if one is interested in the steady state shear flow properties; it is primarily the overall stretching of the chains that is important for the elongational flow properties; and it is the small-scale motions that are of interest in connection with the complex viscosity and other linear viscoelastic properties. Consequently an elastic dumbbell model for a polymer may be adequate for a polymer fluid dynamicist primarily interested in steady-state flows, whereas a more detailed model accounting for rapid vibrational and torsional motions may be required for a polymer chemist studying polymer structure by means of high frequency oscillatory shear and birefringence experiments. The question of "usefulness" must be kept in mind while reading about the various mechanical models in the next few sections.

§11.2 CHAIN MODELS WITH FIXED BOND LENGTHS AND BOND ANGLES

It has been pointed out by Flory[1] that the bond lengths and the angles between adjacent bonds are restricted to quite narrow ranges. At ordinary temperatures the amplitudes of the oscillations in bond lengths and bond angles are about 3% of their

[1] P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969), p. 13.

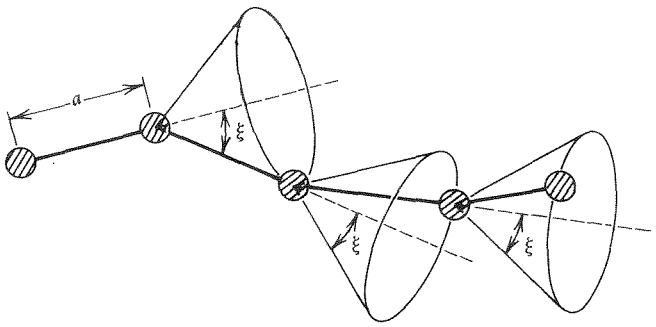


FIGURE 11.2-1. Chain of carbon atoms in the backbone of a polyethylene molecule. ◍, Carbon atom in a polyethylene chain. $\xi = \arccos(\frac{1}{3}) = 70.5°$.

average values. Therefore in constructing a mechanical model of a polymer molecule it seems reasonable to fix the bond lengths and angles at their mean values.

If we consider for a moment a polyethylene chain, $CH_3(CH_2)_nCH_3$, and if we ignore the pendant hydrogen atoms, then the chain can be represented as a set of mass points (often called "beads" in polymer kinetic theory) joined by massless "rods." The angle between successive C–C bonds is restricted to be $\xi = \arccos \frac{1}{3} = 70.5°$ (see Fig. 11.2-1). However, because of the presence of the hydrogen atoms, there are rotational energy barriers that prevent the successive links from rotating freely. Some approximate analytical expressions have been developed for the potential energy of the rotational barriers for polyethylene and other chains, and with these, various quantities, such as mean square end-to-end distance, have been calculated.[2]

A somewhat less detailed model is the *rotational isomeric state model.* In this model one presumes that the details of the rotational energy barrier are not needed, but that each succeeding link in the chain can exist in one of several (usually three) distinct rotational positions. This type of modeling has been used extensively by Flory and his collaborators in their studies of the configurations of specific polymer chains at equilibrium.[3] To date no nonequilibrium calculations have been made for these chain models that account for hindered rotation, with either continuous or discrete rotational states.

This leads us to discuss a still less detailed model in which one ignores altogether the restrictions on the rotations about the chemical bonds although the bond angles are kept fixed. This *freely rotating chain* model was the subject of extensive formal nonequilibruim kinetic theory studies by Kirkwood and his school.[4] Kirkwood assumed that the beads obey a Maxwellian velocity distribution and also that each bead in the chain experiences a Stokes' law drag force as it moves through the surrounding solvent molecules; in this way a bead "friction coefficient" ζ is introduced that accounts in some kind of average way for the resistance encountered by the bead when the chain moves through a succession of configurations. Having made these two assumptions, Kirkwood then formulated the partial differential equation from which the configurational distribution function could in principle be obtained. This partial differential equation has been solved only for potential flows, and very limited calculations of rheological properties have been made (see §16.6). In addition,

[2] A very readable account of this type of modeling can be found in L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Oxford University Press, London (1975), Chapter III.

[3] P. J. Flory, op. cit., Chapters III–VII.

[4] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967); this is a collection of twenty papers dealing with polymer kinetic theory.

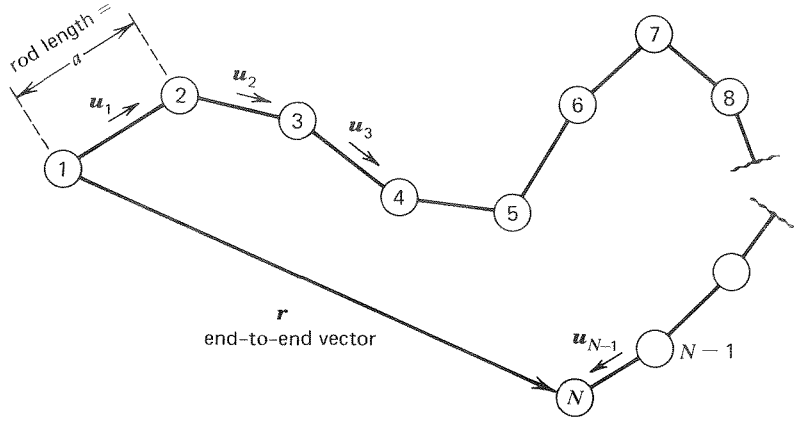


FIGURE 11.3-1. The Kramers freely jointed bead-rod chain model formed from N "beads" and $N - 1$ rigid "rods". The rod orientations are given by the unit vectors $\boldsymbol{u}_k$ ($k = 1, 2, \ldots, N - 1$).

some calculations of equilibrium properties have been given, based not on rigorous statistical mechanics but on a modified random walk calculation in which the constancy of the bond angles is accounted for.[5]

Another chain model, closely related to the Kirkwood-Riseman freely rotating chain, is the Porod-Kratky *wormlike chain*.[6] This is essentially a continuous version of the freely rotating chain, in that the beads have been smoothed out into a continuous wormlike structure of constant curvature with the plane of the curvature varying randomly.

§11.3 THE FREELY JOINTED BEAD-ROD CHAIN MODEL

We turn next to a model which is considerably less detailed, namely the *freely jointed chain* of N beads of mass m and friction coefficient ζ connected by $N - 1$ rigid, massless rods of length a. In this model the beads do not represent the atoms of the polymer chain backbone, but merely some portion of the polymer chain, say 10 or 20 monomer units. The quantities N and a are thus imprecisely defined quantities, but $(N - 1)a$ is the contour length of the true molecule being represented by the model. We have thus sacrificed some rigor in this model for the sake of simplicity. Since this model was the object of study by Kramers[1] in a key paper in polymer kinetic theory, we often refer to it as the *Kramers chain* model; it has also been referred to as the *pearl necklace* model. It is pictured in Fig. 11.3-1.

Although the freely jointed bead-rod chain does not pretend to portray the chemical structure of a linear macromolecule, it does possess a number of features that are characteristic of these molecules: it has a large number of internal degrees of freedom; it can be oriented, stretched, and deformed; it has a constant contour length. These are all properties that are significant in formulating a kinetic theory for the rheological behavior of a polymeric liquid. Keep in mind that the model contains two adjustable constants: the drag coefficient ζ and the rod length a (the bead mass m turns out to be unimportant since

[5] L. R. G. Treloar, loc. cit.; H. Eyring, *Phys. Rev.*, **39**, 746-748 (1932); F. T. Wall, *J. Chem. Phys.*, **11**, 67-71, 485-488, 527-530 (1943).

[6] P. J. Flory, op. cit., Appendix G; G. Porod, *Monatsh. Chem.*, **80**, 251-255 (1949); O. Kratky and G. Porod, *Rec. Trav. Chim.*, **68**, 1106-1122 (1949). H. Yamakawa, *Ann. Revs. Phys. Chem.*, **35**, 23-47 (1984).

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

inertial effects are generally neglected, and the number of beads N is determined from the contour length L by $L = (N - 1)a$).

Because of the importance of the freely jointed chain model in the polymer chemistry literature, we interrupt our discussion of model-building to obtain a few standard results that we need later. In order to obtain these results, it is necessary to have an expression for the configurational distribution function for the chain. In Chapter 12 we derive an expression for the equilibrium distribution function for a single bead-rod chain in a dilute solution starting from the principles of equilibrium statistical mechanics. We find that to a good approximation the distribution function is the "random walk" distribution; that is, the polar angles θ_i and ϕ_i for the ith link in the chain are completely random. The probability that the ith link is found to be within the range $d\theta_i\, d\phi_i$ about θ_i, ϕ_i is then

$$\psi_{i,\mathrm{eq}}(\theta_i, \phi_i)d\theta_i\, d\phi_i = \frac{1}{4\pi} \sin \theta_i\, d\theta_i\, d\phi_i \tag{11.3-1}$$

Since each link is assumed to be oriented independently of all other links, the configurational distribution function for the entire chain at equilibrium is the product of the single link distribution functions:[2]

$$\psi_{\mathrm{eq}}(\theta^{N-1}, \phi^{N-1}) = \prod_{i=1}^{N-1} \psi_{i,\mathrm{eq}} = \left(\frac{1}{4\pi}\right)^{N-1} \prod_{i=1}^{N-1} \sin \theta_i \tag{11.3-2}$$

The average value of any property $B(\theta^{N-1}, \phi^{N-1})$ that depends on the configuration is then given by

$$\langle B \rangle_{\mathrm{eq}} = \iint B\psi_{\mathrm{eq}}\, d\theta^{N-1}\, d\phi^{N-1} \tag{11.3-3}$$

This is the average value over the entire ensemble of systems, where in this case a system is a single polymer molecule. This average value is that which would be measured in some kind of an experiment that is made over a macroscopic time interval. That is, we assume that time averages are the same as ensemble averages. Average values are discussed more fully in Chapter 12.

In the illustrative examples that follow we use this random-walk distribution to obtain expressions for some important statistical quantities: the mean square end-to-end distance, the probability distribution for the end-to-end vector, and the mean tension in the chain.

EXAMPLE 11.3-1 Root-Mean-Square End-to-End Distance

In a dilute solution a polymer molecule is being continually bombarded by the solvent molecules. As a result its configuration is continually changing, as are various derived quantities, such as the end-to-end distance of the molecule. The end-to-end vector is

$$\boldsymbol{r} = \sum_{i=1}^{N-1} a\boldsymbol{u}_i \tag{11.3-4}$$

[2] Here and elsewhere in this volume we use the abbreviated notation θ^{N-1}, ϕ^{N-1} instead of $\theta_1, \phi_1, \theta_2, \phi_2, \ldots, \theta_{N-1}, \phi_{N-1}$ and $\iint d\theta^{N-1}\, d\phi^{N-1}$ for $\int \cdots \int d\theta_1\, d\phi_1\, d\theta_2\, d\phi_2 \cdots d\theta_{N-1}\, d\phi_{N-1}$. Also, note that in Eq. 11.3-1 we choose to include the factor $\sin \theta_i$ in the distribution function rather than in the differential element of area; we do this in order to be consistent with the use of generalized coordinates in the next chapter.

where the $\boldsymbol{u}_i$ are the unit vectors in the directions of the links of the chain. The square of the end-to-end distance is then given by

$$r^2 = (\boldsymbol{r}\cdot\boldsymbol{r}) = a^2 \sum_{i=1}^{N-1}\sum_{j=1}^{N-1} (\boldsymbol{u}_i\cdot\boldsymbol{u}_j) \tag{11.3-5}$$

We are normally interested only in average quantities, that is, quantities averaged over an entire ensemble of systems. In this case the system is a single polymer molecule, and the distribution function in Eq. 11.3-2 describes the distribution of configurations for a large collection of chains. Find the average value of r^2 in a solution at rest (that is, at rest when viewed macroscopically) by using the configurational distribution function in Eq. 11.3-2.

SOLUTION According to Eq. 11.3-3 the average value of r^2 is

$$\langle r^2\rangle_{\text{eq}} = a^2 \sum_i \sum_j \iint (\boldsymbol{u}_i\cdot\boldsymbol{u}_j)\psi_{\text{eq}}\, d\theta^{N-1}\, d\phi^{N-1} \tag{11.3-6}$$

The dot products of the unit vectors can be calculated by noting that the x-, y-, and z-components of $\boldsymbol{u}_i$ are $\sin\theta_i\cos\phi_i$, $\sin\theta_i\sin\phi_i$, and $\cos\theta_i$, respectively; when the integrations are performed we find that

$$\begin{aligned}\langle r^2\rangle_{\text{eq}} &= a^2 \sum_i \sum_j \delta_{ij} \\ &= a^2(N-1)\end{aligned} \tag{11.3-7}$$

in which δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ if $i \neq j$). Therefore the root-mean-square end-to-end distance is

$$\sqrt{\langle r^2\rangle_{\text{eq}}} = \sqrt{N-1}\,a \tag{11.3-8}$$

Since the length of the fully extended chain is $(N-1)a$, a polymer molecule can in the extreme be stretched by a factor of $\sqrt{N-1}$ from its equilibrium value. Since N can be of the order of magnitude of 100 for reasonable models of macromolecules, it can be expected that this enormous change in molecular shape will profoundly effect the optical and rheological properties of polymeric materials in a state of flow.

If instead of the freely jointed chain we use the freely rotating chain with $\xi = \arccos\frac{1}{3}$ we find Eyring's result[3] that $\langle r^2\rangle_{\text{eq}} = 2(N-1)a^2$. This is just 2 times the value for the freely jointed chain.

In obtaining Eq. 11.3-8 and also the Eyring result just quoted, the finite size of the cross-section of the chain is not accounted for. If this "excluded volume effect" is accounted for, the root-mean-square end-to-end distance will be increased still further.[3,4]

EXAMPLE 11.3-2 Equilibrium Distribution Function for the End-to-End Vector

In Eq. 11.3-2 we have given the equilibrium distribution function for the configuration of a freely jointed bead-rod chain model of a polymer molecule. For some purposes we need less complete distribution functions. By way of example, suppose we want only the probability that the first link in

[3] See L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Oxford University Press, London (1975), Chapter VI.

the chain will have an orientation θ, ϕ. This can be obtained in one of two ways. The simplest is to integrate the full chain distribution function over the orientation variables for all links except the first:

$$\psi_{1,\mathrm{eq}}(\theta, \phi) = \underbrace{\int \cdots \int}_{2(N-2)\text{-fold}} \psi_{\mathrm{eq}}(\theta^{N-1}, \phi^{N-1}) d\theta_2 \, d\phi_2 \cdots d\theta_{N-1} \, d\phi_{N-1} \Big|_{\theta_1 = \theta, \phi_1 = \phi} \tag{11.3-9}$$

Alternatively one can evaluate the average of the product of the Dirac delta functions:

$$\psi_{1,\mathrm{eq}}(\theta, \phi) = \underbrace{\int \cdots \int}_{2(N-1)\text{-fold}} \psi_{\mathrm{eq}}(\theta^{N-1}, \phi^{N-1}) \delta(\theta_1 - \theta) \delta(\phi_1 - \phi) d\theta^{N-1} \, d\phi^{N-1} \tag{11.3-10}$$

The delta function has the property that $\int \delta(x - a) f(x) dx = f(a)$. When this property is used it can be seen that Eq. 11.3-10 reduces to Eq. 11.3-9. Often this second way of getting reduced distribution functions is more straightforward to apply. For more on the Dirac delta function, see Appendix E.

Let us now apply this second procedure to get the probability that a polymer molecule has an end-to-end vector in the range $d\boldsymbol{r}$ about $\boldsymbol{r}$. That is, we write

$$P_{\mathrm{eq}}(\boldsymbol{r}) = \int\int \delta\left(\boldsymbol{r} - a \sum_i \boldsymbol{u}_i\right) \psi_{\mathrm{eq}} \, d\theta^{N-1} \, d\phi^{N-1} \tag{11.3-11}$$

To obtain $P_{\mathrm{eq}}(\boldsymbol{r})$ in the random-walk approximation, we have to introduce the distribution function from Eq. 11.3-2 and perform the integration. The mathematical details of the evaluation of the multiple integrals in Eq. 11.3-11 are not given here. If N is very large and the end-to-end distance is smaller than about $0.5\,Na$, it may be shown[4] that $P_{\mathrm{eq}}(\boldsymbol{r})$ is to a very good approximation

$$P_{\mathrm{eq}}(\boldsymbol{r}) \doteq \left(\frac{3}{2\pi(N-1)a^2}\right)^{3/2} e^{-3r^2/2(N-1)a^2} \tag{11.3-12}$$

This result is known as the Gaussian distribution for the end-to-end vector of the freely jointed chain with $N - 1$ links of length a. It can be seen that $P_{\mathrm{eq}}(\boldsymbol{r})$ has a maximum at $\boldsymbol{r} = \boldsymbol{0}$. That is, if one end of the molecule is located at the origin, the most probable location of the other end is also at the origin. This does not mean, however, that the most likely value of the end-to-end distance $r = |\boldsymbol{r}|$ is zero. Indeed we already know that the average value of the square of the end-to-end distance is $(N - 1)a^2$. Show that although the Gaussian distribution for the end-to-end vector is only approximately valid, it still gives the correct value of the mean square end-to-end distance in the random-walk approximation.

SOLUTION Using Eq. 11.3-12 gives

$$\begin{aligned}
\langle r^2 \rangle_{\mathrm{eq}} &= \int r^2 P_{\mathrm{eq}}(\boldsymbol{r}) d\boldsymbol{r} \\
&= \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r^2 \left(\frac{3}{2\pi(N-1)a^2}\right)^{3/2} e^{-3r^2/2(N-1)a^2} r^2 \sin\theta \, dr \, d\theta \, d\phi \\
&= (N-1)a^2
\end{aligned} \tag{11.3-13}$$

in agreement with Eq. 11.3-7. In the next example we see a further use of Eq. 11.3-12.

[4] H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 15; P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley, New York (1969), Chapter VIII. See also Problem 12D.1.

EXAMPLE 11.3-3 Average Tension in a Polymer Chain

The Helmholtz free energy $A = U - TS$ (where U is the internal energy and S is the entropy) of any system at equilibrium at temperature T is given by statistical mechanics as

$$A = -kT \ln Z \tag{11.3-14}$$

where Z is the *partition function*. Aside from a multiplicative constant the partition function is given by the integral of $e^{-\mathscr{H}/kT}$ over the phase space of the system. The Hamiltonian $\mathscr{H}$ is given as the sum of the kinetic and potential energies:

$$\mathscr{H} = \mathscr{K} + \phi \tag{11.3-15}$$

expressed in terms of generalized coordinates and momenta (see Chapter 12).

Here we consider a polymer chain with a fixed end-to-end vector $\boldsymbol{r}$ suspended in a sea of solvent molecules at a temperature T. For an ensemble of such systems it can be shown (see Eq. 12.3-5 with $\sqrt{g} = \prod_i \sin\theta_i$) that in the random-walk approximation the partition function is given, except for a multiplicative factor independent of $\boldsymbol{r}$, by $P_{eq}(\boldsymbol{r})$ as defined in Eq. 11.3-11. Hence the Helmholtz free energy of the polymer chain with end-to-end vector $\boldsymbol{r}$ is

$$A(\boldsymbol{r}) = A^{(0)} - kT \ln P_{eq}(\boldsymbol{r}) \tag{11.3-16}$$

where $A^{(0)}$ does not contain $\boldsymbol{r}$. Use this result to find the average tension in a polymer chain for large values of N and for $|\boldsymbol{r}| < \frac{1}{2}Na$.

SOLUTION When the length of the chain is changed by a small amount at constant T, the change of the Helmholtz free energy is given from Eq. 11.3-16 and Eq. 11.3-12 by

$$\begin{aligned} dA &= -kT\, d \ln P_{eq}(\boldsymbol{r}) \\ &\doteq -kT\, d\left[\frac{-3(\boldsymbol{r}\cdot\boldsymbol{r})}{2(N-1)a^2}\right] \\ &= \frac{3kT}{(N-1)a^2}(\boldsymbol{r}\cdot d\boldsymbol{r}) \end{aligned} \tag{11.3-17}$$

However, we also know that for an isothermal process the change in the Helmholtz free energy of the chain is related to the tension $\boldsymbol{F}^{(c)}$ in the chain by

$$dA = (\boldsymbol{F}^{(c)}\cdot d\boldsymbol{r}) \tag{11.3-18}$$

When these last two expressions are equated we get

$$\left(\left[\boldsymbol{F}^{(c)} - \frac{3kT}{(N-1)a^2}\boldsymbol{r}\right]\cdot d\boldsymbol{r}\right) = 0 \tag{11.3-19}$$

This scalar product must be equal to zero for all infinitesimal increments $d\boldsymbol{r}$, but that can be true only if the vector within the bracket is zero. Consequently

$$\boldsymbol{F}^{(c)}(\boldsymbol{r}) = \frac{3kT}{(N-1)a^2}\boldsymbol{r} \qquad (N \text{ large}, |\boldsymbol{r}| < \tfrac{1}{2}Na) \tag{11.3-20}$$

Thus the freely jointed bead-rod chain acts like a Hookean spring with a force constant given by $H = 3kT/(N-1)a^2$ and length zero in the absence of an external force; that is, its rest length is zero. Since this calculation is based on the Gaussian distribution, Eq. 11.3-20 is often called a *Gaussian spring*; because of the connection with the entropy of the chain the term "entropic spring" is also used.

Now that an expression has been derived for the Hookean spring constant, we can rewrite the expressions for the distribution function for the end-to-end vector and the root-mean-square end-to-end distance as

$$P_{eq}(\boldsymbol{r}) \doteq \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)(\boldsymbol{r}\cdot\boldsymbol{r})} \tag{11.3-21}$$

$$\langle r^2\rangle_{eq} = \frac{3kT}{H} \tag{11.3-22}$$

These expressions are now in forms similar to those appearing in later chapters.

As mentioned previously the Gaussian approximation is good only for large N and extensions r smaller than about $0.5Na$. As a result Eq. 11.3-20 cannot be generally valid, and indeed it allows the chain to be stretched to any length provided that enough force is applied. In actuality the spring must stiffen up as the chain becomes fully extended. To take account of this fact various modified force laws have been proposed; we cite two of these:

i. *Inverse Langevin Force Law* (derivable from molecular arguments):[3]

$$F^{(c)}(r) = \frac{kT}{a}\mathscr{L}^{-1}\left[\frac{r}{(N-1)a}\right] \tag{11.3-23}$$

where $\mathscr{L}^{-1}$ is the function inverse to the Langevin function given by $\mathscr{L}(x) = (\coth x) - x^{-1}$.

ii. *Warner Force Law* (a useful empiricism):[5]

$$F^{(c)}(r) = \frac{3kTr/(N-1)a^2}{[1-(r/(N-1)a)^2]} \tag{11.3-24}$$

Springs obeying this force law are often called *FENE* (finitely extensible nonlinear elastic) springs.

In these last two equations $F^{(c)} = |\boldsymbol{F}^{(c)}|$ denotes the tension in the spring.

These various spring force-law functions are shown in Fig. 11.3-2. Note that the Warner force law has all of the desired physical characteristics: linear behavior at small extensions, and a finite length $(N-1)a$ in the limit of an infinite force; it has the advantage that it is much simpler than the inverse Langevin function.

§11.4 THE FREELY JOINTED BEAD-SPRING MODELS

In the foregoing section we saw that a freely jointed bead-rod chain suspended in a solvent and thereby subjected to random Brownian motion behaves something like a

[5] H. R. Warner, Jr., *Ind. Eng. Chem. Fundamentals*, **11**, 379–387 (1972).

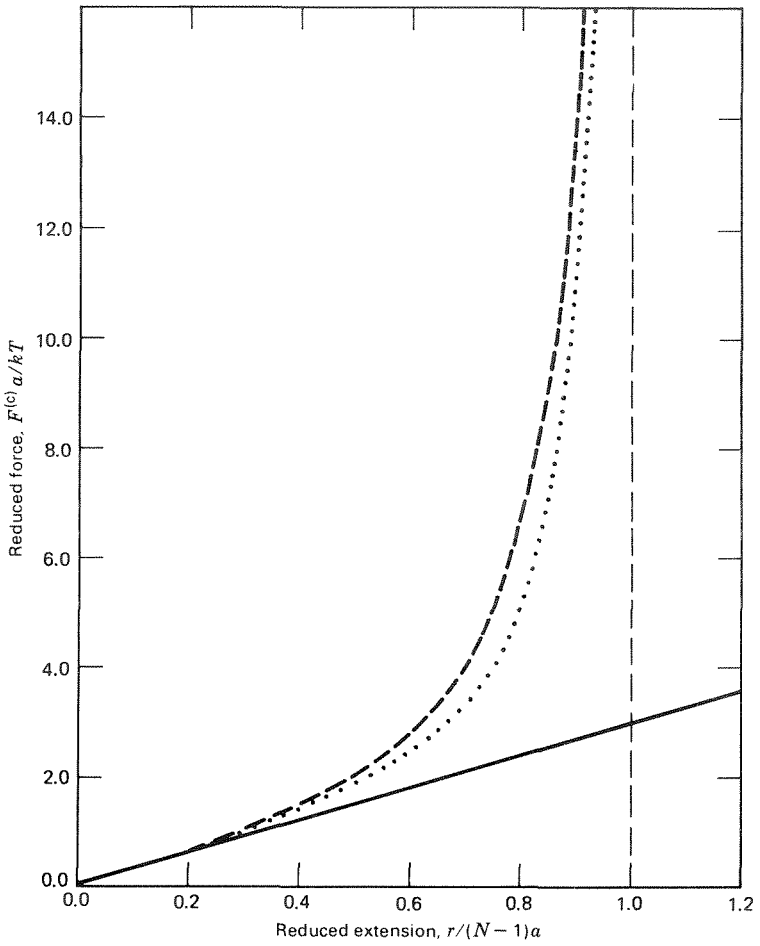


FIGURE 11.3-2. Plots of three approximate expressions for the ensemble average tension $F^{(c)}$ in a freely jointed chain of $(N-1)$ links of length a with end-to-end distance r. ——, Hookean, Eq. 11.3-20; ·····, inverse Langevin, Eq. 11.3-23; - - - -, Warner, Eq. 11.3-24.

spring. A similar result would have been obtained for a freely rotating chain. This suggests that a suitable way to model a linear polymer chain is to replace a portion of the chain containing several hundred backbone atoms by a "spring" and concentrate the masses of the atoms in "beads." This leads to the freely jointed bead-spring chain (see Fig. 11.4-1). Each bead is presumed to experience a drag force as it moves through the solvent, and this force is customarily described by Stokes' law. This model is considerably simpler to handle than the corresponding bead-rod chain because it contains no internal constraints; this point is elaborated on in the next chapter.

If the springs are taken to be Hookean springs, then the bead-spring chain is often referred to as a *Rouse chain*, or a *Rouse–Zimm chain*, the names being associated with the authors of two landmark papers in polymer kinetic theory.[1] This model has been widely

[1] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272-1280 (1953); B. H. Zimm, *J. Chem. Phys.*, **24**, 269-278 (1956). For the corrections of some errors in the latter paper see M. C. Williams, *J. Chem. Phys.*, **42**, 2988-2989 (1965), **43**, 4542 (1965). See also M. C. Williams, *AIChE J.*, **21**, 1-25 (1975) for an extensive literature review on macromolecular modeling.

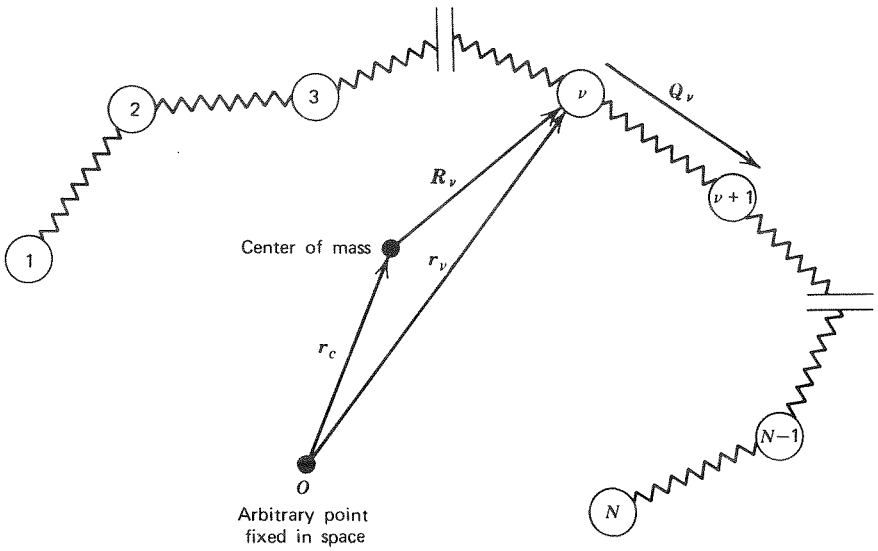


FIGURE 11.4-1. The freely jointed bead-spring chain model formed from N "beads" and $N-1$ "springs". The spring configurations are given by the connector vectors $\boldsymbol{Q}_\nu$ ($\nu = 1, 2, 3, \ldots, N-1$).

used in kinetic theory because it has a large number of internal degrees of freedom and exhibits orientability and stretchability; however it has the distinct disadvantage that it does not have a constant contour length and in fact can be stretched out to any length whatsoever. The model has been particularly popular—and, in fact, probably overused—because the linear spring force law has enabled polymer scientists to obtain a wide spectrum of analytical solutions to equilibrium and nonequilibrium problems alike. The Rouse-Zimm chain contains three model parameters: the number of beads N, the Hooke-law force constant H for the springs, and the Stokes' law friction coefficient ζ.

If one wishes to include finitely extensible springs (the Warner, or "FENE," springs, for example) then the contour length of the chain model cannot exceed a certain limit, and there are four model parameters: N and ζ mentioned above, and then two constants in the spring force law (a spring constant H, and the maximum extensibility of an individual spring Q_0). These finitely extensible chains have had only limited use, inasmuch as it is apparently not possible to get analytical solutions to nonequilibrium kinetic theory problems.

EXAMPLE 11.4-1 Mean-Square End-to-End Distance for a Rouse Chain

It is shown in Chapter 12 that the equilibrium configurational distribution function for the Rouse chain is

$$\psi_{\text{eq}} = \left(\frac{H}{2\pi kT}\right)^{3(N-1)/2} e^{-(H/2kT)\sum_i(\boldsymbol{Q}_i \cdot \boldsymbol{Q}_i)}$$

$$= \prod_{j=1}^{N-1} \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_j^2} \tag{11.4-1}$$

It is not too surprising that this equation appears to be a generalization of Eq. 11.3-21 for the end-to-end vector distribution function for a bead-rod chain in the Gaussian limit. Find the mean-square end-to-end distance.

SOLUTION The mean square end-to-end distance can be found for the Rouse chain by using a derivation similar to that in Example 11.3-1:

$$\langle r^2 \rangle_{eq} = \int \sum_i \sum_j (\boldsymbol{Q}_i \cdot \boldsymbol{Q}_j) \psi_{eq}(\boldsymbol{Q}_1 \cdots \boldsymbol{Q}_{N-1}) d\boldsymbol{Q}^{N-1}$$

$$= \sum_i \int Q_i^2 \prod_{j=1}^{N-1} \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)Q_j^2} \, d\boldsymbol{Q}^{N-1}$$

$$= \sum_i \left(\frac{H}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty Q_i^2 e^{(H/2kT)Q_i^2} Q_i^2 \, dQ_i$$

$$= \frac{3(N-1)kT}{H} \tag{11.4-2}$$

Finally by means of the method outlined in Example 12.5-2 it can be shown that the probability for the end-to-end vector $\boldsymbol{r}$ for the Rouse chain is:

$$P_{eq}(\boldsymbol{r}) = \left[\frac{H}{2(N-1)\pi kT}\right]^{3/2} e^{-[H/2(N-1)kT](\boldsymbol{r} \cdot \boldsymbol{r})} \tag{11.4-3}$$

Equations 11.4-2 and 11.4-3 should be compared with Eqs. 11.3-22 and 11.3-21 respectively. Further discussions of Rouse chains are given in Chapter 12.

§11.5 DUMBBELL MODELS

In the foregoing two sections we discussed chains of N beads connected together linearly with rigid rods or springs. In this section we consider the very simplified models that result when N is set equal to 2—the *dumbbell models*. The *rigid dumbbell*[1] and the *elastic dumbbell*[2] are shown in Fig. 11.5-1. Of course, there are many kinds of elastic dumbbell models depending on the choice of the spring force law. Table 11.5-1 contains a summary of information about various commonly encountered dumbbell models.

The dumbbell models are only very crude representations of polymer molecules. The rigid dumbbell can be regarded as an ultrasimplified model of a rigid linear polymer, such as tobacco mosaic virus (see electron micrograph in Fig. 11.5-2). The model of a rod connecting two point masses does not account for the finite volume of the molecule nor does it even involve the same kinds of hydrodynamics as it rotates and translates through the solvent. Nonetheless it does have the property of being oriented by a solvent flow field, and many of the rheological properties are described qualitatively by this elementary rigid dumbbell model.

[1] W. Kuhn, *Zeits. f. phys. Chem.*, **161**, 1–32 (1932); *Kolloid-Zeitschrift*, **62**, 269–285 (1933); W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 97–127 (1945).

[2] J. J. Hermans, *Physica*, **10**, 777 789 (1943); G. K. Fraenkel, *J. Chem. Phys.*, **20**, 642–647 (1952).

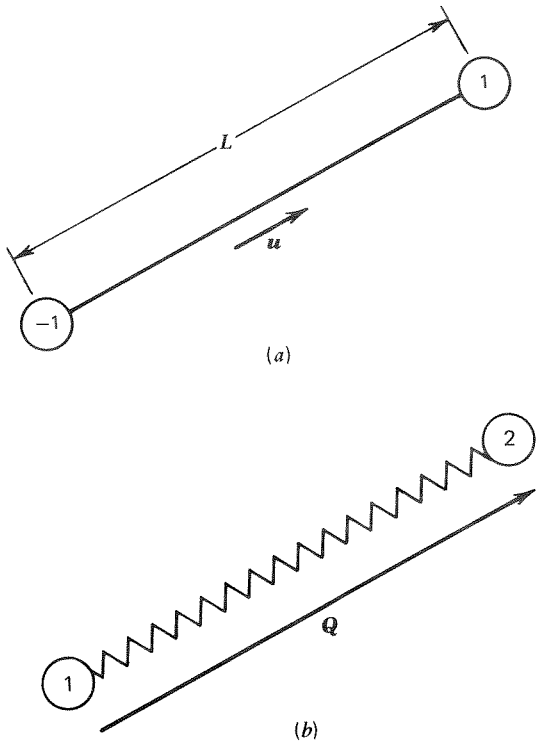


FIGURE 11.5-1. (*a*) Rigid dumbbell model of length L with orientation given by unit vector $\boldsymbol{u}$. (*b*) Elastic dumbbell with configuration given by vector $\boldsymbol{Q}$, whose components are X, Y, Z.

The elastic dumbbell model is also too crude to be of much interest to a polymer chemist, since it in no way accounts for the details of the molecular architecture. It certainly does not have enough internal degrees of freedom to describe the very rapid motions that contribute, for example, to the complex viscosity at high frequencies. On the other hand, the elastic dumbbell model is orientable and stretchable, and these two properties are essential for the qualitative description of steady-state rheological properties and those involving slow changes with time. In fact, the elastic dumbbell models have proven to be very helpful in developing an elementary but broad understanding of the relation between macromolecular motions and rheological phenomena.

Above all, by using the crude dumbbell models it is possible to perform kinetic theory derivations and calculations for nonlinear rheological properties, to continue even further to get constitutive equations, and then finally to solve some nontrivial flow problems. All of this can be done with a limited amount of mathematical effort and analytical results in closed form can be obtained. In other words one can go through the entire program of endeavor—from molecular model to fluid dynamics—for illustrative purposes, in order to point the way towards the task that has ultimately to be performed for more realistic models. The analytical results for the dumbbell models can be used also to check computer simulation procedures in molecular dynamics and Brownian dynamics.

Dumbbell models must, to some extent then, be regarded as mechanical playthings, somewhat disconnected from the real world of polymers. When used intelligently, however, they can be useful pedagogically and very helpful in developing a qualitative understanding of rheological phenomena.

TABLE 11.5-1

Expressions for Spring Forces and Equilibrium Configurational Distribution Functions for Elastic Dumbbells

Name	Connector Force Law and Connector Potential $\boldsymbol{F}^{(c)} = +(\partial/\partial \boldsymbol{Q})\phi^{(c)}$		Comments	Non-Normalized Distribution Function[a] $= \exp(-\phi^{(c)}/kT)$	
Hooke[b] ("Linear")	$\boldsymbol{F}^{(c)} = H\boldsymbol{Q}$	(A)	This spring is infinitely stretchable, and when there is no force in the connector, Q is zero (that is, the beads coalesce).	$e^{-HQ^2/2kT}$	(I)
	$\phi^{(c)} = \frac{1}{2}HQ^2$	(B)			
Fraenkel[c]	$\boldsymbol{F}^{(c)} = H\left(1 - \frac{Q_0}{Q}\right)\boldsymbol{Q}$	(C)	In the absence of tension, the distance between the bead centers is Q_0. When $Q_0 \to 0$ we obtain Hookean springs, and when $H \to \infty$, we get a rigid rod of length Q_0.	$e^{-H(Q-Q_0)^2/2kT}$	(J)
	$\phi^{(c)} = \frac{1}{2}H(Q - Q_0)^2$	(D)			
Tanner[d] ("Linear-Locked")	$\boldsymbol{F}^{(c)} = H\boldsymbol{Q}, \quad Q < Q_0$	(E)	These "linear-locked" springs can stretch only as far as $Q = Q_0$, but for $Q \le Q_0$ they are described by Hooke's law.	$\begin{cases} e^{HQ^2/2kT} & \text{for } Q < Q_0 \\ 0 & \text{for } Q \ge Q_0 \end{cases}$	(K)
	$\phi^{(c)} = \frac{1}{2}HQ^2, \quad Q < Q_0$	(F)			
Warner[e] ("FENE")	$\boldsymbol{F}^{(c)} = \dfrac{H\boldsymbol{Q}}{1 - (Q/Q_0)^2}, \quad Q < Q_0$	(G)	These "finitely extendable nonlinear elastic" (or "FENE") connectors have an upper limiting length of $Q = Q_0$ The parameter b is given by $b = HQ_0^2/kT$.	$\begin{cases} \left[1 - \left(\dfrac{Q}{Q_0}\right)^2\right]^{HQ_0^2/2kT} & \text{for } Q < Q_0 \\ 0 & \text{for } Q \ge Q_0 \end{cases}$	(L)
	$\phi^{(c)} = -\frac{1}{2}HQ_0^2 \ln[1 - (Q/Q_0)^2] \quad Q < Q_0$	(H)			

[a] The normalization constant for the equilibrium distribution function is $J_{eq} = \iiint \exp(-\phi^{(c)}/kT)dX\,dY\,dZ$, in which X, Y, and Z are the Cartesian components of $\boldsymbol{Q}$. For Hookean dumbbells, $J_{eq} = (H/2\pi kT)^{3/2}$, and for FENE dumbbells. $J_{eq} = 2\pi Q_0^3 B(\frac{3}{2}, (b+2)/2)$ in which $B(x, y)$ is the beta function of x and y.

[b] See Example 11.3-3 and Eq. 11.3-20.

[c] G. K. Fraenkel, *J. Chem. Phys.*, **20**, 642–647 (1952); G. Wilemski and G. Tanaka, *Macromolecules*, **14**, 1531–1538 (1981).

[d] R. I. Tanner and J. Stehrenberger, *J. Chem. Phys.*, **55**, 1958–1964 (1971); erratum, *ibid.*, **61**, 2486 (1974); see also R. I. Tanner, *Trans. Soc. Rheol.*, **19**, 37–65 (1975).

[e] H. R. Warner, Jr., *Ind. Eng. Chem. Fundamentals*, **11**, 379–387 (1972); see Fig. 11.3-2 for a graph of Eq. G. See also, R. C. Armstrong, *J. Chem. Phys.*, **60**, 724–728, 729–733 (1974), and X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 251–265 (1985).

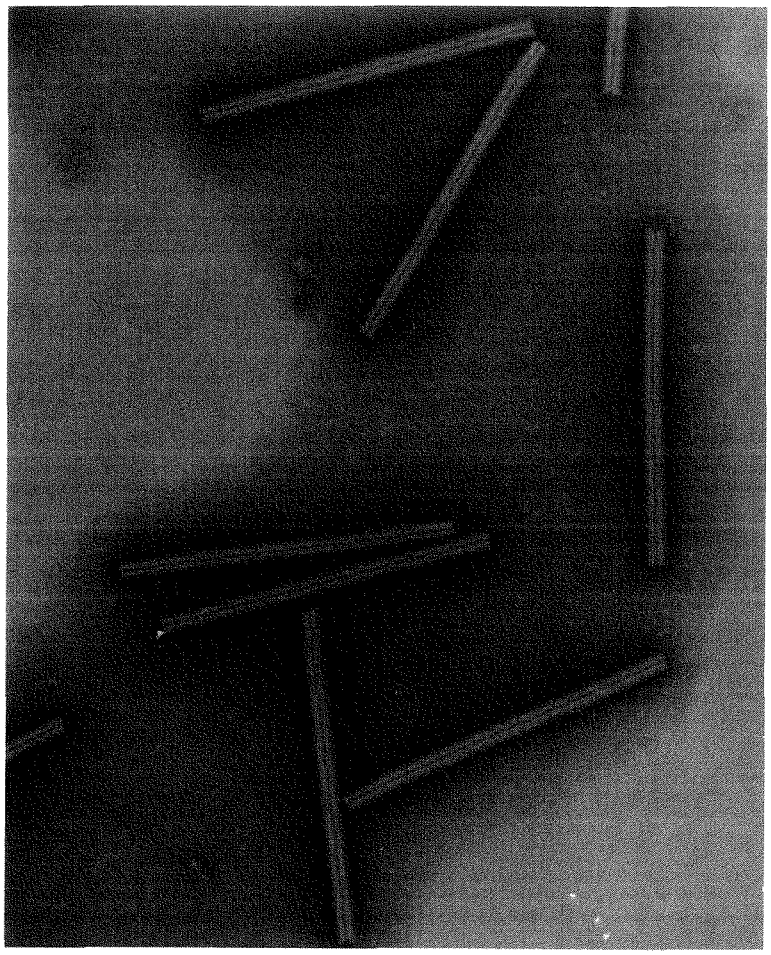


FIGURE 11.5-2. Electron micrograph of tobacco mosaic virus embedded in negative stain. The magnification is $\times 150{,}000$. Courtesy of the Virus Laboratory, University of California, Berkeley.

§11.6 THE GEOMETRY OF CHAINLIKE MOLECULES

Many parts of this book involve the kinetic theory of chainlike macromolecules, modeled as bead-rod or bead-spring chains. In discussions of these models it is helpful to have some standardized notation for the quantities needed to describe the chain configuration. In this section we give the various systems of notation used for describing the configuration of a chain of N identical "beads" joined together linearly by $N-1$ "connectors"; we also give the interrelations among the various systems of notation. The choice of system of notation depends predominantly on the kinds of constraints that are built into the chain, that is, fixed connector lengths, fixed bond angles, and so on. A more complete discussion of constraints and generalized coordinates is given in Chapter 12, but the discussion here should be a useful introduction to the subject.

a. Bead Vectors

The simplest way to give the configuration of a chain model is to specify the locations of all the beads by means of position vectors $\boldsymbol{r}_\nu$ with respect to some fixed

coordinate system (see Fig. 11.4-1). In some discussions we like to use position vectors $\boldsymbol{R}_v = \boldsymbol{r}_v - \boldsymbol{r}_c$ with respect to the center of mass of the chain.

b. Connector Vectors

An alternative way to specify the configuration of a chain is to give the position vector of the center of mass, $\boldsymbol{r}_c$, and the $N-1$ "connector vectors" $\boldsymbol{Q}_k$, which connect pairs of adjacent beads. (See Fig. 11.4-1). That is, we use

$$\boldsymbol{r}_c = \frac{1}{N}\sum_v \boldsymbol{r}_v \tag{11.6-1}$$

$$\boldsymbol{Q}_k = \boldsymbol{r}_{k+1} - \boldsymbol{r}_k \qquad k = 1, 2, \ldots, N-1 \tag{11.6-2}$$

Next we give the relations needed to go back and forth between these two sets of vectors. Here and throughout the book we use the following index conventions:

$v, \mu, \eta \ldots$	Numbering of beads	$1, 2, 3, \ldots, N$
$i, j, k \ldots$	Numbering of connectors	$1, 2, 3, \ldots, N-1$

Then it will usually not be necessary to state explicitly the upper limits on summations, the range of free indices, and the orders of matrices.

We express the relations between the two systems by writing

$$\boldsymbol{Q}_k = \sum_v \bar{B}_{kv}\boldsymbol{r}_v \tag{11.6-3}$$

$$\boldsymbol{r}_v - \boldsymbol{r}_c = \sum_k B_{vk}\boldsymbol{Q}_k \tag{11.6-4}$$

Here the matrix elements $\bar{B}_{kv}$ and B_{vk} are defined by

$$\bar{B}_{kv} = \delta_{k+1,v} - \delta_{kv} \tag{11.6-5}$$

$$B_{vk} = \begin{cases} \dfrac{k}{N} & (k < v) \\ -\left[1 - \left(\dfrac{k}{N}\right)\right] & (k \geq v) \end{cases} \tag{11.6-6}$$

Of course the combination of Eqs. 11.6-3 and 11.6-5 is exactly equivalent to Eq. 11.6-2. In terms of the $\bar{B}_{kv}$ and B_{vk} matrix elements we can define two $(N-1) \times (N-1)$ symmetric, nonsingular matrices (C_{ij}) and (A_{ij}) as follows:

$$\sum_v B_{vi}B_{vj} = C_{ij} = \begin{cases} i(N-j)/N, & \text{if } i \leq j \\ j(N-i)/N, & \text{if } j \leq i \end{cases} \tag{11.6-7}$$

$$\sum_v \bar{B}_{iv}\bar{B}_{jv} = A_{ij} = \begin{cases} 2 & \text{if } i = j \\ -1 & \text{if } i = j \pm 1 \\ 0 & \text{otherwise} \end{cases} \tag{11.6-8}$$

The (A_{ij})-matrix is generally referred to as the *Rouse matrix*[1] and the (C_{ij})-matrix can be called the *Kramers matrix*.[2] These matrices, which are inverse to one another, have eigenvalues a_j and c_j, respectively, given by[3];

$$a_j = \frac{1}{c_j} = 4 \sin^2\left(\frac{j\pi}{2N}\right) \tag{11.6-9}$$

Furthermore, we note for later use that[4]

$$\sum_j c_j = \sum_j C_{jj} = \frac{N^2 - 1}{6} \tag{11.6-10}$$

$$\sum_j \sum_k C_{jk} = \frac{N(N^2 - 1)}{12} \tag{11.6-11}$$

$$\sum_j c_j^2 = \sum_j \sum_k C_{jk}^2 = \frac{(N^2 - 1)(2N^2 + 7)}{180} \tag{11.6-12}$$

$$\sum_i \sum_j \sum_k C_{ik} C_{kj} = \frac{N(N^4 - 1)}{120} \tag{11.6-13}$$

$$\sum_j c_j^3 = \frac{(N^2 - 1)(8N^4 + 29N^2 + 71)}{7560} \tag{11.6-14}$$

$$\prod_j c_j = \det(C_{ij}) = \frac{1}{N} \tag{11.6-15}$$

c. Polar Angles

Another way to specify the chain configuration is to give the location of the center of mass $\boldsymbol{r}_c$, the lengths of the connectors Q_k, and the polar angles θ_k and ϕ_k for the connectors (or alternatively the unit vectors $\boldsymbol{u}_k$ in lieu of the polar angles). This specification is particularly useful for the freely jointed bead-rod chain, inasmuch as the connector lengths are all equal: $Q_k = a$.

In some developments it is convenient to associate with each connector in the chain a triad of unit vectors, $\boldsymbol{s}_k, \boldsymbol{t}_k, \boldsymbol{u}_k$; the third of these is the unit vector in the direction from bead k to bead $k + 1$. The first and second are unit vectors in the positive θ and ϕ directions. The components and spatial derivatives of these unit vectors are summarized in Appendix E, §E.5.

[1] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272-1280 (1953).

[2] H. A. Kramers, *Physica*, **11**, 1-19 (1944), used matrix elements $g_{\mu\nu}$ that differ by a factor of N from the matrix elements C_{ij} used here.

[3] F. B. Hildebrand, *Methods of Applied Mathematics*, Prentice-Hall, Englewood Cliffs, NJ (1952), p. 366, Problem 54; the (A_{ij})-matrix is a symmetric Jacobi matrix.

[4] H. A. Kramers, loc. cit.; O. Hassager, *J. Chem. Phys.*, **60**, 2111-2124 (1974).

d. Included Angles

Another method for giving the chain orientation is to give the center of mass vector $\boldsymbol{r}_c$, the connector lengths Q_k, the polar angles $\theta_1(\equiv\xi_1)$ and $\phi_1(\equiv\xi_{01})$ for the first connector, a set of angles $\xi_2, \xi_3, \ldots, \xi_{N-1}$, and another set of angles $\xi_{12}, \xi_{23}, \ldots, \xi_{N-2,N-1}$. The angle ξ_k is the angle (at bead k) between vectors $\boldsymbol{Q}_{k-1}$ and $\boldsymbol{Q}_k$, and has the range $0 \leq \xi_k < \pi$. The angle $\xi_{k,k+1}$ is the angle (at the connector between beads k and $k+1$) measured clockwise from the plane containing $\boldsymbol{Q}_{k-1}$ and $\boldsymbol{Q}_k$, to the plane containing $\boldsymbol{Q}_k$ and $\boldsymbol{Q}_{k+1}$, when sighting along the direction of the vector $\boldsymbol{Q}_k$; the range of this angle is $0 \leq \xi_{k,k+1} < 2\pi$ and $\xi_{k,k+1}$ is defined to be zero when beads $k-1$ through $k+2$ are coplanar, and when the triangle formed from beads $k-1$, k, $k+1$ overlaps the triangle formed from beads k, $k+1$, $k+2$. (To define the angle ξ_{12} one needs to introduce a fictitious $\boldsymbol{Q}_0$ which is pointing in the direction of the positive z-axis.) The angles ξ_1, ξ_{01}, and ξ_{12} specify the orientation of the entire chain in space, and the Q_k, $\xi_k(k \geq 2)$, and $\xi_{k-1,k}(k \geq 3)$ give the relative internal configuration (see Fig. 11.6-1).

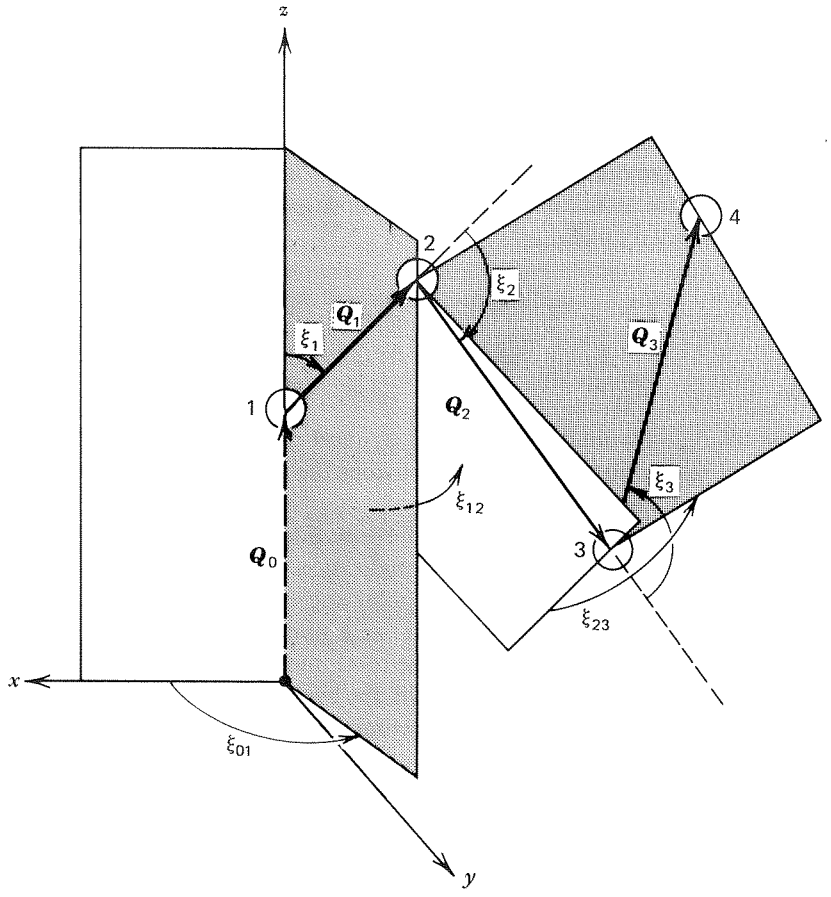


FIGURE 11.6-1. Use of included angles to specify chain configurations.

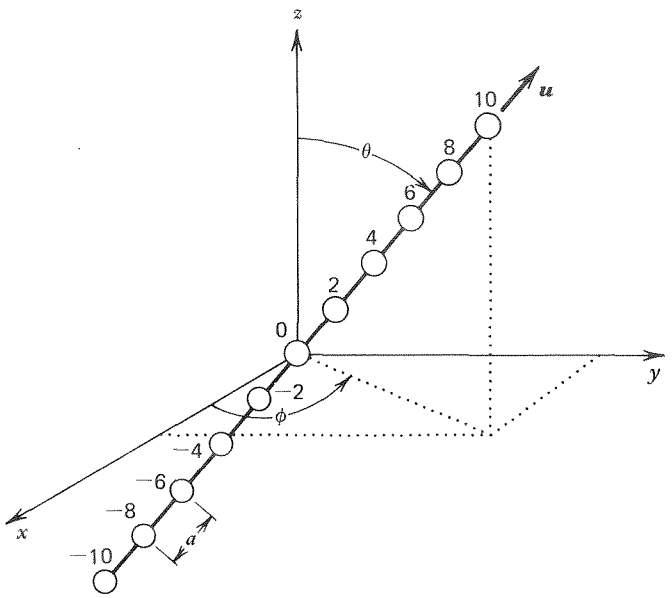


FIGURE 11.6-2. Multibead rod with orientation given by θ and ϕ. A rod with N beads separated by distance a has a total length of $L = (N - 1)a$.

The description of a configuration by means of the included angles is useful for the freely jointed chain (for which the Q_k are constant)[5], and is particularly useful for the freely rotating chain (for which the Q_k and the $\xi_k (k \geq 2)$ are all constants).[6]

A triad of unit vectors can be installed in each connector as described in §11.6c. The unit vectors associated with link k are related to those associated with link $k - 1$ by means of a transformation matrix as follows:

$$\begin{pmatrix} \boldsymbol{s}_k \\ \boldsymbol{t}_k \\ \boldsymbol{u}_k \end{pmatrix} = \begin{pmatrix} C_k c_k & C_k s_k & -S_k \\ -s_k & c_k & 0 \\ S_k c_k & S_k s_k & C_k \end{pmatrix} \begin{pmatrix} \boldsymbol{s}_{k-1} \\ \boldsymbol{t}_{k-1} \\ \boldsymbol{u}_{k-1} \end{pmatrix} \tag{11.6-16}$$

in which $C_k = \cos \xi_k$, $S_k = \sin \xi_k$, $c_k = \cos \xi_{k-1,k}$, and $s_k = \sin \xi_{k-1,k}$. Note that $\boldsymbol{s}_0$, $\boldsymbol{t}_0$, $\boldsymbol{u}_0$ are taken to be $\boldsymbol{\delta}_x$, $\boldsymbol{\delta}_y$, $\boldsymbol{\delta}_z$. Equation 11.6-16 provides the relations between the polar angles θ_i, ϕ_i and the included angles ξ_k, $\xi_{k-1,k}$.

We conclude this section by giving the notation to be used for the linear, rigid multibead-rod model (see Fig. 11.6-2). The configuration of this model is given by specifying the location of the center of mass and the two polar angles θ and ϕ giving its orientation. As may be seen in Fig. 11.6-2 it is convenient to use a numbering system for the beads that makes use of the symmetry of the model; if the total number of beads N is even, the beads are given odd numbers only, whereas if N is odd, the beads are designated by even numbers.

In this section we have discussed the geometrical relations and notation for linear models. Of course there are similar models for star-shaped polymers, comb polymers, and various shapes of rigid biopolymers. Such models are discussed only infrequently in this book, and hence it is not worthwhile to summarize notation for them here.

[5] C. F. Curtiss and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **2**, 392–396 (1977).

[6] P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969).

PROBLEMS

11A.1 Configurational Matrices for Chainlike Models

a. Display the $\bar{B}_{kv}$, B_{vk}, A_{ij}, and C_{ij} in matrix form for $N = 5$.
b. Verify Eqs. 11.6-10 to 11.6-13 using the numbers from the matrices in (a).

11A.2 Eigenvalues of the Rouse Matrix

For a 4-bead Rouse chain, find the eigenvalues of the Rouse matrix by getting the roots of the characteristic equation. Compare the eigenvalues thus obtained with the formula in Eq. 11.6-9.

11A.3 The Angle Between Successive C–C Bonds

Show that the angle between successive C–C bonds in a polyethylene chain is $\xi = \arccos(\frac{1}{3}) = 70.5°$.

11B.1 The Radius of Gyration

The radius of gyration s of a chain is defined by

$$s^2 = \frac{1}{N}\sum_{v=1}^{N}(\boldsymbol{R}_v \cdot \boldsymbol{R}_v) \tag{11B.1-1}$$

where $\boldsymbol{R}_v$ is the bead position vector with respect to the center of mass of the chain. The mean-square radius of gyration for a chain at equilibrium is then

$$\langle s^2\rangle_{eq} = \frac{1}{N}\sum_{v=1}^{N}\int(\boldsymbol{R}_v \cdot \boldsymbol{R}_v)\psi_{eq}\, d\boldsymbol{Q}^{N-1} \tag{11B.1-2}$$

a. Show that for the Rouse freely jointed bead-spring chain

$$\langle s^2\rangle_{eq} = \frac{(N^2-1)kT}{2NH} = \frac{1}{6}\frac{N+1}{N}\langle r^2\rangle_{eq} \tag{11B.1-3}$$

b. Show that for the Kramers freely jointed bead-rod chain

$$\langle s^2\rangle_{eq} = \frac{(N^2-1)a^2}{6N} = \frac{1}{6}\frac{N+1}{N}\langle r^2\rangle_{eq} \tag{11B.1-4}$$

if the random-walk distribution function is used.

c. Kramers[1] has shown that for the freely rotating bead-rod chain with $\xi = \arccos(\frac{1}{3}) = 70.5°$ as the included angle (see Fig. 11.2-1)

$$\langle s^2\rangle_{eq} = \tfrac{1}{6}Na^2\cot^2\tfrac{1}{2}\xi \tag{11B.1-5}$$

in the limit of very large N, where N is the number of beads. Calculate $\sqrt{\langle s^2\rangle_{eq}}$ for a polyethylene chain of molecular weight 10^6 g/mol. Each "bead" represents one carbon atom, and the C–C bond length is 0.15 nm. What is the analogous result for the freely jointed chain?

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

11B.2 Equilibrium Averages for the Random-Walk Chain

a. Verify the step from Eq. 11.3-6 to Eq. 11.3-7.
b. Show further that $\langle u_i u_j \rangle_{eq} = (\frac{1}{3})\delta_{ij}\,\delta$.
c. What is $\langle r \rangle_{eq}$?

11B.3 Probability for the End-to-End Vector

a. What assumptions are implied in Eq. 11.3-12?
b. Verify that $\int P_{eq}(\boldsymbol{r})d\boldsymbol{r} = 1$.
c. What is the probability density that a chain has a length r?

11B.4 Normalization Constants and Mean-Square End-to-End Distance for Elastic Dumbbells

a. In Table 11.5-1, verify that the normalization constant J_{eq} is

$$J_{eq} = \left(\frac{H}{2\pi kT}\right)^{-3/2} \tag{11B.4-1}$$

for Hookean dumbbells.
b. Show that for the Warner (FENE) dumbbells

$$J_{eq} = 2\pi Q_0^3 \mathrm{B}\left(\frac{3}{2}, \frac{b+2}{2}\right) \tag{11B.4-2}$$

where the "beta function" $\mathrm{B}(x, y) = \int_0^1 t^{x-1}(1-t)^{y-1}\,dt = \Gamma(x)\Gamma(y)/\Gamma(x+y)$, in which $\Gamma(x)$ is the gamma function.
c. Show that $\langle Q^2 \rangle_{eq} = 3kT/H$ for Hookean dumbbells.
d. Find $\langle Q^2 \rangle_{eq}$ for FENE dumbbells.

$$\textit{Hint:}\quad \int_0^{Q_0}\left[1-\left(\frac{Q}{Q_0}\right)^2\right]^{b/2} Q^n\,dQ = \left(\frac{Q_0^{n+1}}{2}\right)\mathrm{B}\left[\frac{1}{2}(n+1), \frac{1}{2}(b+2)\right]$$

11B.5 Configuration Matrices for the Simplest "Star" Polymer Model

In Fig. 11B.5 is a model with a center (bead "0") and three side chains leading to beads "1", "2", and "3". All beads have the same mass. Let the bead locations be $\boldsymbol{r}_0, \boldsymbol{r}_1, \boldsymbol{r}_2$, and $\boldsymbol{r}_3$. Let the center of mass location be given by the position vector $\boldsymbol{r}_c$, and the vectors $\boldsymbol{Q}_k$ be defined by $\boldsymbol{Q}_k = \boldsymbol{r}_k - \boldsymbol{r}_0$. Let these various vectors be related by:

$$\boldsymbol{Q}_k = \sum_v \bar{B}_{kv}\boldsymbol{r}_v \tag{11B.5-1}$$

$$\boldsymbol{r}_v = \boldsymbol{r}_c + \sum_k B_{vk}\boldsymbol{Q}_k \tag{11B.5-2}$$

a. Show that $\bar{B}_{kv} = \delta_{kv} - \delta_{v0}$ and that $B_{vk} = \delta_{vk} - \frac{1}{4}$.
b. Then verify that $A_{ij} = \delta_{ij} + 1$ and $C_{ij} = \delta_{ij} - \frac{1}{4}$, and show that the matrices (A_{ij}) and (C_{ij}) are inverse to one another.
c. Show that the eigenvalues of the (A_{ij})-matrix are $a_1 = a_2 = 1$, and $a_3 = 4$.
d. Which will have the greater value of $\langle s^2 \rangle_{eq}$, a Rouse chain with four beads, or the four-bead model considered here?

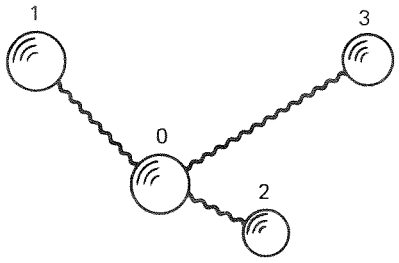


FIGURE 11B.5. Very simple mechanical model of a star polymer.

11D.1 Relation of FENE-Dumbbell Distribution Function to Hookean-Dumbbell Distribution Function

Verify that the normalized equilibrium distribution function ψ_{eq} for FENE dumbbells given in Table 11.5-1 simplifies to the corresponding quantity for Hookean dumbbells in the limit as $Q_0 \to \infty$. To do this use Stirling's approximation for large x:

$$\Gamma(x+1) \sim \left(\frac{x}{e}\right)^x \sqrt{2\pi x} \qquad (x \to \infty) \tag{11D.1-1}$$

and the fact that:

$$(x+\tfrac{1}{2})^x \sim x^x \sqrt{e} \qquad (x \to \infty) \tag{11D.1-2}$$

CHAPTER 12

EQUILIBRIUM CONFIGURATIONS OF POLYMER MOLECULES

In the foregoing chapter we discussed the various bead-rod-spring models that have been used in polymer kinetic theory. The aim of this chapter is to show how to obtain the equilibrium configurational distribution functions for these models and then to estimate some equilibrium properties of polymer systems.

Even though the main object of this volume is the study of nonequilibrium phenomena, there are several good reasons for including a brief survey of equilibrium properties at this point. Equilibrium statistical mechanics enables us to write down immediately the phase-space distribution function, from which the configurational distribution may be obtained; it is the deviation from this distribution function that is of primary interest in later chapters, and, indeed, the equilibrium distribution function may be taken as the starting point for a perturbation-theory development. In addition the study of polymer systems at equilibrium provides a convenient vehicle for introducing the nomenclature associated with molecular geometry and distribution functions to be used later. Finally the equilibrium properties are in themselves of interest in polymer chemistry and engineering.

Here and in later chapters we use classical mechanics and classical statistical mechanics throughout, inasmuch as quantum mechanical effects are of little importance in the study of the rheological properties of very large molecules. It is well known that the quantum effects are appreciable in the transport properties of gases and liquids only at extremely low temperatures and then only for helium and hydrogen.

We start by defining generalized coordinates and momenta for bead-rod-spring models, and then we give the equations of motion in terms of the Hamiltonian for the system. After that we give the general expression for the phase-space distribution function for the bead-rod-spring models at equilibrium; from this distribution function we can obtain a variety of equilibrium properties as average values. In the final section we discuss lower-order distribution functions and changes of variables in distribution functions. A careful study of this chapter provides much of the mathematics and physics needed for the remainder of the book.

§12.1 GENERALIZED COORDINATES AND MOMENTA

We begin by considering a general macromolecular model consisting of N beads of mass m_ν ($\nu = 1, 2, \ldots, N$) connected in an arbitrary way by springs and/or rigid rods. The total mass of the polymer molecule is then $m_p = \sum_\nu m_\nu$.

The location of bead ν is given by the position vector $\boldsymbol{r}_\nu$ ($\nu = 1, 2, \ldots, N$) with respect to an arbitrary origin of coordinates; the velocity of the bead is $\dot{\boldsymbol{r}}_\nu = d\boldsymbol{r}_\nu/dt$ with respect to the same origin. The center of mass $\boldsymbol{r}_c$ of the macromolecule and its velocity $\dot{\boldsymbol{r}}_c$ are defined by

$$\boldsymbol{r}_c = \frac{1}{m_p}\sum_{\nu=1}^{N} m_\nu \boldsymbol{r}_\nu; \qquad \dot{\boldsymbol{r}}_c = \frac{1}{m_p}\sum_{\nu=1}^{N} m_\nu \dot{\boldsymbol{r}}_\nu \tag{12.1-1a,b}$$

It is convenient to introduce another set of bead position vectors and bead velocity vectors by

$$\boldsymbol{R}_\nu = \boldsymbol{r}_\nu - \boldsymbol{r}_c; \qquad \dot{\boldsymbol{R}}_\nu = \dot{\boldsymbol{r}}_\nu - \dot{\boldsymbol{r}}_c \tag{12.1-2a,b}$$

The vector $\boldsymbol{R}_\nu$ locates the νth bead with respect to the center of mass, and $\dot{\boldsymbol{R}}_\nu$ is the velocity relative to the center of mass. The $\boldsymbol{R}_\nu$ and $\dot{\boldsymbol{R}}_\nu$ are not all independent since

$$\sum_{\nu=1}^{N} m_\nu \boldsymbol{R}_\nu = \boldsymbol{0}; \qquad \sum_{\nu=1}^{N} m_\nu \dot{\boldsymbol{R}}_\nu = \boldsymbol{0} \tag{12.1-3a,b}$$

In classical mechanics and classical statistical mechanics it is necessary to use the minimum number of coordinates needed to locate all the particles. For N particles with no constraints (e.g., for beads connected by springs and no fixed angles between adjacent springs), $3N - 3$ "internal coordinates" are needed to specify the locations of the beads in a center-of-mass coordinate system: for N particles with constraints (e.g., for beads joined by rigid rods or with fixed angles between adjacent connector rods) the number of degrees of freedom d in the system is less than $3N - 3$; in general the coordinates required to specify the internal coordinates are then called $Q_1, Q_2, \ldots, Q_d (d \leq 3N - 3)$. Examples from Chapter 11 are the following N-bead chains:

Model	Number of Internal Coordinates	Generalized Coordinates
Freely jointed bead-spring chain	$3N - 3$	$\boldsymbol{Q}_1, \boldsymbol{Q}_2, \ldots, \boldsymbol{Q}_{N-1}$
Freely jointed bead-rod chain	$2N - 2$	$\boldsymbol{u}_1, \boldsymbol{u}_2, \ldots, \boldsymbol{u}_{N-1}$
Freely rotating bead-rod chain (i.e., with fixed bond angles)	N	$\xi_1, \xi_{01}, \xi_{12}, \xi_{23}, \ldots, \xi_{N-2,N-1}$

The choice of generalized coordinates is not unique. For example the internal configuration of the freely jointed bead-rod chain with $N = 3$ may be specified by giving the polar angles for each link $\theta_1, \phi_1, \theta_2, \phi_2$; or one may use the included angles $\xi_1, \xi_{01}, \xi_{12}$, (to specify the orientation of the chain in space) and ξ_2 (to specify the angle between the two rods). The time rate of change of the sth generalized coordinate is designated by $\dot{Q}_s = dQ_s/dt$; these are called "generalized velocities."

We usually use the following conventions for indices:

$\nu, \mu, \eta, \ldots$	to designate beads	$1, 2, \ldots, N$
$s, t, u, v, \ldots$	to designate generalized coordinates	$1, 2, \ldots, d \leq 3N - 3$
$i, j, k, \ldots$	to designate links in chain models	$1, 2, \ldots, N - 1$
$m, n, p, q, \ldots$	to designate Cartesian components	1, 2, 3

The kinetic energy associated with the macromolecular model is then:[1]

$$\begin{aligned}\mathscr{K} &= \frac{1}{2}\sum_{\nu} m_\nu \dot{\boldsymbol{r}}_\nu^2 \\ &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_{\nu} m_\nu \dot{\boldsymbol{R}}_\nu^2 \end{aligned} \tag{12.1-4}$$

Equation 12.1-3b is used to get the second expression, which just states that the total kinetic energy is the sum of the kinetic energy of the center of mass and the kinetic energies of the beads with respect to the center of mass. Equation 12.1-4 may now be rewritten in terms of generalized coordinates by eliminating the $\boldsymbol{R}_\nu$ in favor of the Q_s by use of the chain rule of partial differentiation:

$$\begin{aligned}\mathscr{K} &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_s\sum_t\sum_\nu \left(\sqrt{m_\nu}\frac{\partial}{\partial Q_s}\boldsymbol{R}_\nu\right)\cdot\left(\sqrt{m_\nu}\frac{\partial}{\partial Q_t}\boldsymbol{R}_\nu\right)\dot{Q}_s\dot{Q}_t \\ &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_s\sum_t\sum_\nu (\boldsymbol{b}_{\nu s}\cdot\boldsymbol{b}_{\nu t})\dot{Q}_s\dot{Q}_t \\ &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_s\sum_t g_{st}\dot{Q}_s\dot{Q}_t \end{aligned} \tag{12.1-5}$$

Here we have introduced the *base vectors*[2] $\boldsymbol{b}_{\nu s}$:

$$\boldsymbol{b}_{\nu s} = \sqrt{m_\nu}\frac{\partial}{\partial Q_s}\boldsymbol{R}_\nu \tag{12.1-6}$$

and the components of the *metric matrix* g_{st}:

$$g_{st} = \sum_\nu (\boldsymbol{b}_{\nu s}\cdot\boldsymbol{b}_{\nu t}) \tag{12.1-7}$$

As can be seen in Eq. 12.1-5 the definition of these quantities arises quite naturally in writing the kinetic energy in terms of the generalized coordinates; these quantities may also be interpreted in terms of a hyperspace, although it is really not necessary to make use of this

[1] We use the abbreviation $\boldsymbol{r}_\nu^2$ in lieu of the lengthier $(\boldsymbol{r}_\nu\cdot\boldsymbol{r}_\nu)$

[2] These base vectors satisfy the relation

$$\sum_\nu \sqrt{m_\nu}\boldsymbol{b}_{\nu t} = \boldsymbol{0} \tag{12.1-6a}$$

because of Eq. 12.1-3a.

idea.[3] It is important to note that the base vectors $\boldsymbol{b}_{vs}$ and the metric matrix components g_{st} in general depend on the generalized coordinates Q_s. The determinant of the g_{st} matrix often appears in the following development; we designate this quantity by $g = \det(g_{st})$. We also find it useful to have notation for the components G_{st} of the matrix inverse to the (g_{st})-matrix; that is, we define the G_{st} by

$$\sum_t G_{st} g_{tu} = \delta_{su} \tag{12.1-8}$$

Once the generalized coordinates have been selected for a specific macromolecular model, the g_{st} may be obtained; inverting the matrix to get the G_{st} is in general extremely difficult.

Thus far we have been concerned only with the coordinates needed for specifying the configuration of a bead-spring-rod model for a macromolecule. We now turn to the notation for momenta. The momentum of bead v is $\boldsymbol{p}_v = m_v \dot{\boldsymbol{r}}_v$, and the momentum of the center of mass $\boldsymbol{p}_c$ is $m_p \dot{\boldsymbol{r}}_c$; we note incidentally that the latter can also be obtained by differentiating the kinetic energy with respect to the velocity of the center of mass, thus

$$\boldsymbol{p}_c = \frac{\partial}{\partial \dot{\boldsymbol{r}}_c} \mathscr{K} = m_p \dot{\boldsymbol{r}}_c \tag{12.1-9}$$

The generalized momenta for the internal degrees of freedom are then defined by an analogous differentiation:

$$P_s = \frac{\partial}{\partial \dot{Q}_s} \mathscr{K} = \sum_t g_{st} \dot{Q}_t \tag{12.1-10}$$

[3] Let $\boldsymbol{R}$ be a vector in a $3N$-dimensional space with components $\sqrt{m_1} X_{11}$, $\sqrt{m_1} X_{12}$, $\sqrt{m_1} X_{13}, \ldots, \sqrt{m_N} X_{N1}$, $\sqrt{m_N} X_{N2}$, $\sqrt{m_N} X_{N3}$ (X_{N3} is the z-component of $\boldsymbol{R}_N$). The unit vectors in this space are $\boldsymbol{\delta}_{vn}$ (v = bead number, n = Cartesian component). Then we define the base vectors in the d-dimensional subspace as (cf. §A.8)

$$\boldsymbol{g}_t = \frac{\partial}{\partial Q_t} \boldsymbol{R} = \sum_v \sum_n \frac{\partial}{\partial Q_t} (\boldsymbol{\delta}_{vn} \sqrt{m_v} X_{vn}) \tag{12.1-6b}$$

and the metric matrix components as

$$\begin{aligned} g_{st} &= (\boldsymbol{g}_s \cdot \boldsymbol{g}_t) \\ &= \sum_v \sum_n \left(\sqrt{m_v} \frac{\partial}{\partial Q_s} X_{vn} \right) \left(\sqrt{m_v} \frac{\partial}{\partial Q_t} X_{vn} \right) \end{aligned} \tag{12.1-7a}$$

This may be reorganized by introducing the unit vectors $\boldsymbol{\delta}_n$ in three-space and the three-space position vectors $\boldsymbol{R}_v$:

$$\begin{aligned} g_{st} &= \sum_v \sum_n \sum_m \left(\sqrt{m_v} \frac{\partial}{\partial Q_s} X_{vn} \boldsymbol{\delta}_n \right) \cdot \left(\sqrt{m_v} \frac{\partial}{\partial Q_t} X_{vm} \boldsymbol{\delta}_m \right) \\ &= \sum_v \left(\sqrt{m_v} \frac{\partial}{\partial Q_s} \boldsymbol{R}_v \right) \cdot \left(\sqrt{m_v} \frac{\partial}{\partial Q_t} \boldsymbol{R}_v \right) \\ &= \sum_v (\boldsymbol{b}_{vs} \cdot \boldsymbol{b}_{vt}) \end{aligned} \tag{12.1-7b}$$

In which the 3-space base vectors $\boldsymbol{b}_{vs}$ finally appear.

Note that the generalized momenta may or may not have the dimensions of momentum depending on the dimensions of the generalized coordinates that have been selected. Equation 12.1-10 can be inverted to give

$$\dot{Q}_s = \sum_t G_{st} P_t \tag{12.1-11}$$

When this is substituted into Eq. 12.1-5 we get

$$\mathscr{K} = \frac{1}{2m_p} \boldsymbol{p}_c^2 + \frac{1}{2} \sum_s \sum_t G_{st} P_s P_t \tag{12.1-12}$$

which gives the kinetic energy of the macromolecular model in terms of the momentum of the center of mass and the generalized momenta of the beads.

In the two illustrative examples that follow we show how the notation of this section is used in the description of two important polymer chain models: the bead-rod chain and the bead-spring chain. The results obtained in these two examples will be useful in later sections and chapters.

EXAMPLE 12.1-1 Base Vectors and Metric Matrix Components for the Freely Jointed Bead-Rod Chain with $N = 3$

Consider the Kramers chain with all links of length a and all masses identical (i.e., $m_v = m$ for all v). Obtain the formal expressions for the base vectors, and then display the matrix of the $\boldsymbol{b}_{vs}$ for $N = 3$. Then proceed to get the g_{st} and the determinant of the (g_{st})-matrix for $N = 3$.

SOLUTION We take the generalized coordinates to be the polar angles of the rods: θ_k and ϕ_k. In some formulas we actually use the unit vectors associated with the links, $\boldsymbol{s}_k$, $\boldsymbol{t}_k$, $\boldsymbol{u}_k$, keeping in mind that these are expressible in terms of the polar angles; using the unit vectors just saves having to write out lengthy expressions involving trigonometric functions.

After the generalized coordinates have been selected, the next task is to express the position vectors $\boldsymbol{R}_v$ in terms of the generalized coordinates; to do this we use Eq. 11.6-4:

$$\boldsymbol{R}_v = a \sum_k B_{vk} \boldsymbol{u}_k \tag{12.1-13}$$

Then, making use of the formulas for differentiating the unit vectors (given in §E.5) we find

$$\begin{aligned} \boldsymbol{b}_{v,\theta_k} &= a\sqrt{m} B_{vk} \boldsymbol{s}_k \\ \boldsymbol{b}_{v,\phi_k} &= a\sqrt{m} B_{vk} \boldsymbol{t}_k \sin\theta_k \end{aligned} \tag{12.1-14}$$

When we specialize to $N = 3$, the $\boldsymbol{b}_{vs}$ may be displayed in the following way:

$$\left(\frac{\boldsymbol{b}_{vs}}{a\sqrt{m}}\right) = \begin{pmatrix} -\frac{2}{3}\boldsymbol{s}_1 & -\frac{2}{3}\boldsymbol{t}_1 \sin\theta_1 & -\frac{1}{3}\boldsymbol{s}_2 & -\frac{1}{3}\boldsymbol{t}_2 \sin\theta_2 \\ \frac{1}{3}\boldsymbol{s}_1 & \frac{1}{3}\boldsymbol{t}_1 \sin\theta_1 & -\frac{1}{3}\boldsymbol{s}_2 & -\frac{1}{3}\boldsymbol{t}_2 \sin\theta_2 \\ \frac{1}{3}\boldsymbol{s}_1 & \frac{1}{3}\boldsymbol{t}_1 \sin\theta_1 & \frac{2}{3}\boldsymbol{s}_2 & \frac{2}{3}\boldsymbol{t}_2 \sin\theta_2 \end{pmatrix} \tag{12.1-15}$$

Here the rows correspond to the beads ($v = 1, 2, 3$) and the columns to the four generalized coordinates in the order θ_1, ϕ_1, θ_2, ϕ_2. Then the g_{st} are obtained from Eq. 12.1-7:

$$\left(\frac{g_{st}}{ma^2}\right) = \begin{pmatrix} \frac{2}{3} & 0 & \frac{1}{3}(C_1C_2c + S_1S_2) & \frac{1}{3}C_1S_2s \\ 0 & \frac{2}{3}S_1^2 & -\frac{1}{3}S_1C_2s & \frac{1}{3}S_1S_2c \\ \frac{1}{3}(C_1C_2c + S_1S_2) & -\frac{1}{3}S_1C_2s & \frac{2}{3} & 0 \\ \frac{1}{3}C_1S_2s & \frac{1}{3}S_1S_2c & 0 & \frac{2}{3}S_2^2 \end{pmatrix} \tag{12.1-16}$$

in which $S_1 = \sin\theta_1$, $C_1 = \cos\theta_1$, $s = \sin(\phi_1 - \phi_2)$, $c = \cos(\phi_1 - \phi_2)$. From this matrix we then get

$$g = \det(g_{st}) = \tfrac{4}{27}m^4a^8S_1^2S_2^2\left[1 - \tfrac{1}{4}(C_1C_2 + S_1S_2c)^2\right] \tag{12.1-17}$$

The quantity $(C_1C_2 + S_1S_2c)$ turns out to be just $\cos\xi_2 = (\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)$. To find the G_{st} for this very short two-link chain requires inverting the 4×4 matrix in Eq. 12.1-16.

Performing the analogous operations for a long chain would clearly be exceedingly tedious. If all one needs is the determinant of the (g_{st})-matrix, then some help can be had by using a recursion formula derived by Fixman[4] that allows one to get g_N (g for a chain of N beads) from g_{N-1} and g_{N-2}, aside from a constant multiplicative factor. One first defines h_N by

$$g_N \propto (ma^2)^{2(N-1)}h_N \prod_{k=1}^{N-1} \sin^2\theta_k \tag{12.1-18}$$

and then h_N is given by the recursion relation,

$$h_N = 2h_{N-1} - h_{N-2}\cos^2\xi_{N-1} \tag{12.1-19}$$

in which $h_1 = 1$ and $h_2 = 2$.

EXAMPLE 12.1-2 Base Vectors and Metric Matrix Components for the Freely Jointed Bead-Spring Chain

Obtain the $\boldsymbol{b}_{vs}$ and the g_{st} for a chain of N beads, all of mass m, connected linearly by $N - 1$ springs.

SOLUTION For this model there are $3N - 3$ degrees of freedom. It is sensible to choose as the generalized coordinates the Cartesian components Q_{kp} of the connector vectors $\boldsymbol{Q}_k$ defined by

$$\boldsymbol{Q}_k = \sum_p \boldsymbol{\delta}_p Q_{kp} \tag{12.1-20}$$

where $\boldsymbol{\delta}_p$ is the unit vector in the pth coordinate direction. This complicates the notation somewhat, since where we previously had generalized coordinates with one index (i.e., the "s" in Q_s), we now have two indices (the "kp" in Q_{kp}). From Eq. 11.6-4 we find for the bead locations with respect to the center of mass:

$$\boldsymbol{R}_v = \sum_p \sum_k \boldsymbol{\delta}_p B_{vk} Q_{kp} \tag{12.1-21}$$

[4] M. Fixman, *Proc. Nat. Acad. Sci., U.S.A.*, **71**, 3050-3053 (1974).

The base vectors are then

$$\boldsymbol{b}_{\nu,kp} = \sqrt{m}\frac{\partial}{\partial Q_{kp}}\boldsymbol{R}_\nu = \sqrt{m}B_{\nu k}\boldsymbol{\delta}_p \tag{12.1-22}$$

and the metric matrix components are

$$g_{ip,jq} = \sum_\nu (\boldsymbol{b}_{\nu,ip}\cdot\boldsymbol{b}_{\nu,jq}) = mC_{ij}\delta_{pq} \tag{12.1-23}$$

where Eq. 11.6-7 has been used to introduce the elements C_{ij} of the Kramers matrix. The inverse matrix has components given by

$$G_{ip,jq} = m^{-1}A_{ij}\delta_{pq} \tag{12.1-24}$$

In order to get $g = \det(g_{ip,jq})$ it is convenient to arrange the rows in the sequence $ip = 11, 21, 31, \ldots; 12, 22, 32, \ldots; 13, 23, 33, \ldots$ and the columns, labeled by jq, in the same sequence so that

$$g = \det(g_{ip,jq}) = \begin{vmatrix} D & 0 & 0 \\ 0 & D & 0 \\ 0 & 0 & D \end{vmatrix} \tag{12.1-25}$$

in which D is the $(N-1)\times(N-1)$ matrix with elements mC_{ij}. Then

$$g = [\det(mC_{ij})]^3 = \left(\frac{m^{N-1}}{N}\right)^3 \tag{12.1-26}$$

where Eq. 11.6-15 has been used. We see thus that for the freely jointed bead-spring chain the quantity g can be evaluated for a chain of any length, and that the result is just a constant.

§12.2 HAMILTON'S EQUATIONS OF MOTION

The classical Hamiltonian may be written as the sum of the kinetic energy and the potential energy, expressed in terms of the coordinates and momenta (not velocities!). For a system of N particles *with no constraints* we may use the Cartesian components of the position and momentum vectors of each of the particles as independent coordinates in phase space; then the Hamiltonian is

$$\mathscr{H} = \sum_\nu \frac{1}{2m_\nu}\boldsymbol{p}_\nu^2 + \phi(\boldsymbol{r}^N) \tag{12.2-1}$$

Here ϕ is the potential energy of the system, which depends on the coordinates of all the particles.

The dynamics of the system of particles is described by giving the equations of motion. These are "Hamilton's canonical equations," a set of $6N$ scalar first-order partial differential equations

$$\frac{\partial\mathscr{H}}{\partial\boldsymbol{r}_\nu} = -\dot{\boldsymbol{p}}_\nu; \qquad \frac{\partial\mathscr{H}}{\partial\boldsymbol{p}_\nu} = \dot{\boldsymbol{r}}_\nu \tag{12.2-2a,b}$$

These equations are equivalent to the more familiar Newton's second law of motion, as may be seen as follows: First substitute $\mathscr{H}$ from Eq. 12.2-1 into Hamilton's equations of motion to get

$$\frac{\partial \phi}{\partial \boldsymbol{r}_v} = -\dot{\boldsymbol{p}}_v; \qquad \frac{1}{m_v}\boldsymbol{p}_v = \dot{\boldsymbol{r}}_v \tag{12.2-3a,b}$$

Then combine these two equations and introduce the force on particle v, defined by $\boldsymbol{F}_v = -(\partial/\partial \boldsymbol{r}_v)\phi$ to obtain

$$\boldsymbol{F}_v = m_v \ddot{\boldsymbol{r}}_v \tag{12.2-4}$$

This is Newton's second law of motion for particle v.

For systems *with constraints* the Cartesian coordinates discussed above cannot be used, and the classical Hamiltonian has to be written in terms of generalized coordinates and momenta. Even for systems without constraints it is usually convenient to use the position and momentum of the center of mass as phase-space coordinates along with the appropriate generalized coordinates and momenta; then the Hamiltonian becomes

$$\mathscr{H} = \frac{1}{2m_p}\boldsymbol{p}_c^2 + \frac{1}{2}\sum_s \sum_t G_{st} P_s P_t + \phi(\boldsymbol{r}_c, Q_1, Q_2, \ldots Q_d) \tag{12.2-5}$$

and Hamilton's canonical equations of motion are

$$\text{Center of mass} \quad \frac{\partial \mathscr{H}}{\partial \boldsymbol{r}_c} = -\dot{\boldsymbol{p}}_c; \qquad \frac{\partial \mathscr{H}}{\partial \boldsymbol{p}_c} = \dot{\boldsymbol{r}}_c \tag{12.2-6a,b}$$

$$\text{Internal coordinates} \quad \frac{\partial \mathscr{H}}{\partial Q_s} = -\dot{P}_s; \qquad \frac{\partial \mathscr{H}}{\partial P_s} = \dot{Q}_s \tag{12.2-7a,b}$$

These equations play a key role in the development of the general phase-space kinetic theory in Chapter 17.

§12.3 DISTRIBUTION FUNCTIONS FROM EQUILIBRIUM STATISTICAL MECHANICS

In this section we take as the object of our study a dilute solution of polymer molecules, these molecules being represented by bead-rod-spring models. The solution is at a temperature T and is contained in a volume V; there are n polymer molecules per unit volume. The solvent acts as a "temperature bath"; a typical polymer molecule is being jostled by the solvent molecules, and hence it goes through many configurations, and its various parts (i.e., the beads) can have many different velocities or momenta. We now want to know how the molecules in the solution are distributed over all the possible configuration and momentum coordinates.

In order to simplify the notation we let Q be the abbreviation for the collection of coordinates $Q_1, Q_2, \ldots, Q_d$, and we use the abbreviation dQ for $dQ_1 dQ_2 \ldots dQ_d$; we use similar abbreviated notation for the generalized momenta. We now introduce the *single-molecule-phase-space distribution function* $f_{eq}(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P)$ for the system at equilibrium. This quantity has the following significance: $f_{eq}(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P)d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP$ is the number of

polymer molecules in the solution having a configuration in the range $d\boldsymbol{r}_c\, dQ$ about $\boldsymbol{r}_c$, Q, and having momenta in the range $d\boldsymbol{p}_c\, dP$ around $\boldsymbol{p}_c$, P.

The distribution function f_{eq} is then given by the product of the number of polymer molecules in the system and the probability density; the probability density in turn is given by equilibrium statistical mechanics as proportional to $\exp(-\mathcal{H}/kT)$, where $\mathcal{H}$ is the Hamiltonian of the single polymer molecule in the temperature bath at temperature T; in order to be properly normalized the exponential has to be divided by the integral of the exponential over all the phase-space variables. Therefore, according to the standard formula from equilibrium statistical mechanics,[1,2]

$$f_{eq}(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P) = \frac{nVe^{-\mathcal{H}/kT}}{\iiiint e^{-\mathcal{H}/kT}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP} = \frac{ne^{-\mathcal{H}/kT}}{\iiint e^{-\mathcal{H}/kT}\, dQ\, d\boldsymbol{p}_c\, dP} \tag{12.3-1}$$

The second form given here is possible as long as the potential energy ϕ does not depend on the coordinates of the center of mass; then the integration over $\boldsymbol{r}_c$ in the denominator can be performed to give a factor of V, as indicated above.

In many instances we are interested only in the *configurational distribution function* $\Psi_{eq}(\boldsymbol{r}_c, Q)$. The quantity $\Psi_{eq}\, d\boldsymbol{r}_c\, dQ$ gives the number of polymer molecules in the configuration range $d\boldsymbol{r}_c\, dQ$ about $\boldsymbol{r}_c$, Q. It is obtained by integrating f_{eq} over all momenta:

$$\begin{aligned}\Psi_{eq}(\boldsymbol{r}_c, Q) &= \iint f_{eq}\, d\boldsymbol{p}_c\, dP \\ &= \frac{n\iint e^{-\mathcal{H}/kT}\, d\boldsymbol{p}_c\, dP}{\iiint e^{-\mathcal{H}/kT}\, d\boldsymbol{p}_c\, dP\, dQ} \\ &= n\psi_{eq}(Q)\end{aligned} \tag{12.3-2}$$

We have noted that if, as is usually the case, the potential energy does not depend on the center of mass, the distribution function Ψ_{eq} does not depend on the center of mass and can be replaced by $n\psi_{eq}$. When $\mathcal{H}$ from Eq. 12.2-5 is inserted into the integrals in Eq. 12.3-2, the integral over $\boldsymbol{p}_c$ factors out in both the numerator and the denominator, and hence cancels out. As a result

$$\psi_{eq}(Q) = \frac{\int \exp(-\sum_s \sum_t G_{st} P_s P_t / 2kT) dP\, e^{-\phi(Q)/kT}}{\iint \exp(-\sum_s \sum_t G_{st} P_s P_t / 2kT) e^{-\phi(Q)/kT}\, dP\, dQ} \tag{12.3-3}$$

The integration over the P's can be performed (see Appendix E, §E.3) to give $(2\pi kT)^{d/2}/\sqrt{\det(G_{st})}$. Hence we get, finally, after setting $g(Q) = \det(g_{st}) = 1/\det(G_{st})$:

$$\boxed{\psi_{eq}(Q) = \frac{\sqrt{g(Q)}e^{-\phi(Q)/kT}}{\int \sqrt{g(Q)}e^{-\phi(Q)/kT}\, dQ}} \tag{12.3-4}$$

[1] R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, London (1938), §33.
[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, New York (1940), Chapter 10.

Note that ψ_{eq} is normalized so that $\int \psi_{eq}(Q)dQ = 1$; therefore $\psi_{eq}\, dQ$ is just the probability that the internal configuration is in the range dQ about Q. Equation 12.3-4 is the key equation to be used throughout the remainder of the chapter. In order to get the configurational distribution function, ψ_{eq}, all one needs to know is the potential energy $\phi(Q)$, describing the "springs" in the system, and the geometrical quantity g, which may be obtained from the generalized coordinates describing the mechanical model being used.[3]

Because of the importance of chainlike models, we conclude this section by showing what Eq. 12.3-4 yields for such models when all the bead masses are taken to be the same ($m_\nu = m$):

a. The Freely Jointed Bead-Rod Chain (Kramers Chain)

For this model there are no springs between the beads and no bending potentials at the link junctions, so that $\phi = 0$. Hence Eq. 12.3-4 becomes for a chain of N beads

$$\psi_{eq} = \frac{\sqrt{g}}{\iint \sqrt{g}\, d\theta^{N-1}\, d\phi^{N-1}} \tag{12.3-5}$$

For the chain with three beads ($N = 3$), we can use the expression for g given in Eq. 12.1-17 to get:

$$\psi_{eq}(\theta_1, \phi_1, \theta_2, \phi_2) = \frac{S_1S_2[1 - \frac{1}{4}(C_1C_2 + S_1S_2c)^2]^{1/2}}{\iiiint S_1S_2[1 - \frac{1}{4}(C_1C_2 + S_1S_2c)^2]^{1/2}\, d\theta_1\, d\phi_1\, d\theta_2\, d\phi_2}$$
$$= \frac{\sin\theta_1 \sin\theta_2}{(4\pi)^2}\left[\frac{(1 - \frac{1}{4}\cos^2\xi_2)^{1/2}}{\frac{1}{4}\sqrt{3} + \frac{1}{6}\pi}\right] \tag{12.3-6}$$

This result should be compared with the random-walk distribution in Eq. 11.3-2. Note that equilibrium statistical mechanics when applied to a chain with rigid links, gives a result that deviates from the random walk. The factor given in brackets in Eq. 12.3-6, for $N = 3$, says that the probability of having the links perpendicular to each other, for a given solid angle, is about 15.5% larger than the probability of their being parallel or antiparallel, for the same amount of solid angle. This result, which has been known for a long time,[4] has also

[3] The choice of the generalized coordinates Q_s is arbitrary, and each choice leads to a different g and a different ψ_{eq}. Suppose that we had chosen a set of coordinates Q'_s, so that

$$\psi_{eq}(Q') = \frac{\sqrt{g(Q')}e^{-\phi(Q')/kT}}{\int \sqrt{g(Q')}e^{-\phi(Q')/kT}\, dQ'} \tag{12.3-4a}$$

It must be emphasized that $\psi_{eq}(Q')$ and $\psi_{eq}(Q)$ are *different* functions of their arguments; the same applies to g and ϕ. Since the probability of finding a molecule in any finite region of the configuration space is independent of the choice of generalized coordinates,

$$\psi_{eq}(Q') = \psi_{eq}(Q)\left|\frac{\partial(Q_1, Q_2, \ldots, Q_d)}{\partial(Q'_1, Q'_2, \ldots, Q'_d)}\right| \tag{12.3-4b}$$

Thus we see that the Jacobian of the transformation is $\sqrt{g(Q')/g(Q)}$. A specific example of this is given in Problem 12B.1.

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

been confirmed by Gottlieb[5] by a molecular dynamics calculation. He put a 3-bead-2-rod model into a sea of 47 solvent molecules, assigning them initial random positions and momenta. The interactions between solvent molecules, as well as those between solvent molecules and the beads of the polymer model, were taken to be of the Lennard-Jones type. The equations of motion of classical mechanics for the entire system were then integrated numerically. This computer simulation gave results in general agreement with Eq. 12.3-6, and definitely not with the random walk result (Eq. 12.3-6 without the factor in brackets).

b. The Freely Jointed Bead-Spring Chain (e.g., the Rouse-Zimm Chain)

In these models, if we use the generalized coordinates in Eq. 12.1-20, the quantity g in Eq. 12.3-4 is a constant (see Eq. 12.1-26). Consequently the equilibrium configurational distribution function is

$$\psi_{eq}(\boldsymbol{Q}^{N-1}) = \frac{e^{-\phi/kT}}{\int e^{-\phi/kT}\, d\boldsymbol{Q}^{N-1}} \tag{12.3-7}$$

If, now, we specialize to the chain model used by Rouse and Zimm, in which the beads are linked together by Hookean springs, with a spring constant H, the internal potential energy is then

$$\phi(\boldsymbol{Q}^{N-1}) = \tfrac{1}{2}H \sum_k \boldsymbol{Q}_k^2 \tag{12.3-8}$$

When this is substituted into Eq. 12.3-7 and the integration performed in the denominator we get

$$\begin{aligned}\psi_{eq}(\boldsymbol{Q}^{N-1}) &= \left(\frac{H}{2\pi kT}\right)^{3(N-1)/2} e^{-(H/2kT)\sum_j \boldsymbol{Q}_j^2} \\ &= \prod_j \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_j^2}\end{aligned} \tag{12.3-9}$$

Gottlieb has performed computer simulations for the three-bead-two-spring chain model (using Fraenkel springs) and found good agreement with Eq. 12.3-7. The confirmation of distribution functions by computer simulations is relatively new; these calculations are particularly interesting, since distribution functions are not experimentally accessible. Also, computer simulations can be carried out for mechanical models that lead to mathematical complexities when approached purely analytically. This is particularly true when nonequilibrium calculations are involved.[6]

§12.4 AVERAGE VALUES

Experimentally accessible quantities are inevitably the result of measurements on a sample containing an enormous number of molecules. Consequently the sensing device in the experiment detects the response of molecules in a very wide variety of configurations. To

[5] M. Gottlieb and R. B. Bird, *J. Chem. Phys.*, **65**, 2467 2468 (1976); M. Gottlieb, *Computers in Chemistry*, **1**, 155-160 (1977).

[6] P. J. Dotson, *J. Chem. Phys.*, **79**, 5730-5731 (1983).

make a comparison between experiment and theory, we therefore have to be able to compute averages of physical quantities over all configurations and all momenta.

The average value of a function $B(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P)$ in the phase space of a single polymer molecule is

$$\langle B\rangle_{eq} = \frac{\iiiint Bf_{eq}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP}{\iiiint f_{eq}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP}$$

$$= \frac{1}{nV}\iiiint Bf_{eq}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP \tag{12.4-1}$$

It is this average that is of concern in connecting molecular dynamics with physical, macroscopic observables. Another average that is particularly useful in later chapters is the average of the quantity B over all the momenta:

$$[\![B]\!]_{eq} = \frac{\iint Bf_{eq}\, d\boldsymbol{p}_c\, dP}{\iint f_{eq}\, d\boldsymbol{p}_c\, dP}$$

$$= \frac{1}{\Psi_{eq}}\iint Bf_{eq}\, d\boldsymbol{p}_c\, dP \tag{12.4-2}$$

Throughout the entire book we shall always use the angular brackets to indicate an average over a phase space and the double brackets to designate a momentum-space average. Note that the momentum-space average can be used to rewrite the phase-space average formally in this way:

$$\langle B\rangle_{eq} = \frac{1}{nV}\iint [\![B]\!]_{eq}\Psi_{eq}\, d\boldsymbol{r}_c\, dQ \tag{12.4-3}$$

The factor nV appears in Eqs. 12.4-1 and 12.4-3 because of the way that f_{eq} was defined in Eq. 12.3-1.

If the quantity B depends only on the configuration coordinates $\boldsymbol{r}_c$ and Q, then Eq. 12.4-3 becomes

$$\langle B\rangle_{eq} = \frac{1}{nV}\iint B\Psi_{eq}\, d\boldsymbol{r}_c\, dQ \tag{12.4-4}$$

If the quantity B depends only on the internal configuration coordinates Q, and if the potential energy ϕ also depends only on the internal coordinates Q, the integration over $\boldsymbol{r}_c$ can be performed and the average value of B becomes just an integral over the internal configuration space:

$$\langle B\rangle_{eq} = \int B\psi_{eq}\, dQ \tag{12.4-5}$$

If now the expression for ψ_{eq} from Eq. 12.3-4 is inserted into this integral we obtain

$$\boxed{\langle B\rangle_{eq} = \frac{\int B\sqrt{g}e^{-\phi/kT}\, dQ}{\int \sqrt{g}e^{-\phi/kT}\, dQ}} \tag{12.4-6}$$

This much-used result does carry with it the restriction that both B and ϕ be functions of the internal coordinates Q only. In order to use this result it is necessary to have the quantity g, the determinant of the metric matrix for the macromolecule configuration space. As we have seen in Example 12.1-1, obtaining an expression for g is a difficult problem even for some relatively simple models, when constraints are present. When there are no constraints—that is, when the model contains springs rather than rods—and when Cartesian components are used, g is a constant and it is not necessary to calculate $\sqrt{g}$. In the illustrative example that follows, it is shown how to use Eq. 12.4-3.

EXAMPLE 12.4-1 Equilibrium Averaged Internal Kinetic Energy for Any Bead-Rod-Spring Model

According to Eq. 12.1-12 the kinetic energy is the sum of two parts: that associated with the center of mass $\mathscr{K}_c = (1/2m_p)\boldsymbol{p}_c^2$ and that associated with the internal degrees of freedom, $\mathscr{K}_{\text{int}} = (1/2)\sum_s \sum_t G_{st} P_s P_t$. Find the average value of $\mathscr{K}_{\text{int}}$ at equilibrium. Keep in mind that the G_{st} in general depend on the Q's. Assume that the potential energy is independent of $\boldsymbol{r}_c$.

SOLUTION Inasmuch as the quantity to be averaged, $\mathscr{K}_{\text{int}}$, contains no $\boldsymbol{r}_c$ and since the potential energy is independent of $\boldsymbol{r}_c$, we can write Eq. 12.4-3 as

$$\langle \mathscr{K}_{\text{int}} \rangle_{\text{eq}} = \int [\![\mathscr{K}_{\text{int}}]\!]_{\text{eq}} \psi_{\text{eq}} \, dQ$$

$$= \frac{1}{2} \sum_s \sum_t \int G_{st} [\![P_s P_t]\!]_{\text{eq}} \psi_{\text{eq}} \, dQ \tag{12.4-7}$$

The momentum-space average of $P_s P_t$ is then

$$[\![P_s P_t]\!]_{\text{eq}} = \frac{\iint P_s P_t e^{-\mathscr{H}/kT} \, d\boldsymbol{p}_c \, dP}{\iint e^{-\mathscr{H}/kT} \, d\boldsymbol{p}_c \, dP} \tag{12.4-8}$$

Because $\mathscr{H} = \mathscr{K}_c + \mathscr{K}_{\text{int}} + \phi$, the integration over $\boldsymbol{p}_c$ and the factor $\exp(-\phi/kT)$ in the numerator and denominator cancel one another, and we end up with

$$[\![P_s P_t]\!]_{\text{eq}} = \frac{\int P_s P_t \exp[-(1/2kT) \sum_u \sum_v G_{uv} P_u P_v] dP}{\int \exp[-(1/2kT) \sum_u \sum_v G_{uv} P_u P_v] dP} \tag{12.4-9}$$

The integrations can be performed by using standard matrix methods (see §E.3) with the result that

$$[\![P_s P_t]\!]_{\text{eq}} = \frac{(2\pi kT)^{d/2} \sqrt{g} \, kT g_{st}}{(2\pi kT)^{d/2} \sqrt{g}} = kT g_{st} \tag{12.4-10}$$

When this is substituted into Eq. 12.4-7 we obtain finally

$$\langle \mathscr{K}_{\text{int}} \rangle_{\text{eq}} = \frac{1}{2} kT \sum_s \sum_t \int G_{st} g_{st} \psi_{\text{eq}} \, dQ$$

$$= \frac{1}{2} kT \sum_s \int \delta_{ss} \psi_{\text{eq}} \, dQ$$

$$= \frac{1}{2} dkT \tag{12.4-11}$$

in which d is the number of internal degrees of freedom of the macromolecular model. This result just shows that at equilibrium there is a contribution of $(1/2)kT$ for each degree of freedom.

§12.5 CONTRACTED DISTRIBUTION FUNCTIONS

In Section 12.3 we started with the distribution function f_{eq} in the phase space of a single polymer molecule. By integrating over the momenta we obtained the distribution function Ψ_{eq} in the configuration space of a polymer molecule. When the potential energy is independent of the center of mass, a further integration leads to the definition of a distribution function ψ_{eq} in the internal configuration space of a single macromolecule.

This process of "contraction" to a smaller and smaller variable-space can, of course, be continued. For example, let us consider the Rouse chain for which we know the equilibrium distribution function in Eq. 12.3-9. Suppose we wish to know what the distribution function is for the first link in the chain only; that is, we want to know the probability $\psi_{1,eq}(\boldsymbol{Q})d\boldsymbol{Q}$ that the connector vector $\boldsymbol{Q}_1$ of the first spring will be in the range $d\boldsymbol{Q}$ about $\boldsymbol{Q}$. This distribution function may be obtained by integrating Eq. 12.3-9 over the variables $\boldsymbol{Q}_2, \boldsymbol{Q}_3, \ldots, \boldsymbol{Q}_{N-1}$ and then replacing $\boldsymbol{Q}_1$ by $\boldsymbol{Q}$:

$$\begin{aligned}\psi_{1,eq}(\boldsymbol{Q}) &= \int\cdots\int \psi_{eq}(\boldsymbol{Q}^{N-1})d\boldsymbol{Q}_2\, d\boldsymbol{Q}_3 \ldots d\boldsymbol{Q}_{N-1}|_{\boldsymbol{Q}_1=\boldsymbol{Q}} \\ &= \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_1^2} \prod_{k=2}^{N-1} \int \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_k^2}\, d\boldsymbol{Q}_k|_{\boldsymbol{Q}_1=\boldsymbol{Q}} \\ &= \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}^2} \end{aligned} \tag{12.5-1}$$

Another method for getting the same result is to integrate over the entire configuration space, including a Dirac delta-function to select just the information needed in the final distribution function:

$$\begin{aligned}\psi_{1,eq}(\boldsymbol{Q}) &= \langle \delta(\boldsymbol{Q}_1 - \boldsymbol{Q})\rangle_{eq} \\ &= \int \delta(\boldsymbol{Q}_1 - \boldsymbol{Q})\psi_{eq}(\boldsymbol{Q}^{N-1})d\boldsymbol{Q}^{N-1} \\ &= \int \delta(\boldsymbol{Q}_1 - \boldsymbol{Q})\left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_1^2}\, d\boldsymbol{Q}_1 \\ &\quad \cdot \int\cdots\int \left[\prod_{k=2}^{N-1}\left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_k^2}\right] d\boldsymbol{Q}_2\, d\boldsymbol{Q}_3 \ldots d\boldsymbol{Q}_{N-1} \\ &= \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}^2} \end{aligned} \tag{12.5-2}$$

In formal developments we usually prefer to use the Dirac delta-function procedure; also in getting some contracted distribution functions we find that the delta-function method is easier to exploit. Example 12.5-1 is an illustration of this point.

In Eq. 12.5-2 $\psi_{1,eq}(\boldsymbol{Q})dQ_x\, dQ_y\, dQ_z$ is the probability that the first link has a connector vector with Cartesian components in the range $dQ_x\, dQ_y\, dQ_z$ about Q_x, Q_y, Q_z. If we want the probability $\psi_{1,eq}(Q, \theta, \phi)dQ\, d\theta\, d\phi$—the probability that the first link has a

length within the range dQ about Q, and an orientation within the range $d\theta\, d\phi$ about θ, ϕ—then this can be obtained from Eq. 12.5-2 by multiplying by the appropriate Jacobian

$$\psi_{1,\mathrm{eq}}(Q,\theta,\phi) = \psi_{1,\mathrm{eq}}(Q_x, Q_y, Q_z)\cdot\frac{\partial(Q_x, Q_y, Q_z)}{\partial(Q,\theta,\phi)}$$
$$= \psi_{1,\mathrm{eq}}(Q_x, Q_y, Q_z)Q^2\sin\theta \tag{12.5-3}$$

Finally if we want just the distribution of the connector length for the first link, we can integrate over the polar angles θ, ϕ:

$$\psi_{1Q,\mathrm{eq}}(Q) = \iint \psi_{1,\mathrm{eq}}(Q,\theta,\phi)d\theta\, d\phi$$
$$= 4\pi Q^2\left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)Q^2} \tag{12.5-4}$$

We have illustrated here how one goes from a single molecule phase-space distribution function all the way down to the distribution of lengths in one link of the chain; this has been done for a Rouse chain, but similar developments can be made for other models as well.

EXAMPLE 12.5-1 Distribution Function for the Vector Between Two Beads of a Rouse Chain

(a) Let $\boldsymbol{r}_{\mu\nu}$ be the vector from bead μ to bead ν. Obtain the probability density $P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu})$ that the vector $\boldsymbol{r}_{\mu\nu}$ be in the range $d\boldsymbol{r}_{\mu\nu}$ about $\boldsymbol{r}_{\mu\nu}$.

(b) Use the result in (a) to evaluate $\langle 1/r_{\mu\nu}\rangle_{\mathrm{eq}}$.

SOLUTION **(a)** The distribution function for the bead-to-bead vector is obtained from the complete chain distribution function by using the Dirac delta-function method; here, in order to be specific, we take $\nu > \mu$:

$$P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu}) = \int \delta\left(\boldsymbol{r}_{\mu\nu} - \sum_{j=\mu}^{\nu-1}\boldsymbol{Q}_j\right)\psi_{\mathrm{eq}}(\boldsymbol{Q}^{N-1})d\boldsymbol{Q}^{N-1} \tag{12.5-5}$$

Into this we substitute Eq. 12.3-9 for the Rouse chain distribution function and Eq. E.4-5 for a representation of the Dirac delta function:

$$P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu}) = \int\left\{\frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty}\exp\left[i\left(\boldsymbol{r}_{\mu\nu} - \sum_{j=\mu}^{\nu-1}\boldsymbol{Q}_j\right)\cdot\boldsymbol{s}\right]d\boldsymbol{s}\right\}$$
$$\cdot\left\{\prod_{h=1}^{N-1}\left(\frac{H}{2\pi kT}\right)^{3/2}\exp\left[-\frac{H}{2kT}\boldsymbol{Q}_h^2\right]\right\}d\boldsymbol{Q}^{N-1} \tag{12.5-6}$$

The integrals over $\boldsymbol{Q}_k$ outside the range $h = \mu$ to $h = \nu - 1$ can be performed, and the order of integration can be changed to give

$$P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty}\exp(i\boldsymbol{r}_{\mu\nu}\cdot\boldsymbol{s})\prod_{h=\mu}^{\nu-1}\left(\frac{H}{2\pi kT}\right)^{3/2}$$
$$\cdot\left\{\int\exp\left[-\frac{H}{2kT}(\boldsymbol{Q}_h\cdot\boldsymbol{Q}_h) - i(\boldsymbol{Q}_h\cdot\boldsymbol{s})\right]d\boldsymbol{Q}_h\right\}d\boldsymbol{s} \tag{12.5-7}$$

The integral within braces is known (see Eq. E.3-6) and when it is evaluated we get

$$P_{eq}(\boldsymbol{r}_{\mu\nu}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty} \exp(i\boldsymbol{r}_{\mu\nu}\cdot\boldsymbol{s}) \prod_{h=\mu}^{\nu-1}\left(\frac{H}{2\pi kT}\right)^{3/2} \cdot\left\{\left(\frac{2\pi kT}{H}\right)^{3/2}\exp\left[-\frac{kT}{2H}(\boldsymbol{s}\cdot\boldsymbol{s})\right]\right\}d\boldsymbol{s}$$

$$= \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty}\exp\left[-(\nu-\mu)\frac{kT}{2H}(\boldsymbol{s}\cdot\boldsymbol{s}) + i(\boldsymbol{s}\cdot\boldsymbol{r}_{\mu\nu})\right]d\boldsymbol{s} \tag{12.5-8}$$

If $\nu < \mu$ we have the same result except for the fact that $(\nu - \mu)$ is replaced by $(\mu - \nu)$; therefore, the result in Eq. 12.5-8 can be made to apply to all values of $\nu \neq \mu$ by replacing $(\nu - \mu)$ by $|\nu - \mu|$. Once again we have an integral of the form of Eq. E.3-6 which is then evaluated to give the final result:

$$P_{eq}(\boldsymbol{r}_{\mu\nu}) = \left(\frac{H}{2|\nu-\mu|\pi kT}\right)^{3/2}\exp\left(-\frac{H}{2|\nu-\mu|kT}\boldsymbol{r}_{\mu\nu}^2\right) \tag{12.5-9}$$

For the special case that $\nu = 2$ and $\mu = 1$, this result simplifies to that in Eq. 12.5-2. When $\nu = N$ and $\mu = 1$, Eq. 12.5-9 simplifies to Eq. 11.4-3 for the probability density for the end-to-end vector $\boldsymbol{r}$.

(b) To get the equilibrium average value of $1/r_{\mu\nu}$ we now have to do one more integration:

$$\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{eq} = \left(\frac{H}{2|\nu-\mu|\pi kT}\right)^{3/2}\int\frac{1}{r_{\mu\nu}}\exp\left(-\frac{H}{2|\nu-\mu|kT}\boldsymbol{r}_{\mu\nu}^2\right)d\boldsymbol{r}_{\mu\nu} \tag{12.5-10}$$

This integral is easily performed in spherical coordinates, with the result that

$$\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{eq} = \sqrt{\frac{2H}{|\nu-\mu|\pi kT}} \tag{12.5-11}$$

This result is used in Chapter 15.

EXAMPLE 12.5-2 Configurational Distribution Function for a Bead-Spring Chain with Infinitely Stiffened Springs

Write the distribution function for a chain with N beads connected linearly with Fraenkel springs, for which $\phi = (H/2)\sum_k (Q_k - a)^2$ (see Table 11.5-1). Then let the Fraenkel spring constant H go to infinity so that the springs approach rigid rods of length a. Do you get the result of Eq. 12.3-6?

SOLUTION For the Fraenkel-spring chain the analog of Eq. 12.3-9 is

$$\psi_{eq}(\boldsymbol{Q}^{N-1}) = \frac{\prod_k F_k}{\prod_k \int F_k\, d\boldsymbol{Q}_k} \tag{12.5-12}$$

where $F_k = \exp[-(H/2kT)(Q_k - a)^2]$. If we now switch to polar coordinates, we have

$$\psi_{eq}(Q^{N-1}, \theta^{N-1}, \phi^{N-1}) = \frac{\prod_k F_k Q_k^2 \sin\theta_k}{\prod_k \iiint F_k Q_k^2 \sin\theta_k\, dQ_k\, d\theta_k\, d\phi_k} \tag{12.5-13}$$

We now integrate over the length coordinates Q_k to get

$$\psi_{eq}(\theta^{N-1}, \phi^{N-1}) = \frac{\prod_k \sin\theta_k}{(4\pi)^{N-1}} \tag{12.5-14}$$

Thus after the integration, the factors involving the Q_k in numerator and denominator cancel, and in this cancellation the parameters H and a of the Fraenkel spring have disappeared. Hence, if we "freeze" the connectors by letting H go to infinity we still get the result in Eq. 12.5-14, which is just the random-walk distribution (see Eq. 11.3-2).

Several points need to be made with regard to Example 12.5-2. Chain models with "stiffened springs" are *not* the same as chain models with "rigid rods." Furthermore there is no unique way to take the limit of stiffened springs, whereas the rigid-rod models are unique. It should be noted that the phenomenon encountered here also arises in Example 12.4-1 where the internal kinetic energy of a bead-spring chain with stiffened Fraenkel springs is $(3/2)(N-1)kT$, whereas that of a Kramers bead-rod chain is $(N-1)kT$. For a very interesting discussion of this problem of freezing out degrees of freedom, which is not normally addressed in books on statistical mechanics, see the article by van Kampen.[1]

Finally we need to address the question of whether it is better to use a stiffened-spring chain model or one with rigid rods. Although only limited calculations are available that would enable us to compare the two types of models in nonequilibrium situations, it is very likely that quantitative differences between them would be small for chains with a large number of links. Furthermore the discrepancy between the two types of models is probably small compared to the discrepancy between either model and the true system. Generally the choice of mechanical model will be made by selecting the one which is mathematically most convenient. For more on bead-rod chains see §§16.5 and 16.6.

PROBLEMS

12A.1 Deviation from Random-Walk Distribution

a. How much does Eq. 12.3-6 deviate from the corresponding random-walk distribution?
b. Plot the functions in Eqs. 12C.1-1 and 12D.1-6, and interpret the results.

12B.1 Equilibrium Properties of a Dilute Polymer Solution Modeled as a Suspension of Elastic Dumbbells

The choice of generalized coordinates is arbitrary. Here we work through some of the subjects covered in this chapter for elastic dumbbells, using two different sets of generalized coordinates:

I. X, Y, Z (the Cartesian components of the connector vector $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$)
II. Q, θ, ϕ (the polar coordinates for the connector vector $\boldsymbol{Q}$; in this discussion we use $S \equiv \sin\theta$, $C \equiv \cos\theta$, $s \equiv \sin\phi$, $c \equiv \cos\phi$)

a. Express $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ in terms of the generalized coordinates; take the mass of each bead to be m.

b. Find the (g_{st})- and (G_{st})-matrices:

$$\text{I.} \quad (g_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{m}{2}; \qquad (G_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{2}{m} \tag{12B.1-1a,b}$$

$$\text{II.} \quad (g_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & Q^2 & 0 \\ 0 & 0 & Q^2S^2 \end{pmatrix} \frac{m}{2}; \qquad (G_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & Q^{-2} & 0 \\ 0 & 0 & Q^{-2}S^{-2} \end{pmatrix} \frac{2}{m} \tag{12B.1-2a,b}$$

c. Next obtain the Hamiltonian:

$$\text{I.} \qquad \mathscr{H} = \frac{1}{4m}\boldsymbol{p}_c^2 + \frac{1}{m}(P_X^2 + P_Y^2 + P_Z^2) + \phi^{(c)} \tag{12B.1-3}$$

$$\text{II.} \qquad \mathscr{H} = \frac{1}{4m}\boldsymbol{p}_c^2 + \frac{1}{m}(P_Q^2 + Q^{-2}P_\theta^2 + Q^{-2}S^{-2}P_\phi^2) + \phi^{(c)} \tag{12B.1-4}$$

How are the P's related to the generalized velocities? In these equations $\phi^{(c)} = \frac{1}{2}HQ^2 = \frac{1}{2}H(X^2 + Y^2 + Z^2)$ for Hookean dumbbells.

d. Next show that

$$\text{I.} \qquad \psi_{eq}(X, Y, Z) = \frac{[e^{-\phi^{(c)}/kT}]}{\iiint [e^{-\phi^{(c)}/kT}]dX\,dY\,dZ} \tag{12B.1-5}$$

$$\text{II.} \qquad \psi_{eq}(Q, \theta, \phi) = \frac{[e^{-\phi^{(c)}/kT}]Q^2 \sin\theta}{\iiint [e^{-\phi^{(c)}/kT}]Q^2 \sin\theta\,dQ\,d\theta\,d\phi} \tag{12B.1-6}$$

Note that

$$\psi_{eq}(Q, \theta, \phi) = \psi_{eq}(X, Y, Z)\cdot\left|\frac{\partial(X, Y, Z)}{\partial(Q, \theta, \phi)}\right| \tag{12B.1-7}$$

e. Next evaluate the integrals in the denominators of the above expressions for ψ_{eq} for Hookean dumbbells.

f. Obtain the mean square end-to-end distance $\langle Q^2\rangle_{eq}$ for Hookean dumbbells.

g. Finally prove that for any kind of elastic dumbbell

$$\langle \boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle_{eq} = kT\boldsymbol{\delta} \tag{12B.1-8}$$

Here $\boldsymbol{F}^{(c)}$ is the force in the connector, defined by

$$\boldsymbol{F}^{(c)} = \boldsymbol{F}_1^{(\phi)} = -\frac{\partial}{\partial \boldsymbol{r}_1}\phi^{(c)} = +\frac{\partial}{\partial \boldsymbol{Q}}\phi^{(c)} = \frac{\boldsymbol{Q}}{Q}\phi^{(c)\prime} = \boldsymbol{u}\phi^{(c)\prime} \tag{12B.1-9}$$

where $\phi^{(c)\prime} \equiv d\phi^{(c)}/dQ$ and $\boldsymbol{u}$ is the unit vector in the direction from bead "1" to bead "2." First show that

$$\begin{aligned}\langle \boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle_{eq} &= \frac{\int \boldsymbol{u}\boldsymbol{u}\phi^{(c)\prime}(e^{-\phi^{(c)}/kT})Q\,dQ}{\int (e^{-\phi^{(c)}/kT})dQ} \\ &= \frac{\int_0^\infty \phi^{(c)\prime}(e^{-\phi^{(c)}/kT})Q^3\,dQ \int \boldsymbol{u}\boldsymbol{u}\,d\boldsymbol{u}}{\int_0^\infty (e^{-\phi^{(c)}/kT})Q^2\,dQ \int d\boldsymbol{u}}\end{aligned} \tag{12B.1-10}$$

in which $d\boldsymbol{u} \equiv \sin\theta\,d\theta\,d\phi$. Use Appendix E to evaluate the integrals over $\boldsymbol{u}$. Then integrate the Q-integral by parts to obtain Eq. 12B.1-8.

12B.2 Equilibrium Distribution Function for a Bead-Spring Chain with Finitely Extensible Springs

Obtain an expression analogous to Eq. 12.3-9 for $\psi_{eq}(\boldsymbol{Q}^{N-1})$ for a chain model that has FENE springs (see Problem 11B.4b).

12B.3 Two-Link Distribution Function for a Rouse Chain

In §12.5 we obtained the one-link distribution function for a Rouse chain, $\psi_{1,\mathrm{eq}}(\boldsymbol{Q})$ which is the probability density that spring "1" have a configuration $\boldsymbol{Q}$. Find the analogous quantity for two links, $\psi_{12,\mathrm{eq}}(\boldsymbol{Q}, \boldsymbol{Q}')$, which gives the probability density that spring "1" has a connector vector $\boldsymbol{Q}$ and that spring "2" has a connector vector $\boldsymbol{Q}'$.

12C.1 Probability of End-to-End Vector for a Three-Bead Kramers Chain[1]

a. The probability density $P(\boldsymbol{r})$ for the end-to-end vector for a three-bead Kramers chain is given in Eq. 12D.1-6 in the random-walk approximation. Show that in the absence of this approximation ($0 < r < 2a$)

$$P_{\mathrm{eq}}(\boldsymbol{r}) = \frac{1}{8\pi a^2 r}\left[\frac{\sqrt{1 - \frac{1}{4}[1 - \frac{1}{2}(r/a)^2]^2}}{\frac{1}{4}\sqrt{3} + \frac{1}{6}\pi}\right] \tag{12C.1-1}$$

b. Use the result of (a) to obtain $\langle r^2 \rangle_{\mathrm{eq}}$.

12C.2 Change of Variables in Distribution Functions

In Eq. 12.3-6 we give ψ_{eq} for the 3-bead-2-rod chain, with the polar angles $\theta_1, \phi_1, \theta_2, \phi_2$ as the independent variables. Show that, in terms of the included angles:

$$\psi_{\mathrm{eq}}(\xi_1, \xi_{01}, \xi_2, \xi_{12}) = \frac{\sin \xi_1 \sin \xi_2 \sqrt{1 - \frac{1}{4}\cos^2 \xi_2}}{4\pi^2(\sqrt{3} + \frac{2}{3}\pi)} \tag{12C.2-1}$$

12D.1 Probability of End-to-End Vector for a Bead-Rod Chain (Random-Walk Approximation)[2,3]

a. Use the Dirac delta-function method for getting the probability density $P_{\mathrm{eq}}(\boldsymbol{r})$ for the freely jointed bead-rod chain in the random-walk approximation. Show that this leads to

$$P_{\mathrm{eq}}(\boldsymbol{r}) = \frac{1}{(2\pi)^3(4\pi)^{N-1}} \int_{-\infty}^{+\infty} e^{i(\boldsymbol{r}\cdot\boldsymbol{s})}\left[\int e^{-ia\boldsymbol{u}\cdot\boldsymbol{s}}\, d\boldsymbol{u}\right]^{N-1} d\boldsymbol{s} \tag{12D.1-1}$$

in which $\boldsymbol{u}$ is a unit vector with polar angles θ, ϕ, and $d\boldsymbol{u} = \sin\theta\, d\theta\, d\phi$. In the inner integral imagine that the coordinates are rotated so that $\boldsymbol{s}$ is in the direction of the z-axis; then the inner integral can be evaluated in spherical coordinates since $\int_0^\pi (\exp(\alpha\cos\theta))\sin\theta\, d\theta = (2/\alpha)\sinh\alpha$. Show that this leads to

$$P_{\mathrm{eq}}(\boldsymbol{r}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty} e^{i(\boldsymbol{r}\cdot\boldsymbol{s})}\left(\frac{\sin as}{as}\right)^{N-1} d\boldsymbol{s} \tag{12D.1-2}$$

[1] M. Gottlieb and R. B. Bird, *J. Chem. Phys.*, **65**, 2467-2468 (1976); M. Gottlieb, *Computers in Chemistry*, **1**, 155-160 (1977).
[2] H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), Sec. 5.
[3] P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969).

Once again rotate coordinates and perform the integration in spherical coordinates to get Rayleigh's equation:[4]

$$P_{eq}(r) = \frac{1}{2\pi^2 r}\int_0^\infty (\sin rs)\left(\frac{\sin as}{as}\right)^{N-1} s\,ds \tag{12D.1-3}$$

b. It can be shown[2] that part of the integrand in Eq. 12D.1-3 can be expanded thus:

$$\left(\frac{\sin as}{as}\right)^{N-1} = e^{-(N-1)a^2s^2/6}\left[1 - \frac{1}{180}(N-1)(as)^4 + \cdots\right] \tag{12D.1-4}$$

Show that when this expansion is used, Eq. 12D.1-3 yields

$$P_{eq}(r) = \left(\frac{3}{2\pi(N-1)a^2}\right)^{3/2} e^{-3r^2/2(N-1)a^2} \cdot\left\{1 - \frac{3}{20(N-1)}\left[5 - \frac{10r^2}{(N-1)a^2} + \frac{3r^4}{(N-1)^2a^4}\right] + \cdots\right\} \tag{12D.1-5}$$

When N is very large and $r^2 \ll (N-1)a^2$, this simplifies to Eq. 11.3-12.

c. Show that for $N = 3$ the integral in Eq. 12D.1-3 can be evaluated analytically to give

$$P_{eq}(r) = \frac{1}{8\pi a^2 r}, \qquad 0 < r < 2a \tag{12D.1-6}$$

12D.2 Effect of Ring-Closure on Radius of Gyration[5]

Consider a flexible closed-ring model formed by inserting a spring between beads "1" and "N" in the Rouse bead-spring chain model. All springs have a spring constant H.

a. Do Eqs. 11.6-1 through 9 need to be modified for this model? Explain.

b. How does Eq. 12.3-9 have to be modified?

c. Show that for this model

$$\langle s^2\rangle = \frac{\sum_k\sum_l C_{kl}\int (\boldsymbol{Q}_k\cdot\boldsymbol{Q}_l)\exp[-(H/2kT)\sum_i\sum_j D_{ij}(\boldsymbol{Q}_i\cdot\boldsymbol{Q}_j)]d\boldsymbol{Q}^{N-1}}{N\int \exp[-(H/2kT)\sum_i\sum_j D_{ij}(\boldsymbol{Q}_i\cdot\boldsymbol{Q}_j)]d\boldsymbol{Q}^{N-1}} \tag{12D.2-1}$$

in which $D_{ij} = (\delta_{ij} + 1)$; for later use verify that $D_{ij}^{-1} = \delta_{ij} - (1/N)$. Let d_i be the eigenvalues of the (D_{ij})-matrix; these are N and 1, the latter being $(N-2)$-fold.

d. Next introduce a new set of internal coordinates by letting

$$\boldsymbol{Q}_k = \sum_i \Omega_{ki}\boldsymbol{Q}'_i \tag{12D.2-2}$$

where the Ω_{ki} are the elements of an $(N-1)\times(N-1)$ orthogonal matrix which diagonalizes the (D_{ij})-matrix. Show that the introduction of these new coordinates leads to

$$\langle s^2\rangle = \frac{1}{N}\sum_k\sum_l\sum_j C_{ki}\,\Omega_{kj}\Omega_{ij}\frac{\int_0^\infty Q_j'^4\exp[-(H/2kT)d_jQ_j'^2]dQ_j'}{\int_0^\infty Q_j'^2\exp[-(H/2kT)d_jQ_j'^2]dQ_j'} \tag{12D.2-3}$$

[4] Lord Rayleigh, *Phil. Mag.*, **37**, 321-347 (1919).

[5] B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301-1314 (1949).

e. Perform the integrations in this equation and obtain finally

$$\langle s^2 \rangle = \frac{3kT}{NH} \sum_j \sum_k C_{jk} D_{kj}^{-1} = \frac{(N^2 - 1)kT}{4NH} \tag{12D.2-4}$$

Compare this result with that in Problem 11B.1 and note that the ring closure cuts the value of $\langle s^2 \rangle$ in half.

12D.3 Arbitrary Bead-Spring Models with No Constraints

Consider a molecular model consisting of beads, not necessarily all of the same mass, connected in an arbitrary manner by springs, with *no constraints*. In such a model, the beads may be numbered in any manner, and "connector vectors" $\boldsymbol{Q}_k$ can be introduced as in Eq. 11.6-2. There will, however, not always be a one-to-one correspondence between springs and connector vectors.

a. Show that if the Cartesian components of these connector vectors are used as the coordinates Q_s, then the base vectors, $\boldsymbol{b}_{vs}$, and the components of the metric matrices, g_{st} and G_{st}, are independent of the Q_s.

b. For these models the full set of $\boldsymbol{r}_v$ may be used as the independent variables in lieu of $\boldsymbol{r}_c$ and the Q_s. Show that for any function $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N) = F(\boldsymbol{r}_c, Q_1, Q_2, \ldots Q_d)$

$$\frac{\partial f}{\partial \boldsymbol{r}_v} = \frac{m_v}{m_p} \frac{\partial F}{\partial \boldsymbol{r}_c} + \sum_s \left(\frac{\partial Q_s}{\partial \boldsymbol{r}_v} \right) \frac{\partial F}{\partial Q_s} \tag{12D.3-1}$$

$$\frac{\partial F}{\partial \boldsymbol{r}_c} = \sum_v \frac{\partial f}{\partial \boldsymbol{r}_v}; \qquad \frac{\partial F}{\partial Q_s} = \sum_v \frac{1}{\sqrt{m_v}} \left(\boldsymbol{b}_{vs} \cdot \frac{\partial f}{\partial \boldsymbol{r}_v} \right) \tag{12D.3-2,3}$$

c. Apply Eq. 12D.3-1 with $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N) = \boldsymbol{r}_\mu$ to get

$$\sum_s \frac{1}{\sqrt{m_\mu}} \boldsymbol{b}_{\mu s} \left(\frac{\partial Q_s}{\partial \boldsymbol{r}_v} \right) = \left(\delta_{v\mu} - \frac{m_v}{m_p} \right) \boldsymbol{\delta} \tag{12D.3-4}$$

Use this relation to prove that

$$\sum_s \sum_t G_{st} \boldsymbol{b}_{vs} \boldsymbol{b}_{\mu t} = \left(\delta_{v\mu} - \frac{\sqrt{m_v m_\mu}}{m_p} \right) \boldsymbol{\delta} \tag{12D.3-5}$$

To obtain this, begin by multiplying Eq. 12D.3-4 by $\sqrt{m_\mu}\, \boldsymbol{b}_{\mu t}$ and summing on μ. Then multiply the resulting equation by G_{tu} and sum on t. Next multiply by $(1/\sqrt{m_\mu})\boldsymbol{b}_{\mu u}$ and sum on u, after which Eq. 12D.3-4 can be used again to get the desired result. Equation 12D.3-5 is used in Chapters 16 and 18.