Kinetic Theory of Polymeric Liquids

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Most chemists have encountered in their university study some kind of elementary kinetic theory of dilute gases. In many textbooks of physics or physical chemistry, simple kinetic theory arguments about momentum transfer lead to an expression[1,2] for the viscosity μ of a dilute gas, in which the molecules are modeled as rigid spheres of mass m and diameter σ: $\mu \approx \sqrt{mkT}/\sigma^2$ (here kT is the Boltzmann constant times the absolute temperature). That is, relatively crude arguments lead to the dependence of the gas viscosity on the temperature and on the molecular mass and diameter. Of course, a much more refined kinetic theory has been developed, in which the deviations are found from the simple relation cited above.[1] Also the modeling of the molecules has become more realistic, with the inclusion of van der Waals attractive forces, interactions among dipole and quadrupole moments, and noncentral intermolecular forces.

It is unfortunate that the simple kinetic theory for dilute polymer solutions has not found its way into the textbooks, since it gives considerable insight into structure-property relationships. When the polymer molecules are modeled crudely as elastic dumbbells, it is possible to develop the kinetic theory equations in just a few pages;[3] such derivations have been given in the physics and chemistry research literature as early as 40 years ago, although not in suitable form for textbook use.

For gases and for liquids made up of small molecules, the mechanical response is completely described by two "material constants": the viscosity μ and the density ρ. The viscosity[1,4] appears as the scalar proportionality constant between the stress tensor τ and the rate-of-strain tensor $\gamma_{(1)}$:

$$\tau = -\mu\gamma_{(1)} \tag{1}$$

The Cartesian component τ_{ij} of the stress tensor gives the force in the positive j direction acting across a unit surface perpendicular to the i direction, the force being exerted by the material of lesser i on the material of greater i. The Cartesian components of the rate-of-strain tensor are given by $\gamma_{(1)ij} = \partial v_j/\partial x_i + \partial v_i/\partial x_j$, where v_i is the ith component of the velocity vector and x_i is the ith Cartesian coordinate. Although the linear "Newtonian" expression in eq 1 has been found to be entirely satisfactory for gases and simple liquids, it has been thoroughly established that polymeric liquids (polymer solutions and undiluted polymers (or "melts")) are "non-Newtonian"; that is, eq 1 is not an appropriate "constitutive equation" (the relation between τ and one

or more kinematic tensors) for liquids containing long-chain molecules.

What is the evidence for this? There are many relatively simple experiments[4,5] that show major *qualitative* differences between Newtonian fluids and polymeric fluids:

a. When a rotating rod is inserted into a beaker of a Newtonian liquid, the fluid surface near the rod is lower than that near the beaker wall, because of centrifugal effects. When the rotating rod is inserted into a polymeric fluid, the fluid surface near the rod is higher than that near the beaker wall; that is, there are additional forces that can overcome the centrifugal forces and make the fluid climb up the rotating rod. The "rod-climbing" phenomenon is called the "Weissenberg effect".

b. When a Newtonian liquid is allowed to flow down a tilted trough, the fluid surface is found to be flat (except for meniscus effects at the wall). Polymeric fluids in the same experiment exhibit a small, but measurable, bulging of the fluid surface.

c. When a Newtonian liquid is forced through a horizontal tube by means of a pressure difference and then the driving force is suddenly removed, the liquid stops moving. When the same thing is done for a polymeric liquid, it will "recoil" when the driving force is removed—that is, the fluid begins to retreat in the direction from whence it has come. It is as if the fluid "remembers" where it has been, but as it begins retreating it gradually "forgets" and never returns to its original configuration (the way a rubber band will after it has been stretched). One often hears the anthropomorphic term "fluids with fading memory" applied to polymeric liquids.

d. When a cylinder with its axis in the z direction is suspended in a Newtonian fluid and caused to oscillate in the x direction with very small amplitude, a secondary flow is induced such that the fluid far from the cylinder is pulled in toward the cylinder along the $+$ and $-y$ axis and then propelled away from it in along the $+$ and $-x$ axis; this is the "acoustical streaming" effect. For the polymeric liquids, on the other hand, the direction of the induced secondary flow is reversed, with the fluid being sucked in along the x axis and expelled along the y axis.

These fascinating polymer flow phenomena (and many others!) cannot be described by Newtonian fluid

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(1) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York (2nd Corrected Printing), 1964, Chapter 1.

(2) R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena", Wiley, New York, 1960.

(3) R. B. Bird, O. Hassager, R. C. Armstrong, and C. F. Curtiss, "Dynamics of Polymeric Liquids, Vol. 2: Kinetic Theory", Wiley, New York, 1977 [2nd edition in preparation].

(4) R. B. Bird, R. C. Armstrong, and O. Hassager, "Dynamics of Polymeric Liquids, Vol. 1: Fluid Mechanics", Wiley, New York, 1977 [2nd edition in preparation].

(5) R. B. Bird and C. F. Curtiss, *Phys. Today,* **37** (1), 36–43 (1984).

mechanics at all—that is, by solving the equation of continuity, the equation of motion, and the Newtonian "constitutive equation" (eq 1) simultaneously. To describe the flow of polymers, we have to a different constitutive equation. There have been many attempts to develop empirical constitutive equations, but guessing a tensorial relation to describe many rheological phenomena is a far more difficult assignment than the analogous problem in thermodynamics of guessing the equation of state for describing the pVT behavior of compressed gases and liquids (since van der Waals' first guess back in about 1870, countless empiricisms have been and are still being proposed). In the past several decades considerable insight into the constitutive equations for polymeric fluids has been provided by kinetic theory. Such studies also enable us to say something about molecular orientation and stretching in various kinds of flow fields.

The challenge to be addressed in this article, then, is the development of constitutive equations for polymeric solutions and undiluted polymers ("melts") by the use of kinetic theories; in these theories the constituent polymer molecules have to be modeled by some kind of simple mechanical system that portrays the essential structure and dynamical response.

The Material Functions

In order to test the kinetic theory results, there has to be a body of experimental data on a variety of simple, carefully controlled flow systems, in which the flow field and one or more stress components can be measured. The rapidly growing science of designing and interpreting such measurements is called "rheometry".[6] Here we do not discuss the experimental devices, techniques, and measurement errors but give only the definitions of a few of the "material functions" that are currently being measured.

In a *steady shear flow* $v_x = \dot{\gamma}y$, $v_y = 0$, and $v_z = 0$, it is possible to measure the shear stress and two normal-stress differences. It is then conventional to define three material functions, the viscosity (η), the first normal stress coefficient (Ψ_1), and the second normal stress coefficient (Ψ_2) by

$$\tau_{yx} = -\eta\dot{\gamma} \tag{2a}$$

$$\tau_{xx} - \tau_{yy} = -\Psi_1\dot{\gamma}^2 \tag{2b}$$

$$\tau_{yy} - \tau_{zz} = -\Psi_2\dot{\gamma}^2 \tag{2c}$$

These "viscometric functions", η, Ψ_1, and Ψ_2, are all functions of the shear rate $\dot{\gamma}$; both η and Ψ_1 are known to be positive for polymer solutions and melts, and Ψ_2 is negative and smaller than Ψ_1 in magnitude (experimental values of $-\Psi_2/\Psi_1$ between about 0.01 and 0.3 have been reported in the literature, but recently arguments have been advanced[27] that suggest that 0.25 should be an upper bound, at least for small values of the shear rate $\dot{\gamma}$). The rod-climbing effect is strongly dependent on Ψ_1 and also somewhat dependent on Ψ_2; the bulging of the liquid surface in the tilted trough experiment depends only on Ψ_2.

In a *steady elongational flow*, $v_z = \dot{\epsilon}z$, $v_x = -(^1/_2)\dot{\epsilon}x$, and $v_y = -(^1/_2)\dot{\epsilon}y$, one normal stress difference can be measured

$$\tau_{zz} - \tau_{xx} = -\bar{\eta}\dot{\epsilon} \tag{3}$$

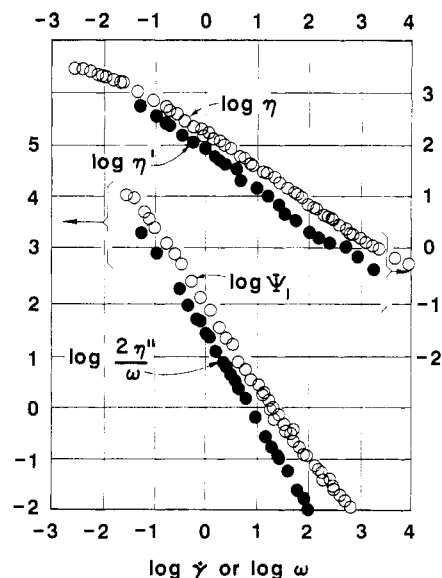(6) K. Walters, "Rheometry", Wiley, New York, 1975.

Figure 1. Material functions for a 1.5% polyacrylamide (Separan AP30) solution in a 50/50 mixture (by weight) of water and glycerine. The functions $\eta(\dot{\gamma})$, $\eta'(\omega)$, and $\eta''(\omega)$ are in Pa·s, and $\Psi_1(\dot{\gamma})$ is in Pa·s²; both $\dot{\gamma}$ and ω are in s⁻¹. The data are taken from J. D. Huppler, E. Ashare, and L. A. Holmes, *Trans. Soc. Rheol.*, 11, 159–179 (1967).

and $\bar{\eta}$ is called the elogational viscosity; $\bar{\eta}$ is a function of the elongation rate $\dot{\epsilon}$.

Many time-dependent flows have been studied by polymer chemists. A particularly important one is the small-amplitude sinusoidal shear flow $v_x = \text{Re}\{\dot{\gamma}^0e^{i\omega t}\}y$, $v_y = 0$, and $v_z = 0$, in which $\dot{\gamma}^0$ is in general a complex quantity and ω is the frequency of oscillation; the notation $\text{Re}\{\}$ means "the real part of". Then because the amplitude of the oscillation is quite small, the shear stress is also sinusoidal: $\tau_{yx} = \text{Re}\{\tau_{yx}^0e^{i\omega t}\}$. We now define a complex viscosity η^* by

$$\tau_{yx}^0 = -\eta^*\dot{\gamma}^0 \tag{4}$$

and $\eta^* = \eta' - i\eta''$ is a function of the frequency ω. The normal stresses can also be measured, and they oscillate with a frequency of 2ω about a nonzero mean.

In Figure 1 we show some sample data for $\eta(\dot{\gamma})$, $\Psi_1(\dot{\gamma})$, $\eta'(\omega)$, and $\eta''(\omega)$. Keep in mind that for a Newtonian fluid η and η' are both constant (the viscosity μ) and η'' and Ψ_1 are zero.

Many other time-dependent shear and elongational experiments have been performed[4,6-8] and other types of flows as well (e.g., biaxial stretching, eccentric-disk flows, squeezing flows). These experiments provide the basic data against which the kinetic theories have to be tested; one cannot overemphasize the need for carefully measured material functions on well-characterized liquids. In addition, data on flow birefrigence[8] and light scattering are important in testing molecular theories.

Molecular Models

Polymers are molecules of very large molecular weight, and there is an enormous variety in their chemical architecture. In this discussion we consider

(7) A. S. Lodge, "Elastic Liquids", Academic Press, New York, 1964. A. S. Lodge, "Body Tensor Fields in Continuum Mechanics", Academic Press, New York, 1974.
(8) H. Janeschitz-Kriegl, "Polymer Melt Rheology and Flow Birefringence", Springer-Verlag, Berlin, 1983.
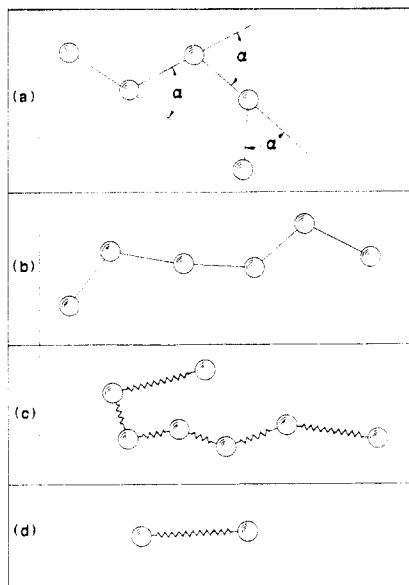
Figure 2. Mechanical models for representing chainlike polymer molecules in kinetic theory: (a) Kirkwood–Riseman freely rotating bead–rod chain, (b) Kramers freely jointed bead–rod chain, (c) Rouse–Zimm freely rotating bead–spring chain, (d) elastic dumbbell model.

for the most part those polymers which are formed by stringing together certain repeating groups of atoms (monomers) in such a way that an extremely long chain is formed. Such a chain can be oriented in space, and in addition it has a lot of flexibility resulting from the large number of internal degree of freedom. The chain can appear in a coiled-up configuration, or it can be stretched out into a long string-like configuration. In Figure 2 we show several mechanical models that have been used in the kinetic theory of flexible, chainlike polymers: (a) the Kirkwood–Riseman freely rotating chain is made up of "beads" joined together by massless "rods", but the angles between successive rods are fixed; (b) the Kramers freely jointed chain is composed of beads joined by rods, with universal joints at the beads; (c) the Rouse–Zimm chain is constructed from beads and "springs", with universal joints; and (d) the elastic dumbbell is made up of just two beads and a spring. These models have been listed in decreasing order of complexity, but each model is supposed to represent a long, extensible molecule that can undergo rotational and uncoiling motions. The constant angles between the rods in the Kirkwood–Riseman chain describes inherent stiffness in the polymer chains, which the other models do not describe. The elastic dumbbell model clearly is incapable of mimicking the responses associated with the many internal degrees of freedom of a polymer molecule; on the other hand, its very simplicity has made it a favorite for study, and it has in fact been quite useful in the development of an understanding of the relation between molecular motions and rheological phenomena.

To some extent the choice of molecular model depends on the contemplated use of the kinetic theory results. To describe the mean-square end-to-end distance or the radius of gyration of polymer molecules at *equilibrium*, statistical mechanics provides an explicit expression for the distribution function, and therefore rather complete molecular models can be used (such as the rotational isomeric state model used by Flory[9]). To

describe the *small-amplitude oscillatory experiment* used for studying linear viscoelastic responses, one needs a model with many internal degrees of freedom, particularly if it is desired to describe effects at high frequencies; the Rouse–Zimm chain model has proven to be quite useful in this instance. To describe the *steady-state shear flow* experiment, where the overall rotation of the molecule is the principal molecular motion involved, it is not particularly necessary to use a model with many beads since the small scale motions are not activated in the flow. To describe an *elongational flow* experiment (and also shear flows with very large velocity gradients), in which the molecules are being stretched out considerably, a model that has a finite extensibility is required, such as the Kramers chain or an elastic dumbbell with a nonlinear spring that can be stretched only to a finite limit. If one wishes to be able to describe and interrelate all three of these types of nonequilibrium experiments quantitatively, then a more comprehensive model such as the Kirkwood–Riseman chain has to be used, since it can describe chain orientation, some small scale motions, finite extensibility, and chain stiffness.

Kinetic Theory for Dilute Polymer Solutions. Illustrated with the Elastic Dumbbell Model (Reference 3, Chapter 10)

In this section we show, by example, how one sets up the basic equations of the kinetic theory for polymers in a dilute solution. This presentation follows a simple, intuitive procedure, which enables one to formulate the problem by using only configuration-space ideas. This procedure is, however, inadequate if it is desired to use molecular models that contain constraints (fixed distances and/or angles); for that purpose it is preferable to use a more general phase-space treatment (ref 3, chapter 14). In addition the phase-space treatment makes clearer the assumptions inherent in the more traditional configuration-space treatments.

The simplest mechanical model of a polymer molecule is the elastic dumbbell of Figure 2d in which two beads are joined by a spring. The interbead vector, from bead "1" to "2" is called $\mathbf{Q}$, and the tension in the spring is called $\mathbf{F}^{(c)}$. Each bead is presumed to experience a Stokes' drag force with a friction coefficient ζ; the latter is the drag force divided by the bead velocity relative to the fluid velocity. The polymer solution hs a velocity field that is homogeneous: $\mathbf{v} = \mathbf{v}_0 + [\kappa \cdot \mathbf{r}]$, where κ is in general a function of time and $\mathbf{r}$ is the position vector. We want to know the probability, ψ-$(\mathbf{Q},t)$ d$\mathbf{Q}$, that a dumbbell in the solution will have a configuration in the range d$\mathbf{Q}$ about $\mathbf{Q}$ at time t.

To get the configurational distribution function $\psi(\mathbf{Q},t)$, we first write down the equation of continuity in the configuration space:

$$\frac{\partial \psi}{\partial t} = -\left(\frac{\partial}{\partial \mathbf{Q}} \cdot [[\dot{\mathbf{Q}}]] \psi \right) \tag{5}$$

In essence all this equation says is that when a dumbbell leaves one configuration, it must turn up in another. Here $[[\dot{\mathbf{Q}}]]$ is the velocity-space average of the time rate of change of the configuration vector $\mathbf{Q}$. This quantity in turn can be obtained by making a force balance on

(9) P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley, New York, 1969.

each of the beads and then subtracting the two equations in order to get the balance of the forces for the internal motion:

$$-\zeta([[\dot{\mathbf{Q}}]] - [\kappa\cdot\mathbf{Q}]) - 2kT\frac{\partial}{\partial\mathbf{Q}}\ln\psi - 2\mathbf{F}^{(c)} = 0 \quad (6)$$

The first term accounts for the *hydrodynamic drag* forces on the beads, the second term describes the *Brownian motion* forces, and the third term accounts for the forces transmitted through the *connecting spring*. When the force balance is solved for $[[\dot{\mathbf{Q}}]]$, and when the latter is substituted into the continuity equation, we get the "diffusion equation"—the second-order partial differential equation for the configurational distribution function:

$$\frac{\partial\psi}{\partial t} = -\left(\frac{\partial}{\partial\mathbf{Q}}\cdot\left\{[\kappa\cdot\mathbf{Q}]\psi - \frac{2kT}{\zeta}\frac{\partial}{\partial\mathbf{Q}}\psi - \frac{2}{\zeta}\mathbf{F}^{(c)}\psi\right\}\right) \quad (7)$$

Once the flow pattern and the spring force law have been chosen (i.e., once κ and $\mathbf{F}^{(c)}$ are specified), then the "diffusion equation" can in principle be solved to get the distribution of configurations of the dumbbells.

Macroscopic properties of the solution—mechanical, electrical, or thermal—can then be calculated by taking appropriate averages using the distribution function $\psi(\mathbf{Q},t)$. Here we are concerned with the mechanical (i.e., rheological) properties and the macroscopic quantity of interest is then the stress tensor τ, which appears in the equation of motion $\rho D\mathbf{v}/Dt = -\nabla p - [\nabla\cdot\tau] + \rho\mathbf{g}$. The stress tensor accounts for the various mechanisms by which forces are transmitted through the fluid: by the motion of the *solvent molecules*, by the *tensions in the springs* of the dumbbells, and by the *momentum transport of the beads* of the dumbbells. The contribution due to the tensions in the springs must be averaged over all the possible configurations of the dumbbells. The final expression is the "Kramers form" of the stress tensor:

$$\tau = -\eta_s\gamma_{(1)} - n\langle\mathbf{Q}\mathbf{F}^{(c)}\rangle + nkT\delta \quad (8)$$

in which η_s is the solvent viscosity, δ is the unit tensor, n is the number density of dumbbells (i.e., polymer molecules) in the solution, and $\langle\ \rangle$ stands for $\int(\ )\psi(\mathbf{Q},t)$ $d\mathbf{Q}$. A second expression for the stress tensor can be obtained by eliminating the spring force from the above expression by using the second tensorial moment of the diffusion equation (eq 7). The expression thus obtained is the "Giesekus form" of the stress tensor

$$\tau = -\eta_s\gamma_{(1)} + \frac{n\zeta}{4}\langle\mathbf{Q}\mathbf{Q}\rangle_{(1)} \quad (9)$$

The subscript on $\langle\mathbf{Q}\mathbf{Q}\rangle_{(1)}$ indicates the "contravariant convected time derivative" $\tau_{(1)} = \partial\tau/\partial t + \{\mathbf{v}\cdot\nabla\tau\} - \{(\nabla\mathbf{v})^\dagger\cdot\tau + \tau\cdot\nabla\mathbf{v}\}$.

The discussion above for the elastic dumbbell model has emphasized the two main parts of the kinetic theory: (i) the derivation of a diffusion equation for the configurational distribution function $\psi(\mathbf{Q},t)$ and (ii) the establishment of an expression for the stress tensor τ (or other macroscopic quantity). For more complex models the kinetic theory has the same general structure; however, for models that have built-in constraints (fixed interbead distances or fixed angles between the rods) generalized coordinates must be used, and the

formulation of the theory becomes somewhat more involved.[3,10] It should be evident that in the modeling the hydrodynamics has been treated only very roughly, with an isotropic, linear hydrodynamic drag law being postulated. Various refinements in the basic dumbbell model can be introduced in which one accounts for the solvent velocity field perturbation at one bead owing to the motion of the other beads ("hydrodynamic interaction"); there is a rather extensive literature on this particular modification of the elementary theory (ref 3, section 10.6). Other modifications are nonisotropic drag coefficients,[11] ζ varying with interbead distance,[12] and inclusion of a dashpot in parallel with the spring.[13] These various "improved" dumbbell models have been very helpful in elucidating the relation between models and rheological phenomena. However, they should not be taken too seriously, inasmuch as the multibead chain models of Figure 2 will ultimately provide much more reliable results.

Distribution Function and Constitutive Equation for Hookean Dumbbells (Reference 3, Section 10.4)

The simplest elastic dumbbell model is one with a linear spring, so that the spring connector force law is $\mathbf{F}^{(c)} = H\mathbf{Q}$, in which H is the Hookean spring constant. For this type of dumbbell the diffusion equation for $\psi(\mathbf{Q},t)$ (eq 7) has been solved to give[14]

$$\psi(\mathbf{Q},t) = \frac{(H/2\pi kT)^{3/2}}{\sqrt{\det\alpha}}\exp[-(H/2kT)(\alpha^{-1}:\mathbf{Q}\mathbf{Q})] \quad (10a)$$

$$\alpha(t) = \delta - \frac{1}{\lambda_H}\int_{-\infty}^{t}\exp[-(t-t')/\lambda_H]\gamma_{[0]}(t,t')\,dt' \quad (10b)$$

in which $\lambda_H = \zeta/4H$ is the characteristic (relaxation) time for the elastic dumbbell solution and $\gamma_{[0]}$ is a finite strain tensor. The finite strain tensor is defined in terms of the motion of the fluid. If a fluid particle is at a position $\mathbf{r}$ at time t, then its position $\mathbf{r}'$ at some previous time t' is given by the "displacement function": $\mathbf{r}' = \mathbf{r}'(\mathbf{r},t,t')$; a displacement gradient tensor $\mathbf{E}$ can then be defined as $\mathbf{E} = [(\partial/\partial\mathbf{r}')\mathbf{r}]^\dagger$, and finally the finite strain tensor[4] is given as $\gamma_{[0]} = \delta - \{\mathbf{E}\cdot\mathbf{E}^\dagger\}$. It is curious that the kinematic tensor that appears in the differential equation is $\kappa = (\nabla\mathbf{v})^\dagger$, whereas the kinematic tensor appearing in the solution (i.e., the finite strain tensor) is related to $\mathbf{E}$. These two tensors are not simply related as may be seen from

$$\mathbf{E}(t,t') = \delta + \int_{t'}^{t}\kappa''\,dt'' + \int_{t'}^{t}\int_{t'}^{t}\{\kappa'''\cdot\kappa''\}\,dt'''\,dt'' + \dots \quad (11)$$

(10) C. F. Curtiss and R. B. Bird, *Physics A: Amsterdam*, *118A*, 191–204 (1983).

(11) H. Giesekus, *J. Non-Newtonian Fluid Mech.*, 11, 69–109 (1982); 12, 367–374 (1983); R. B. Bird and J. M. Wiest, *J. Rheol. (N.Y.)*, 29, 519–532 (1985).

(12) R. I. Tanner, *Trans. Soc. Rheol.*, 19, 557–582 (1975); X.-J. Fan, R. B. Bird, and M. Renardy, *J. Non-Newtonian Fluid Mech.*, 18, 255–272 (1985).

(13) G. G. Fuller and L. G. Leal, *J. Non-Newtonian Fluid Mech.*, 8, 271–310 (1981). C..W. Manke and M. C. Williams, *Macromolecules*, in press.

(14) A. S. Lodge and Y. Wu, *Rheol. Acta*, 10, 539–553 (1971); P. H. van Wiechen and H. C. Booij, *J. Eng. Math.*, 5, 89–98 (1971); H. King and D. F. James, *J. Chem. Phys.*, 78, 4743–4748, 4749–4754 (1983).

which is valid for the homogeneous flow field being considered here; the abbreviated notation $\kappa'' = \kappa(t'')$ has been used.

We note in passing that the tensor α plays an important role in the changes of the thermodynamic functions that occur when a polymer solution goes from a state of equilibrium to a state of flow. The changes in internal energy, entropy, and Helmholtz free energy, associated with the polymer solute, are[15] $\Delta U = \frac{1}{2}nkT$ tr$(\alpha - \delta)$, $\Delta S = nk$ ln $(\det \alpha)^{1/2}$, and $\Delta A = \frac{1}{2}nkT[tr(\alpha - \delta) - $ln $(\det \alpha)]$. In a steady-state shear flow with shear rate $\dot{\gamma}$, it can be shown that the internal energy increase is $\Delta U = nkT\lambda_H^2\dot{\gamma}^2$ and the entropy increase is $\Delta S = nk$ ln $(1 + \lambda_H^2\dot{\gamma}^2)^{1/2}$.

Once the solution to the partial differential equation for $\psi(\mathbf{Q},t)$ has been obtained, the configurational distribution function can then be substituted into the expression for the stress tensor to get the constitutive equation

$$\tau = -\eta_s\gamma_{(1)} + \int_{-\infty}^{t}\left\{\frac{nkT}{\lambda_H}\exp[-(t - t')/\lambda_H]\right\}\gamma_{[0]}(t,t') \, dt' \tag{12}$$

This gives the stresses in an element of fluid in terms of the strains that the fluid element has suffered throughout all of the past history of the motion; the exponential function describes the "rapidly fading memory".

Alternatively one can get the constitutive equation by eliminating $\langle \mathbf{QQ} \rangle$ between eq 8 (written with $\mathbf{F}^{(c)} = H\mathbf{Q}$) and eq 9 to get

$$\tau = -\eta_s\gamma_{(1)} + \tau_p \tag{13a}$$

$$\tau_p + \lambda_H\tau_{p(1)} = -nkT\lambda_H\gamma_{(1)} \tag{13b}$$

When this procedure is used, the constitutive equation for τ_p, the polymer contribution to the stress tensor, is given as a differential equation; this result can be converted into the integral form above by using standard continuum mechanical arguments.[4,7]

We have now shown, for one very elementary model, how one goes from the mechanical model to the complete constitutive equation. We see exactly how the various model parameters (ζ, H, n, η_s) arise in the final constitutive relation; two of the parameters occur grouped together in the time constant $\lambda_H = \zeta/4H$, and this quantity has to be determined ultimately from experimental data.

Having obtained a constitutive equation we next must test it against measured material functions. From the Hookean dumbbell constitutive equation we can, for example, obtain the viscometric functions defined in eq 2. For dilute solutions (for which the theory is intended) the functions $\eta(\dot{\gamma})$, $\Psi_1(\dot{\gamma})$, and $-\Psi_2(\dot{\gamma})$ are known experimentally to be monotone decreasing functions of the shear rate (see Figure 1), but the Hookean dumbbell model gives constant values for all three of them, with $\Psi_2 = 0$. One can also make comparisons with data for unsteady-state shear flows, for elongational flows, and still other flows, and it is found that in most of these other experiments, the model prediction is rather poor.

As a consequence one has to conclude that the simple Hookean dumbbell model, although mathematically tractable, is not sufficiently good to describe even qualitatively some of the observed phenomena.

The next question is: how can the model be improved upon? At this point one can try several different modifications. One modification is to join N beads by $N - 1$ Hookean springs to form a chain (ref 3, chapter 12); this model does give much better results in linear viscoelasticity[16] (for example, in small amplitude oscillatory motions), but it still yields viscometric functions that are independent of the shear rate. Another modification is the use of a finitely extensible nonlinear spring in the elastic dumbbell model since real molecules cannot be stretched out beyond some finite limit; we see in the next section that this simple modification of the basic model gives much better results. However, replacing the linear spring by a nonlinear one is only one of many modifications that have been tried.[11,13]

An Approximate Constitutive Equation for Finitely Extensible Nonlinear Elastic (FENE) Dumbbells (Reference 3, Section 10.5)

A rather simple nonlinear-spring force law is[3,17]

$$\mathbf{F}^{(c)} = \frac{H\mathbf{Q}}{1 - (Q^2/Q_0^2)} \quad (Q \leq Q_0) \tag{14}$$

This kind of spring is Hookean at small values of the bead separation and cannot be stretched beyond a separation of Q_0. For this model there are two time constants: $\lambda_H = \zeta/4H$ and $\lambda_Q = \zeta Q_0^2/12kT$; instead of the latter we use the ratio $b = 3\lambda_Q/\lambda_H = HQ_0^2/kT$. Comparisons of calculated rheological properties with experimental data[18,19] indicate that realistic values for the parameter b are in the range from 30 to 300. The Kramers stress tensor expression is now (from eq 8):

$$\tau = -\eta_s\gamma_{(1)} - nH\left\langle \frac{\mathbf{QQ}}{1 - (Q^2/Q_0^2)} \right\rangle + nkT\delta \tag{15}$$

We would now like to eliminate the $\langle \ \rangle$ quantities between eq 9 and 15, following the method we used for Hookean dumbbells, but this obviously cannot be done. However, we can get an approximate constitutive equation if we replace eq 15 by

$$\tau \doteq -\eta_s\gamma_{(1)} - nH\frac{\langle \mathbf{QQ} \rangle}{1 - \langle Q^2/Q_0^2 \rangle} + (1 - \epsilon b)nkT\delta \tag{16}$$

That is, we replace the average of the ratio by the ratio of averages and then try to compensate somewhat for the error thus introduced by including an extra isotropic contribution containing the parameter ϵ. We then choose ϵ to be $2/[b(b + 2)]$ in order to ensure that eq 16 is correct at equilibrium. Then one can eliminate the two averages $\langle \mathbf{QQ} \rangle$ and $\langle Q^2/Q_0^2 \rangle$ from eq 9, eq 16, and the trace of eq 16 to get the following approximate constitutive equation (almost the same equation was obtained by Tanner[20] by a different procedure):

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

(16) J. D. Ferry, "Viscoelastic Properties of Polymers", 3rd ed., Wiley, New York, 1980.
(17) H. R. Warner, Jr., *Ind. Eng. Chem. Fundam.*, **11**, 379–387 (1972).
(18) R. L. Christiansen and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **3**, 161–177 (1977/1978).
(19) Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **9**, 157–178, 179–194 (1981).

$$Z\tau_{\rm p} + \lambda_H\tau_{\rm p(1)} - \lambda_H[\tau_{\rm p} - (1- \epsilon b)nkT\delta]\overset{\cdot}{D} \ln Z/Dt =$$
$$-(1 - \epsilon b)nkT\lambda_H\gamma_{(1)} \quad (17a)$$

$$Z = 1 + (3/b)[(1 - \epsilon b) - {\rm tr}(\tau_{\rm p}/3nkT)] \quad (17b)$$

In the limit that b becomes infinite (Hookean dumbbells), the quantity Z goes to unity and the constitutive equation simplifies to eq 13; thus Z is seen to describe the influence of the nonlinear springs. Although eq 17 is an approximate constitutive equation, it leads to results which are in remarkably good agreement with those one gets by solving the diffusion equation (eq 7) numerically and then computing the components of the stress tensor from eq 15.[21]

The constitutive equation in eq 17 has been found to describe quite well the viscosity curves for several moderately concentrated polymer solutions,[19] and it seems to describe a number of other rheological properties qualitatively. It has also been used to solve several flow problems;[14,22,23] once the velocity fields have been obtained, the trace of eq 16 can be used to get the molecular stretching $\langle Q/Q_0{}^2 \rangle$. For this particular model then we can go through the entire sequence: *molecular model → constitutive equation → solution to fluid dynamics problem → molecular stretching in a flow field*. It is this sequence of activities that we would like to be able to carry out for more realistic molecular models, such as multibead chains, which have a spectrum of relaxation times.

Model of Interacting Kramers Chains as a Model for a Polymer Melt

There are two kinds of theories for polymer melts: the older ones are the *network theories*[24] in which the melt is envisioned as a temporary network formed by the transient physical junctions between the strands of the constituent molecules; the newer ones are the *mean field theories*,[25,26] in which one modifies the dilute solution theory and looks just at the motion of a single molecule as it moves about with its motion drastically limited by the other molecules in its immediate vicinity. In the network theories one has to make empirical statements about the rates of junction creation and destruction, whereas in the mean field theories one has to make empirical statements about the drag force on the beads and the Brownian motion forces—and both of these now being taken to be nonisotropic; the Brownian motion is presumed to be acting only along the polymer backbone, and the resultant back-and-forth wiggling is called "reptation".

We discuss here the results of a mean-field theory[26] in which the polymer molecules are represented by Kramers chains. Then the use of the nonisotropic hydrodynamic drag and the reptational Brownian motion leads after considerable effort and several simplifying assumptions to the following constitutive equation (the Curtiss–Bird equation):

$$\tau = NnkT\Big[\tfrac{1}{3}\delta - \int_{-\infty}^{t}\mu(t - t')\mathbf{A}(t,t')\,dt' -$$
$$\epsilon\lambda\kappa: \int_{-\infty}^{t}\nu(t - t')\mathbf{B}(t,t')\,dt'\Big] \quad (18a)$$

$$\mu(s) = -(\lambda/2)d\nu/ds \quad (18b)$$

$$\nu(s) = \frac{16}{\pi^2\lambda}\sum_{\alpha,{\rm odd}}\frac{1}{\alpha^2}e^{-\pi^2\alpha^2 s/\lambda} \quad (18c)$$

$$\mathbf{A} = (1/4\pi)\int [1 + (\gamma^{[0]}\!:\!\mathbf{uu})]^{-3/2}\mathbf{uu}\,d\mathbf{u} \quad (18d)$$

$$\mathbf{B} = (1/4\pi)\int [1 + (\gamma^{[0]}\!:\!\mathbf{uu})]^{-3/2}\mathbf{uuuu}\,d\mathbf{u} \quad (18e)$$

Here N is the number of beads in the Kramers bead-rod chain, a is the length of a rod in the chain, $\lambda = N^{3+\beta}\zeta a^2/2kT$ is the time constant, $\gamma^{[0]} = \{\Delta^\dagger\!\cdot\!\Delta\} - \delta$ is another finite strain tensor (Δ is the tensor inverse to $\mathbf{E}$), $\mathbf{u}$ is a unit vector described by polar angles θ and ϕ, and $d\mathbf{u} = \sin\theta\,d\theta\,d\phi$ is an element of area on a unit sphere. The model contains a total of five constants: the number of beads in the chain N, the rod length a, the bead friction factor ζ, the "link tension coefficient" ϵ which is between zero and unity, and the "chain constraint exponent β which appears to be about 0.3–0.5; several of these parameters (ζ, β, and a) are lumped together in the time constant λ, which has to be determined from experiments. The constitutive equation emerging from the Doi–Edwards kinetic theory is, apart from a multiplicative constant, a special case of eq 18 with $\epsilon = 0$ and $\beta = 0$.

In the final constitutive equation there are two integral terms, one containing a second-order tensor, $\mathbf{A}$, and another containing a fourth-order tensor, $\mathbf{B}$. Both integrals have the same structure: the integrand is a product of a term (μ or ν) involving only the time constant of the fluid, and another term involving only the kinematics of the flow field ($\mathbf{A}$ or $\mathbf{B}$). Note that this same type of factorization manifested itself in eq 12 for the dilute solution of elastic dumbbells. It has been shown recently[27] that this model (eq 13) for a polymer melt shows rod climbing[28] if $\epsilon > {}^1/_8$; the Doi–Edwards theory (even for polydisperse systems) cannot describe rod climbing.

Extensive comparisons have been made between the rheological properties calculated for this model and the experimental measurements for monodisperse liquids made of chainlike polymers.[29] It is possible to choose values of N, λ, and ϵ to fit the experimental data for several different types of polymeric liquids (both undiluted polymers and very concentrated solutions). The constitutive equation given above has recently been used for making fluid dynamics calculations.[30] The theory has been extended to polydisperse systems by Curtiss;[31] the time constant for species α in the mixture is found to be $\lambda_\alpha = \bar{N}^{1+\beta}N_\alpha{}^2\zeta a^2/2kT$, where $\bar{N}$ is the number average of N_α (number of beads in chain of molecular weight M_α). If one uses the log-normal dis-

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

(21) X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 125–144 (1985).

(22) Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **12**, 135–152 (1983).

(23) L. E. Wedgewood and R. B. Bird, in "Integration of Fundamental Polymer Science and Technology"; Elsevier: London, (1985).

(24) A. S. Lodge, R. C. Armstrong, M. H. Wagner, and H. H. Winter, *Pure Appl. Chem.*, **54**, 1349–1359 (1983).

(25) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1789–1801, 1802–1817, 1818–1832 (1978); **75**, 38–54 (1979).

(26) C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016–2025, 2026–2033 (1981).

(27) O. Hassager, *J. Rheol. (N.Y.)*, **29**, 361–364 (1985).

(28) D. D. Joseph, G. S. Beavers, A. Cers, C. Dewald, A. Hoger, and P. T. Than, *J. Rheol. (N.Y.)*, **28**, 325–346 (1984).

(29) R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1105 (1982); R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4747–4757 (1982); H. H. Saab, R. B. Bird, and C. F. Curtiss, *ibid.*, **77**, 4758–4766 (1982).

(30) D. S. Malkus and B. Bernstein, *J. Non-Newtonian Fluid Mech.*, **16**, 77–116 (1984).

(31) C. F. Curtiss, to appear in Chapter 19 of the 2nd edition of ref 3.

Table I
Constants in the Retarded-Motion Expansion from Kinetic Theory Calculations[a] (Made Dimensionless with a_k)

order k	const	FENE dumbbells (dilute solution)[b]	multibead rods (dilute solution)[c]	freely jointed bead-rod chain (melt)[d]
1	b_1/a_1	$\dfrac{\eta_s}{a_1} - \dfrac{b}{b+5}$	$\dfrac{\eta_s}{a_1} + [1 - \dfrac{2}{5}(1 - \dfrac{\lambda_2}{\lambda_1})]$	$\dfrac{1}{60} + \dfrac{\epsilon}{90}$
2	b_2/a_2	$-\dfrac{b^2}{(b-5)(b+7)}$	$-\dfrac{3}{5}$	$-\dfrac{1}{600}$
2	b_{11}/a_2	0	$-\dfrac{12}{35}(1 - \dfrac{\lambda_2}{\lambda_1})$	$-\dfrac{1}{1050} + \dfrac{c}{1050}$
3	b_3/a_3	$\dfrac{b^3(2b + 11)/(2b + 7)}{(b-5)(b+7)(b+9)}$	$\dfrac{3}{5}$	$\dfrac{17}{100\,800}$
3	b_{12}/a_3	$\dfrac{4b^3/(2b+7)}{(b+5)(b+7)(b+9)}$	$\dfrac{12}{35}[1 - \dfrac{1}{2}(1 - \dfrac{\lambda_2}{\lambda_1})]$	$\dfrac{17}{117\,600} - \dfrac{17\epsilon}{352\,800}$
3	$b_{1:11}/a_3$	$\dfrac{3b^3/(2b+7)}{(b+5)^2(b+7)(b+9)}$	$\dfrac{3}{35}[1 + \dfrac{6}{5}(1 - \dfrac{\lambda_2}{\lambda_1})]$	$\dfrac{17}{705\,600}$
	a_k	$nkT\lambda_H{}^k$	$nkT\lambda_1{}^k$	$NnkT\lambda^k$

[a] The coefficients tabulated here are for the "retarded-motion expansion", a constitutive equation that expresses the stress tensor for flows in which the velocity is changing slowly in space and time (see ref 4, Chapters 8 and 9): $\tau =$ $-[b_1\gamma_{(1)} + b_2\gamma_{(2)} + b_{11}\{\gamma_{(1)}\cdot\gamma_{(1)}\} + b_3\gamma_{(3)} + b_{12}\{\gamma_{(1)}\cdot\gamma_{(2)} + \gamma_{(2)}\cdot\gamma_{(1)}\} + b_{1:11}(\gamma_{(1)}:\gamma_{(1)})\gamma_{(1)} + ...]$ in which $\gamma_{(1)} = \nabla v + (\nabla v)^\dagger$ and the higher order rate-of-strain tensors are defined by $\gamma_{(n+1)} = \dfrac{D}{Dt}\gamma_{(n)} - \{(\nabla v)^\dagger\cdot\gamma_{(n)} + \gamma_{(n)}\cdot\nabla v\}$. Note that $b_1 \equiv \eta_0$, $b_2 \equiv -\Psi_{1,0}/2$, and $b_{11} \equiv \Psi_{2,0}$ where the subscript zero designates zero-shear-rate properties; the D/Dt operator is the "substantial derivative". [b] The constants for the FENE dumbbell with no hydrodynamic interaction were obtained by R. C. Armstrong, 60, 724-728 (1974); the parameters λ_H and b are defined after eq 14. [c] The constants for the multibead rod with Rotne-Prager-Yamakawa hydrodynamic interaction were obtained by X. J. Fan, using R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, 14, 85-101 (1984). The time constants λ_1 and λ_2 are abbreviations for $\lambda_N(h,\xi^2)$ and $\lambda_N(2h,-\xi^2)$ in the Bird-Curtiss publication. For osculating beads the quantity $[1 - (\lambda_2/\lambda_1)]$ varies monotonically with the number of beads from -0.5000 for $N = 2$ to -0.0284 for $N = 6$ and from $+0.0102$ for $N = 7$ to $+0.3082$ for $N = 70$. [d] The constants for an undiluted system of interacting Kramers bead-rod chains are taken from C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, 74, 2016-2025, 2026-2033 (1981). The parameters N, λ, and ϵ are defined after eq 18.

tribution of molecular weights, this theory gives for the steady-state shear compliance $J_e^0 = \Psi_{1,0}/2\eta_0^2 \sim (\bar{M}_Z/\bar{M}_W)$,[4] whereas one experimental data correlation gives[32] an exponent of 3.7. The Doi–Edwards theory[25] gives an exponent of 9.

Uses of the Kinetic Theory Results

Most kinetic theories involve lengthy and tedious developments, and few people have the patience to work their way through them. However, as may be seen in the several examples cited above, the final results can often be cast in readily understandable form, and the constants that appear in the final constitutive equation usually have simple physical meanings. The kinetic theory results that are now being obtained can be used in a number of ways:

a. Kinetic theory provides constitutive equations for numerical solution to flow problems. The numerical solutions of nontrivial flow problems require long and expensive computational work.[33] Realistic flow problems often involve complex flow geometries with very unusual combinations of stretching and shearing flows. The constitutive equations obtained from kinetic theory probably have a better chance of success then do empirical equations, provided that sensible physical ideas are incorporated in the theory.

b. The constitutive equations generated by kinetic theory can often suggest useful forms for empirical constitutive equations. In the kinetic theory develop-

ment one is compelled to use rather simple molecular models and to make some mathematical and physical assumptions in the derivations. Nonetheless the constitutive equations produced by kinetic theory have suggested the kinds of kinematic tensors that should be used, the kind of factorization that may be profitable to explore in integral models, and the kinds of nonlinearities that might appear in differential models.

c. Kinetic theory has also provided the basis for interrelating various rheological properties and also for suggesting relations between rheological properties and optical properties (such as flow birefringence and light scattering) or transport properties (such as translational diffusivity).

d. Kinetic theory gives information about the molecular stretching and molecular orientation in flow fields, and this kind of information is of interest in polymer processing.

e. By studying the rheological consequences of various kinds of modeling, one can begin to get information about the structure-property relationships. For example, molecular theory predicts that steady elongational viscosity for dilute solutions should be a monotone function of the elongation rate[3] whereas the same quantity for polymer melts should go through a maximum and then decrease with elongation rate.[29] Also, a table given on pp 627–629 of ref 3 shows how the zero-shear-rate viscometric functions are affected by chain length, molecule stiffness, symmetry, location of side groups, and chain stretchability.

f. Kinetic theory also gives information about some of the constants and functions that appear in various

(32) M. Kotaka, *Macromolecules*, 17, 895-898 (1984).
(33) M. J. Crochet, A. R. Davies, and K. Walters, "Numerical Simulation of Non-Newtonian Flow"; Elsevier: Amsterdam, 1984.

continuum-mechanics expansions. As one example, we give in Table I the values of the constants in the retarded motion expansion (through third order) from several different molecular theories. For a wide range of models we find that the second- and third-order constants can be arranged in order of decreasing magnitude: $|b_2| > |b_{11}|$ (b_{11} changes sign for multibead rods), and $b_3 > b_{12} > b_{1:11}$. As another example, we point out the fact that for the multibead-rod model the kernel functions in a memory-integral expansion have been obtained.[34]

g. Kinetic theory calculations provide important background material which will be necessary in order to check the techniques of nonequilibrium Brownian dynamics that will be useful for probing the details of molecular motions in polymeric liquids.[35]

h. Kinetic theory can provide valuable information about the behavior of polymer blends. Most industrial polymers are polydisperse (they are mixtures of polymers of various molecular weights), and the kinetic theory of mixtures can show what the effect of polydispersity will be on various macroscopic properties.

i. The kinetic theory of polymers gives results from time to time that suggest experiments that need to be done. For example, according to the FENE dumbbell model there should be an overshoot in the mean-square end-to-end distance at the start up of a steady shear flow;[19] this suggests that one should do a light-scattering study of this flow system. The multibead–rod theory cited earlier suggests that there should be a change in the sign of the second normal-stress coefficient as one goes from short rods to long rods (see footnote c, in Table I); perhaps this sign change could be observed in the tilted-trough experiment.[36] Many molecular models lead to a relation between the normal stress coefficient Ψ_1 and the relaxation of the shear stress τ_{yx}, after the cessation of steady shear flow (see eq 12.4–33 of ref 3); this relation has not been sufficiently well tested for well-characterized fluids. In addition, Mochimaru's recent calculations[19] suggest that there should

be "velocity overshoot" in unsteady Couette flow.

Challenges for the Future

Considerably more work needs to be done in obtaining constitutive relations from kinetic theory; the evaluation of each new molecular model must include a fairly complete comparison with experimental data on material functions, but, as pointed out earlier, such data are in short supply for well-characterized fluids.

Much help will be obtained in the future from Brownian dynamics and molecular dynamics simulation techniques; such techniques will become more important with the widespread availability of supercomputers. The simulations should be very helpful in assessing some of the assumptions in kinetic theories, such as the "reptation" idea in undiluted polymers, and the "equilibration-in-momentum-space" assumption common to all dilute solution theories. These techniques should also be used to study nonhomogeneous flows, wall effects, differential migration separations, and molecular stretching in converging–diverging flows.

The various assumptions in all kinetic theories need to be challenged. For example, the widespread use of Stokes law expressions to describe polymer–solvent and polymer–polymer interactions needs to be investigated. One crucial question here is whether or not the Stokes law interactions can describe quantitatively various observed recoil phenomena.

The constitutive equations suggested by molecular theory need to be used in fluid dynamics calculations, particularly those that are relevant to polymer processing, rubber technology, lubricant behavior, and biomedical problems.[37,38]

(34) R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, 14, 85–101 (1984).

(35) P. J. Dotson, *J. Chem. Phys.*, 79, 5730–5731 (1983); Ph.D. Thesis, University of Wisconsin, 1984. H. H. Saab, R. B. Bird, X. J. Fan, and P. J. Dotson, University of Wisconsin Rheology Research Center, Report No. 97 (Nov 1984).

(36) M. Keentok, A. G. Georgescu, A. A. Sherwood, and R. I. Tanner, *J. Non-Newtonian Fluid Mech.*, 6, 303–324 (1980).

(37) J. R. A. Pearson, "Mechanics of Polymer Processing", Elsevier: London, 1985.

(38) R. I. Tanner, "Engineering Rheology", Oxford University Press: London, 1985.