Stresses in Concentrated Polymer Solutions: Part I. Shear Dependence of Viscosity

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A method is suggested for calculating stresses in sheared polymeric liquids. It synthesizes Kirkwood's correlation function techniques and Fixman's formulation for the stress tensor P. The dependence of P on powers of solute concentration, in the concentrated solution range, arises from a consideration of intermolecular forces. A non-Newtonian viscosity, characterized by only two parameters (low shear viscosity limit η_o and time constant λ), is derived from simple choices of functions which appear in the expression for P.

The task of formulating constitutive models for the mechanical response of viscoelastic liquids has occupied rheologists for many years. The goals of these efforts have been diverse, ranging from the need to predict non-Newtonian flow performance in processing equipment to the hope of elucidating mechanisms of molecular behavior.

Most engineering work has utilized continuum rheological models, because many of them describe nonlinear fluid phenomena in a fairly realistic and readily applied fashion (*1, 22, 23*). However, such models frequently lack a molecular interpretation and, however useful they may be for curve-fitting duty, are looked upon as essentially empirical by materials scientists.

On the other hand, molecular models are often too cumbersome, conceptually or mathematically, to be easily applied to practical flow problems. The goal of devising a molecular theory which will provide a simple but realistic relationship between stress and shear rate has not yet been reached. This work suggests another approach to the problem.

POLYMER SOLUTION THEORY

One of the most important sectors of rheological interest is that of polymers, their melts, and solutions. Most molecular studies have been concerned with either very dilute solutions or very concentrated solutions (or melts, which behave similarly). With regard to polymer-polymer forces, dilute-solution theory needs to consider only *intra*molecular forces, since the macromolecule is assumed to be surrounded by an infinite sea of solvent (*2, 6, 8, 12, 14* to *18, 24* to *29, 32, 36*). Methods of describing these system under theta conditions are well accepted and results are quite realistic (*5*). Current research involves efforts to eliminate the theta restriction (*6*), to improve certain other physical approximations made for the sake of tractability (*6, 27*), and to devise more satisfactory models of the polymer molecule itself (*9*).

The less well-defined systems of concentrated solutions have frequently been described as flowing networks composed of entangled polymer chains (*3, 19, 35*), and *inter*molecular polymer forces accommodated as junctions in the network. These concepts, however, lead to the introduction of such functions as a *junction lifetime* (*19*) or a *chain-breakage coefficient* (*35*) which have not been derived in detail.

Between the conceptual extremes of the isolated molecule and the rubberlike network lies the broad middle ground of moderately concentrated solutions. There seems to have been little effort directed specifically toward describing the flow of these important materials. Ferry has had some success in extending dilute solution theory, on an intuitive basis, directly to melts (*5*). The continuum model of Spriggs and Bird (*30*) is a nonlinear generalization of the mathematical structure of many dilute solution molecular models and seems to describe well the behavior of concentrated solutions.

INTERMOLECULAR FORCES FOR FLEXIBLE CHAINS

Basically, the problem is to find a method of treating the forces between distinct polymer chains in a flowing medium. Whereas *intra*molecular forces have been systematically described in dilute-solution theory, we find a near vacuum of results for predicting *inter*molecular forces. This is unfortunate, since the latter interactions are probably dominant in polymeric systems most commonly encountered.

Recently, Fixman has proposed a description of stresses in solutions of flexible linear polymers (*6*). The polymer model is the familiar pearl necklace chain. Each solute molecule is represented as a series of N identical segments which interact with other segments through spring forces, excluded-volume forces, and hydrodynamic forces. The solvent is represented as a continuous phase, creating frictional resistance to segmental motion. Fixman's Equation A16, rewritten with a change of notation, describes the total stress tensor **P** as

$$\mathbf{P} = \mathbf{P}_o + n\sum_{i}^{N} <\mathbf{R}_i{}^1\nabla_i \mathrm{U}> + \frac{1}{2}n^2 <\mathbf{r}\nabla_r V> \qquad (1)$$

where stresses due to the solvent and to externally imposed isotropic pressures are represented by $\mathbf{P}_o$. The number-concentration of polymer molecules is n; position of a segment relative to the center of mass of its own molecule is $\mathbf{R}_i{}^1$; the interaction potential between that segment and all other segments in solution is U; the position vector between two molecular centers is $\mathbf{r}$; and the net interaction potential between those two molecules is V. The relationship between position coordinates, illustrated in Figure 1, is

$$\mathbf{x}_i \equiv \mathbf{r}_m + \mathbf{R}_i{}^{(m)} \qquad (2a)$$

$$\mathbf{r}_m - \mathbf{r}_n \equiv \mathbf{r}_{mn}\ [= \mathbf{r} \text{ in Equation } (1)] \qquad (2b)$$

The averages <> are defined as

$$<\mathbf{R}_i{}^1\nabla_i U> \equiv \int \Psi\ (\{\mathbf{x}^M\})\ \mathbf{R}_i\nabla_i U\ (\{\mathbf{x}^M\})\ d\mathbf{x}^M \qquad (3a)$$

$$<\mathbf{r}\nabla_r V> \equiv \int g(\mathbf{r})\mathbf{r}\nabla_r V(\mathbf{r})\,d\mathbf{r} \qquad (3b)$$

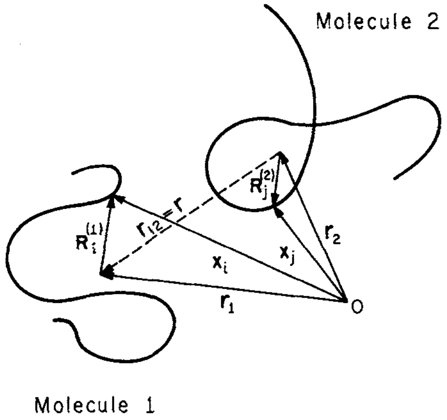

Fig. 1. Illustration of position coordinates referring to polymer molecules and segments.

where Ψ is a distribution function in the coordinate space of all M segments and $g(\mathbf{r})$ is a pair correlation function for intermolecular interactions (*9*).

Fixman's deviation of Equation (1) involved two physical approximations. First, $U(\mathbf{x}_1, \ldots \mathbf{x}_M)$ must be a pairwise additive potential $U = \frac{1}{2} \sum_{i \neq j}^{M} \sum^{M} u_{ij}(\mathbf{x}_i - \mathbf{x}_j)$.

Second, the kinetic energy of segmental motion relative to molecular center-of-mass motion is negligible:

$$||n\mathbf{ww}|| >> \left\| \sum_{i}^{M} <\delta(\mathbf{x} - \mathbf{x}_i)(\mathbf{v}_i - \mathbf{w})(\mathbf{v}_i - \mathbf{w})> \right\| \qquad (4)$$

where $\mathbf{w}(\mathbf{x})$ is the average polymer velocity and hence also macroscopic fluid velocity at point $\mathbf{x}$.

It is important to point out that Equation (1) does not represent simply an arbitrary series expansion of $\mathbf{P}$ in powers of n, but rather is developed directly from the equations of motion of solvent and solute, subject to the two aforementioned restrictions. Not surprisingly, it is reminiscent in form of the equations developed for stresses in a sheared pure fluid composed of simple molecules (*10, 11*). It also resembles the description of equilibrium pressure for imperfect gases—where the ∇V term gives the virial coefficients (*11*)—and for polymer solutions, where the ∇V term leads to osmotic pressure (*8*).

REDUCED FORMS

Equation (1) is very easily applied to dilute solutions. Then the ∇V is unimportant for two reasons: not only is n^2 very small, but $V(\mathbf{r})$ itself becomes negligible as $\mathbf{r}$ increases. Thus the force on the i^{th} segment is not a function of the positions of segments belonging to separated molecules, and $\nabla_i U(\{\mathbf{x}^M\})$ may be replaced by $\nabla_i U^o(\{\mathbf{x}^N\})$ or $-\mathbf{F}_i(\mathbf{R}_1{}^1, \ldots \mathbf{R}_N{}^1)$. Then we have the familiar reduced form

$$\mathbf{P} - \mathbf{P}_o = -n \sum_{i}^{N} <\mathbf{R}_i{}^1 \mathbf{F}_i> \qquad (5)$$

which has been frequently used (*15* to *18*, *26*, *32*, *36*), although obtained in different ways.

If polymer concentrations become very high (volume fraction $\geqq 0.1$), Equation (1) may be inadequate. The primary difficulty would be that U is no longer expected to be a pairwise additive. This would necessitate the use of averages taken over three-body cooperative interactions, with terms in n^3 becoming important. This would correspond to the presence of entanglements, and the form of Equation (1) would probably change considerably.

However, some experimental investigations give us reasonable hope that Equation (1) will be satisfactory for most purposes. They show that stress data for concentrated solutions, taken over wide ranges of temperature, shear rate, and concentration, may be reduced to master curves if a reducing factor of n^2 is used (*4*, *20*, *21*, *33*). This seems to correspond to the prediction of Equation (1), if the ∇V term is dominant.

With this motivation, then, we shall concern ourselves solely with the ∇V term. This may be inadequate by itself, since the ∇U term might also contribute importantly with a weight of n^2 in sufficiently concentrated solutions. If nothing else, the present plan should permit an estimate of the intermolecular forces in some intermediate range of concentration, where $\nabla_i U \approx -\mathbf{F}_i$. Thus we shall investigate another reduced form:

$$\mathbf{P} - \mathbf{P}_o \doteq \frac{1}{2} n^2 \int \mathbf{r} \nabla V(\mathbf{r}) g(\mathbf{r}) d\mathbf{r} \qquad (6)$$

INTERMOLECULAR POTENTIAL

Consider a single polymer molecule, whose segment distribution about its center of mass can be described by a probability density $\nu(\mathbf{R})$. The presence of another molecule at position $\mathbf{r}$ (where $\mathbf{r}$ is the vector between molecular centers) will lead to a repulsive force on each segment of the first molecule. The net force on this molecule, a sum over its segments at all $\mathbf{R}$, is assumed representable as the gradient of $V(\mathbf{r})$:

$$V(\mathbf{r}) = A \int \nu(\mathbf{R}) \nu(\mathbf{r} + \mathbf{R}) d\mathbf{R} \qquad (7)$$

This was a derived (not assumed) result of Fixman's equilibrium theory (*6*), which $A_{\text{eq.}} = \epsilon^{(2)} V_p{}^2$. Here, V_p is the partial molecular volume of polymer in solution, and $\epsilon^{(2)} \equiv d^2\epsilon/dv_p{}^2$ where ϵ is the free energy of mixing segments with solvent to an average volume fraction v_p. This interpretation of A, although an equilibrium concept, should be realistic for moderate shear rates. At higher shear rates, the use of $\epsilon^{(2)}$ could not be simply justified.

Equation (7) can be used if $\nu(\mathbf{R})$ is known as a function of concentration and shear rate. The concentration dependence has been discussed by Flory (*8*) and by Fixman (*7*). Shear effects on $\nu(\mathbf{R})$ seem to have been studied only in dilute solution (*25*, *36*).

PAIR CORRELATION FUNCTION

There exist several techniques for estimating $g(\mathbf{r})$ (*11*). We shall adopt that of Kirkwood and co-workers (*14*), which has been used to calculate the stresses in single-component systems composed of simple spherical molecules.* Their formalism should be equally applicable to systems of polymer molecules; thus we shall briefly review Kirkwood's theory here.

According to generalized Brownian motion concepts, a dynamical equation can be written for $f^{(2)}(\mathbf{p}_1, \mathbf{r}_1, \mathbf{p}_2, \mathbf{r}_2, t)$, a time-smoothed distribution function in the twelve-dimensional phase space of molecular pairs. This equation, involving the friction parameter ξ as a perturbation from equilibium, can be integrated over momentum coodinates $\mathbf{p}_i$ to give an equation of conservation for pair density, $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t)$. A change of variables $(\mathbf{r}_1, \mathbf{r}_2) \rightarrow (\mathbf{X}, \mathbf{r})$ and the introduction of the pair correlation function

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* The viscosity of liquid argon was calculated to be about 50% of the experimental value (*14*). A Lennard-Jones potential was used for $V(\mathbf{r})$.

$$g(\mathbf{X}, \mathbf{r}) \equiv \frac{n^{(2)}(\mathbf{X}, \mathbf{X}+\mathbf{r})}{n(\mathbf{X})n(\mathbf{X}+\mathbf{r})} \qquad (8)$$

produce the steady state dynamical equation for g, which, if **X** dependence is unimportant, is

$$\nabla \cdot \{\nabla g - g\nabla \ln g_o\} = \left(\frac{\xi}{2kT}\right) \mathbf{r} \cdot \mathbf{G} \cdot \nabla g \qquad (9)$$

where **G** is a shear rate tensor* and $g_o = g_o(r)$ is the zero shear (equilibrium) form of g usually termed the radial distribution function. The shear dependence of $g(\mathbf{r})$ is assumed describable by a series perturbation with the parameter $\xi\mathbf{G}$:

$$g \doteq g_o\left[1 + \frac{\xi}{2kT}(\mathbf{e}_r \cdot \mathbf{G} \cdot \mathbf{e}_r)\psi(r) + \ldots\right]$$
$$= g_o\left[1 + \left(\frac{\xi\gamma}{kT}\right)(\sin\theta\cos\theta\cos\phi)\psi(r) + O(\xi^2\gamma^2)\right] \qquad (10)$$

This series is truncated after the linear term in γ because of the smallness of $(\xi\gamma)$ and to be consistent with the many linear approximations inherent in Equation (9). Combination of Equations (9) and (10) yields

$$\frac{d}{dr}\left[r^2 g_o(r)\frac{d\psi(r)}{dr}\right] - 6g_o(r)\psi(r) = r^3\frac{dg_o(r)}{dr} \qquad (11)$$

whose solution is essential to evaluation of Equation (6), rewritten as

$$\mathbf{P} - \mathbf{P}_o \doteq \frac{1}{2}n^2\int[\mathbf{r}\nabla V]g_o\,d\mathbf{r}$$
$$+ \frac{1}{2}n^2\left(\frac{\xi\gamma}{kT}\right)\int[\mathbf{r}\nabla V]g_o\psi\sin\theta\cos\theta\cos\phi\,d\mathbf{r} \qquad (12)$$

Thus equilibrium information $g_o(r)$ is necessary to complete the estimate of **P**. This can be obtained experimentally, for example by light scattering, or from knowledge of $V(r)$ (*8, 11*).

The fact that $g(\mathbf{r})$ is calculated only as far as a linear term in γ does not rule out nonlinear relationships $\mathbf{P}(\gamma)$. This is seen in Equation (12), where $V(\mathbf{r})$ is a function of γ because the polymer segment distribution is undoubtedly influenced by shear. However, nonlinearities in γ are not important in Equation (10) because the *combined* perturbation parameter $\xi\gamma$ is small. Thus Equation (12) seems capable of describing non-Newtonian viscosity and normal stress effects, although probably not to extreme values of γ.

A SIMPLE ILLUSTRATION

We shall now demonstrate the use of Equation (12) with a viscosity calculation, while introducing the simplest possible functions for $\nu(\mathbf{R})$ and $g_o(r)$. For high polymers, the dilute solution range of concentration ($g_o \to 1$) may be exceeded at concentrations well under 1%. As n increases, the molecules coil more compactly to avoid the segments of nearby molecules, and g_o approaches delta function behavior (*7*). Eventually, intramolecular repulsive forces limit this tendency, and segments of separate molecules begin to intermingle. At high concentrations, each segment is subject to a nearly random distribution of intersegmental forces which tend to cancel each other; consequently $g_o(r)$ again approaches unity (*7, 8*). We shall try to represent a solution of rather high concentration by the approximation

$$g_o(r) \doteq 1 \qquad (13)$$

This, in turn, results in a great simplification in Equation (11), which becomes

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = 6\psi \qquad (14)$$

A general solution for $\psi(r)$ is

$$\psi = C_1r^2 + \frac{C_2}{r^3} \qquad (15)$$

but since $g(r)$ must remain finite as $r \to \infty$ we set $C_1 = 0$. At this point, Equation (12) has become

$$\mathbf{P} - \mathbf{P}_o \doteq -\mathbf{I}\left[\frac{1}{2}n^2\int V d\mathbf{r}\right]$$
$$+ \frac{1}{2}\left(\frac{n^2\xi C_2}{kT}\right)\gamma\int(\mathbf{r}\nabla V)\frac{\sin\theta\cos\theta\cos\phi}{r^3}d\mathbf{r} \qquad (16)$$

where **I** is the unit tensor.

Next, $V(\mathbf{r})$ must be obtained from $\nu(\mathbf{R})$, which is shear-dependent. Our choice for the function ν, expressed in terms of a dimensionless shear rate m, is

$$\nu(\mathbf{R}) = \nu(X, Y, Z)$$
$$= \mathcal{N}e^{-B[(X-mZ)^2 + (1+m^2)Y^2 + (1+m^2)Z^2]} \qquad (17)$$

$$m = \lambda\gamma \qquad (18)$$

$$B = \frac{B_o}{1+m^2} \qquad (19)$$

$$\mathcal{N} = \frac{(B_o/\pi)^{3/2}}{\sqrt{1+m^2}} \qquad (20)$$

The factor $\mathcal{N}$ normalizes the probability distribution $\int\nu(\mathbf{R})d\mathbf{R} = 1$. Equation (17) is, of course, not derived and is thus simply a built-in part of the model. (Note that the possibility of entanglements is ignored.)

However, the use of Equation (17) is motivated by more than the hope for mathematical tractability. Physically, this $\nu(\mathbf{R})$ describes a shear-deformable molecule. Its particular dependence on γ is a low-order analog of the γ dependence of the exact segment distribution function for one molecule in a dilute theta solution (*36*). When $m = 0$, Equation (17) reduces to the simple Gaussian distribution which is usually used to characterize equilibrium in theta solutions and melts (*8*).

Substitution of Equation (17) into Equation (7) leads to the intermolecular potential

$$V(\mathbf{r}) = \mathcal{M}e^{-\frac{B}{2}[x^2 + (1+m^2)y^2 + (1+4m^2)z^2 - 2mxz]} \qquad (21)$$

$$\mathcal{M} = \frac{\mathcal{M}_o}{\sqrt{1+m^2}} = \left(\frac{B_o}{2\pi}\right)^{3/2}\frac{A}{\sqrt{1+m^2}} \qquad (22)$$

with $\mathcal{M}_o$ independent of shear rate.

Now, to compute viscosity, we must find the symmetrized shear component of **P** from Equation (12):

$$P_{xz}^{(s)} = \frac{1}{2}(P_{xz} + P_{zx}) = \eta_s\gamma - \frac{1}{4}\left(\frac{n^2\xi C_2}{kT}\right)\gamma\int\int\int$$
$$\left[x\frac{\partial V}{\partial z} + z\frac{\partial V}{\partial x}\right]\frac{xz}{(x^2+y^2+z^2)^{5/2}}dxdydz \qquad (23)$$

Taking $V(\mathbf{r})$ from Equation (21), we obtain the viscosity η:

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* $\mathbf{G} \equiv \nabla\mathbf{v} + (\nabla\mathbf{v})^T = \gamma\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ in Cartesian coordinates.

$$\eta = \frac{P_{xz}^{(s)}}{\gamma} = \eta_s - \left(\frac{n^2 \xi C_2 B \mathcal{M}}{2kT}\right) \int\int\int \mathcal{I}(\mathbf{r}; m)\, e^{-\frac{B}{2}[(x-mz)^2 + (1+m^2)y^2 + (1+3m^2)z^2]}\, dxdydz \quad (24)$$

$$\mathcal{I}\,(\mathbf{r}; m) = [2(1 + 2m^2)x^2z^2 - mx^3z - mxz^3]/(x^2 + y^2 + z^2)^{5/2} \quad (25)$$

The integral is evaluated in the Appendix. Results may be expressed in terms of a dimensionless parameter η_r:

$$\eta_r \equiv \frac{\eta - \eta_s}{\eta_o - \eta_s} = \left[\frac{15}{4} \cdot \frac{2kT}{\pi n^2 \xi C_2 \mathcal{M}_o}\right] (\eta - \eta_s) \quad (26)^*$$

$$\eta_r = \frac{15}{4} a \{b + c + d(e + c)F - 2dcE\} \quad (27)$$

$$a = \frac{1}{m^2(1 + 4m^2)(1 + 3m^2)^2 \sqrt{1 + m^2}} \quad (28)$$

$$b = -1 - \frac{10}{3} m^2 + 9m^4 + 30m^6 + 16m^8 \quad (29)$$

$$c = \frac{m}{\sqrt{1 + 4m^2}} \left(1 + 4m^2 + \frac{13}{3} m^4 + 20m^6 + 32m^8\right) \quad (30)$$

$$d = \left(\frac{1 + m^2}{2m\sqrt{1 + 4m^2}}\right)^{1/2} \quad (31)$$

$$e = (1 + m^2)\left(1 + \frac{7}{3} m^2 - 10m^4 - 16m^6\right) \quad (32)$$

The functions $F = F(\Phi, \kappa)$ and $E = E(\Phi, \kappa)$ are elliptic integrals of the first and second kinds, respectively (*13*), with

$$\kappa^2 = \frac{1}{2} + \frac{m^3}{(1 + m^2)\sqrt{1 + 4m^2}} \quad (33)$$

$$\sin^2\Phi = \frac{2m}{1 + 3m^2} [(1 + 2m^2)\sqrt{1 + 4m^2} - m(1 + 4m^2)] \quad (34)$$

From this we find: $\frac{1}{2} \leqq \kappa^2 < 1$ and $0 \leqq \sin^2\Phi < 1$.

In Equations (27) to (34) and hereafter we use

$$m = \sqrt{\lambda^2 \gamma^2} \quad (18a)$$

which cannot change sign. This is a consequence of the transformations detailed in the Appendix, and is not an arbitrary substitution for the purpose of desirable invariance.

The complicated behavior of Equations (27) to (34) defies inspectional analysis. Furthermore, numerical estimates of $\eta_r(m)$ are difficult, because many significant figures must be retained within the curvy brackets of Equation (27). However, one interesting point can be made without explicit calculation: odd powers of shear rate appear in Equations (30), (31), (33), and (34). This does not violate the symmetry arguments usually voiced in opposition, because m cannot change sign when the shear reverses direction [Equation (18*a*).] This result may tend to justify the practice, long in disrepute, of curve-fitting viscosity data with functions containing odd powers of γ (*5*).

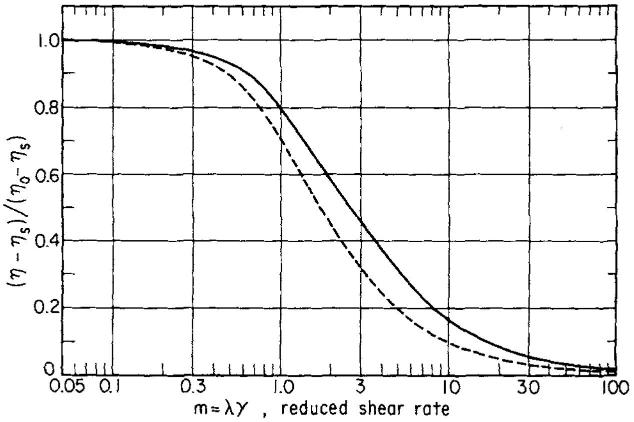

Fig. 2. Non-Newtonian viscosity η_r predicted by Equations (27) to (34). η_o-η_s is the low-shear limit, λ is a time constant, and γ is the shear rate. Dotted line represents $(1+m^2)^{-1/2}$, a much simpler function with very similar properties, and could be used equally well to represent non-Newtonian flow.

The full shear-rate dependence of η_r is displayed in Figure 2, and is seen to be qualitatively very much like the non-Newtonian flow curve exhibited by concentrated polymer solutions. Two limiting forms of η_r are of special interest:

$$m \rightarrow 0: \quad \eta_r = 1 - \frac{9}{14} m^2 \ldots \quad (35)$$

$$m \rightarrow \infty: \quad \eta_r = \frac{5}{3}\left(\frac{1}{m}\right) \quad (36)$$

It may seem surprising that no term of order m appears in Equation (35), since such terms are evident in Equations (30), (31), and (34). However, the coefficient of m vanishes identically. The high-shear behavior ($\sim m^{-1}$) might be compared with the dilute-solution theories of Rouse ($\eta' \sim \bar{m}^{-1/2}$) and of Zimm ($\eta' \sim \bar{m}^{-1/3}$) for experiments with small-amplitude oscillatory shear at reduced frequency $\bar{m} = \lambda\omega$. A continuum formulation which can incorporate the Rouse and Zimm relaxation spectra will make analogous predictions in steady shear (*30*).

APPLICATIONS AND COMPARISONS

The complicated shear dependence of the present model removes it from the realm of engineering utility. However, we find that a much simpler function will behave in much the same way. In Figure 2, we plot also $1/\sqrt{1 + m^2}$ and observe that it differs from η_r principally in being displaced along the m axis.† This suggests that many non-Newtonian flow problems could be solved by using the model

$$\eta_r = \frac{1}{\sqrt{1 + \sigma^2 m^2}} \quad (37a)$$

$$m_\sigma = \sigma m; \quad \sigma \cong 0.6 \quad (37b)$$

with accuracy comparable to that obtained with Equations (26) to (34). At least we could hope that the equation of motion would be integrable analytically if Equation (37) were used. As far as the writer knows, this simple empirical model has never before been given a theoretical justification.

Finally, some remarks about data comparisons are in order. It is well known (*31*) that without great difficulty

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* Here C_2 absorbs the minus sign which precedes the integral in Equation (24).

† We note that $1/\sqrt{1 + m^2}$ appears as one factor in $\eta_r(m)$ [see Equation (28)]. It seems ironic that the other factors and terms in η_r combine to produce a simple effect as an m shift.

one can select viscosity data to make a favorable comparison with almost any model. Partly for this very reason, we shall omit such a demonstration in the present case. Furthermore, we admit that the high-shear prediction of $\eta_r \sim m^{-1}$ will never be matched by real fluids. (This occurs here because the intermolecular contribution to shear stress reaches a plateau value which cannot be exceeded.) Such a prediction is a consequence of pushing the one-time-constant model beyond the bounds of its physical foundations, and of ignoring the *intra*molecular contributions which will become important at high shear. We may, perhaps, consider $\eta_{r\infty} \sim m^{-1}$ to represent a limiting case which may only be approached by extremely non-Newtonian liquids in the power law region of shear rates. However, the $\eta(m)$ behavior at lower shear is sufficiently realistic to describe a variety of materials, particularly solutions of monodisperse polymers.

SUMMARY

The foregoing exposition is intended to suggest a somewhat different approach to the description of stresses in flowing polymer solutions. Emphasis is placed on the importance of an *inter*molecular force contribution to the total stress, a factor treated heretofore solely through the concepts of network elasticity. The present formulation synthesizes Kirkwood's perturbation of the pair correlation function, and Fixman's derivation of a stress representation, and extends their application to nonlinear flow behavior. Combined limitations of all steps suggest that high shear-rate behavior and extremely high concentration effects (for example, physical entanglements between polymer molecules) may not fit within this framework.

The theory is illustrated by choosing physically plausible and mathematically tractable expressions for the intermolecular radial distribution function and the intramolecular segment density probability. Viscosity predictions in closed form show rather realistic non-Newtonian characteristics, with only two parameters: a low-shear limit

$$\eta_o = \frac{n^2 A B_o^{3/2} \xi C_2}{15\sqrt{2\pi}\, kT} \tag{38}$$

and a time constant λ. We note that several unspecified constants encountered during the development (ξ, C_2, B_o, A) are contained in η_o and apparently cannot be evaluated separately from flow data alone.

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NOTATION

A = undetermined constant relating intermolecular potential to segment distribution ($A_{\text{eq.}} = \epsilon^{(2)} V_p^{\,2}$), Equation (7), (g.)(cm.^{5})/sec.^{2}
$B(m)$ = scale factor related to molecular size, used to characterize the segment distribution, Equation (17); [$B_o = B(0)$], cm.$^{-2}$
C_2 = undetermined integration constant, cm.^{5}
$\mathbf{F}_i$ = force exerted on i^{th} polymer segment in dilute solution, (g.)(cm.)/sec.^{2}
g = pair correlation function (g_o = radial distribution function)
$\mathbf{G}$ = shear rate tensor (γ = magnitude of shear rate in simple shear flow), sec.$^{-1}$
k = Boltzmann constant = 1.38×10^{-6}, (g.)(sq. cm.)/(sec.^{2})(deg.^{1})
m = $\lambda\gamma$ or $\sqrt{\overline{\lambda^2\gamma^2}}$, dimensionless shear rate
M = nN, number density of polymer segments in solution, cm.$^{-3}$
$\mathcal{M}(m)$ = characterizes intermolecular potential corresponding to a specific choice of $\nu(\mathbf{R})$, Equation (22) [$\mathcal{M}_o = \mathcal{M}(0)$], (g.)(sq. cm.)/sec.^{2}
n = number density of polymer molecules, cm.$^{-3}$
N = number of statistical segments in each polymer molecule
$\mathcal{N}$ = normalization parameter for $\nu(\mathbf{R})$, Equation (20), cm.$^{-3}$
$\mathbf{P}_m, \mathbf{r}_m$ = momentum and position coordinates of polymer molecule m
$\mathbf{P}, P_{ij}$ = total stress tensor and its ij component, (g.)(cm.)/sec.^{2}
$\mathbf{r}$ = $\mathbf{r}_m - \mathbf{r}_n$, vector between centers of two polymer molecules, cm.
$\mathbf{R}$ = position with respect to center of a polymer chain, cm.
$\mathbf{R}_i^1$ = position of the i^{th} sement, referred to the center of the chain to which it belongs, cm.
s = transformation parameter, Equation (A-4)
T = absolute temperature, deg.$^{-1}$
u_{ij} = potential energy between two polymer segments, g./(sq. cm.)(sec.^{2})
U = $\frac{1}{2}\sum\sum_{i \neq j} u_{ij}$, potential of mean force due to presence of all segments, (g.)(sq. cm.)/sec.^{2}
$\mathbf{v}_i$ = velocity of i^{th} segment, cm./sec.
v_p = volume fraction of polymer in solution
V_p = partial molecular volume of polymer, cc.
$V(\mathbf{r})$ = intermolecular potential energy, Equation (7), (g.)(sq. cm.)/sec.^{2}
$\mathbf{w}$ = average velocity of polymer = macroscopic fluid velocity, cm./sec.
x,y,z = components of $\mathbf{r}$, cm.
$\mathbf{x}_i$ = position of i^{th} segment, referred to arbitrary origin, cm.

Greek Letters

$\alpha_x, \alpha_y, \alpha_z$ = functions of shear rate, Equation (A-7)
β = $\cos\theta$
δ = variable of polar integration, Equation (A22) ($\delta_1 = \delta$ at $\beta = 1$)
$\delta(x)$ = Dirac delta function, cm.$^{-3}$
ϵ = free energy density of mixing polymer segments with solvent, g./(cm.)(sec.^{2})
$\eta(m)$ = viscosity [$\eta_o = \eta(0)$]; (g.)(cm.)/sec.
η_r = $(\eta - \eta_s)/(\eta_o - \eta_s)$
θ = polar coordinate, rad.
κ^2 = parameter of elliptic integrals, Equation (A26)
λ = time constant for polymer chain response, sec.
ν = probability density for distribution of segments about their own molecule, cm.$^{-3}$
ξ = friction coefficient between polymer molecules (*not* simply related to a monomeric friction factor), g./sec.
π = 3.14 . . . . .
σ = m shift factor, needed to superpose $1/\sqrt{1 + \sigma^2 m^2}$ with the theoretical η_r
ϕ = azimuthal coordinate, rad.
Φ = $\sin^{-1} \delta_i$ = amplitude of elliptic integrals, Equation (A25)
$\psi(r)$ = range-dependent factor in g/g_o perturbation, Equation (10)
Ψ = distribution function in coordinate space of all segments, cm.$^{-3M}$
ω = angular frequency of oscillatory simple shear, rad./sec.$^{-1}$

LITERATURE CITED

1. Bird, R. B., *Can. J. Chem. Eng.*, **43**, 161 (1965).
2. Bueche, F., *J. Chem. Phys.*, **22**, 603 (1954).
3. Chömpff, A. J., Ph.D. thesis, Tech. Hogeschool Delft, Nederland (1965).
4. DeWitt, T. W., H. Markovitz, F. J. Padden, and L. J. Zapas, *J. Colloid Sci.*, **10**, 174 (1955).
5. Ferry, J. D., "Viscoelastic Properties of Polymers," Wiley, New York (1961).
6. Fixman, M., *J. Chem. Phys.*, **42**, 3831 (1965).
7. *Ibid.*, **35**, 889 (1961).
8. Flory, P., "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y. (1953).
9. Harris, R., and J. E. Hearst, *J. Chem. Phys.*, **44**, 2595 (1966).
10. Hill, T., "Statistical Mechanics," McGraw-Hill, New York (1956).
11. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
12. Irving, J. H., and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 817 (1950).
13. Jahnke, J. H., and F. Emde, "Tables of Functions," 4 ed., Dover, New York (1945).
14. Kirkwood, J. G., F. P. Buff, and M. S. Green, *J. Chem. Phys.*, **17**, 988 (1949).
15. Kirkwood, J. G., and R. J. Plock, *ibid.*, **24**, 665 (1956).
16. Kirkwood, J. G., and J. Riseman, *ibid.*, **16**, 565 (1948).
17. Kotaka, T., *ibid.*, **30**, 1566 (1959).
18. Kramers, H. A., *ibid.*, **14**, 415 (1946).
19. Lodge, A. S., "Elastic Liquids," Academic Press, New York, (1964); *Trans. Faraday Soc.*, **52**, 120 (1956); Soc. Rheol., Cleveland meeting (1965).
20. Markovitz, H., and D. Brown, *Trans. Soc. Rheol.*, **7**, 137 (1963).
21. Markowitz, H., and B. Williamson, *ibid.*, **1**, 25 (1957).
22. Matsuhisa, Seikichi, and R. B. Bird, *A.I.Ch.E. J.*, **11**, 588 (1965).
23. Oldroyd, J. G., *Proc. Roy. Soc.* (*London*), **A245**, 278 (1958).
24. Pao, Y., *J. Polymer Sci.*, **61**, 413 (1962).
25. Peterlin, A., *J. Chem. Phys.*, **33**, 1799 (1960).
26. Prager, S., *Trans. Soc. Rheol.*, **1**, 53 (1957).
27. Pyun, C. W., and M. Fixman, *J. Chem. Phys.*, **42**, 3838 (1965).
28. Rouse, P., *ibid.*, **21**, 1272 (1953).
29. Scheraga, H. A., *ibid.*, **23**, 1526 (1955).
30. Spriggs, T. W., and R. B. Bird, *Ind. Eng. Chem. Fundamentals*, **4**, 182 (1965).
31. Spriggs, T. W., J. D. Huppler, and R. B. Bird, *Trans. Soc. Rheol.*, **10**, to be published.
32. Williams, M. C., *J. Chem. Phys.*, **42**, 2988 (1964); **43**, 4542 (1965).
33. ———, *A.I.Ch.E. J.*, **11**, 467 (1965).
34. ———, Ph.D. thesis, Univ. Wisconsin, Madison (1964).
35. Yamamoto, M., *Phys. Soc. Japan*, **11**, 413 (1956); **12**, 1148 (1957); **13**, 1200 (1958).
36. Zimm, B. H., *J. Chem. Phys.*, **24**, 269 (1956).

APPENDIX

The integral in Equations (24) and (25) may be evaluated after a unitary transformation of coordinates $(x, y, z) \rightarrow (\bar{x}, \bar{y}, \bar{z})$:

$$x = \frac{\bar{x} - s\bar{z}}{\sqrt{1 + s^2}} \tag{A1}$$

$$y = \bar{y} \tag{A2}$$

$$z = \frac{s\bar{x} + \bar{z}}{\sqrt{1 + s^2}} \tag{A3}$$

where

$$s = -2m - \sqrt{1 + 4m^2} \tag{A4}$$

This permits the exponent in Equation (24) to appear as a diagonalized quadratic form and the denominator of J to remain unchanged. Hence, returning to the original notation, we can write (after some algebra)

$$\eta_r = \{[40]J^{40} + [04]J^{04} + [22]J^{22}\} \frac{1}{\sqrt{1 + m^2}} \tag{A5}$$

where the integrals are

$$J^{ij} = \iiint \frac{x^i z^j}{(x^2 + y^2 + z^2)^{5/2}} e^{-\frac{B}{2}(\alpha_x x^2 + \alpha_y y^2 + \alpha_z z^2)} dxdydz \tag{A6}$$

with

$$\alpha_x = 1 + 2m^2 + m\sqrt{1 + 4m^2} \tag{A7}$$

$$\alpha_y = 1 + m^2 \tag{A8}$$

$$\alpha_z = 1 + 2m^2 - m\sqrt{1 + 4m^2} \tag{A9}$$

The coefficients in Equation (A5) are

$$[40] = \frac{1 + 2m^2 + m\sqrt{1 + 4m^2}}{2(1 + 4m^2)} \tag{A10}$$

$$[04] = \frac{1 + 2m^2 - m\sqrt{1 + 4m^2}}{2(1 + 4m^2)} \tag{A11}$$

$$[22] = -\frac{(1 + 2m^2)(1 - 8m^2)}{(1 + 4m^2)} \tag{A12}$$

Integrals such as J^{13} and J^{31}, which should also appear in Equation (A5), are not displayed, because they vanish for reasons of symmetry.

To perform the necessary integrations, we rewrite Equation (A6) in spherical coordinates:

$$J^{ij} = \iiint r \sin^{i+1}\theta \cos^j\theta \cos^i\phi \, e^{-\frac{B}{2} r^2 h(\theta,\phi)} dr d\theta d\phi \tag{A13}$$

where

$$h = \alpha_x \sin^2\theta \cos^2\phi + \alpha_y \sin^2\theta \sin^2\phi + \alpha_z \cos^2\theta \tag{A14}$$

We may immediately integrate over r:

$$J^{ij} = \frac{1}{B} \int_0^{\pi} \sin^{i+1}\theta \, \cos^j\theta d\theta \int_0^{2\pi} \frac{\cos^i\phi}{h(\theta, \phi)} d\phi \tag{A15}$$

The ϕ integrals may be written in terms of the double angle ψ:

$$\frac{1}{2^{i/2}} \int_0^{2\pi} \frac{(1 + \cos\psi)^{i/2}}{S + P\cos\psi} d\psi \tag{A16}$$

where

$$S(\theta) = \left(\frac{\alpha_x + \alpha_y}{2}\right) + \left[\alpha_z - \left(\frac{\alpha_x + \alpha_y}{2}\right)\right] \cos^2\theta \tag{A17}$$

$$P(\theta) = \left(\frac{\alpha_x - \alpha_y}{2}\right) \sin^2\theta \tag{A18}$$

A contour integration, or an appeal to a good table of integrals, is needed to evaluate Equation (A16). This still leaves the θ integral, which we rewrite in terms of the new variable $\beta = \cos\theta$:

$$J^{40} = \frac{\pi}{2B} \int_{-1}^{1} (1 - \beta^2)^2 \left[1 - \left(\frac{S - P}{P}\right) + \right.$$

$$\left(\frac{S-P}{P}\right)\sqrt{\frac{S-P}{S+P}}\,\Bigg]\frac{d\beta}{P} \qquad (A19)$$

$$J^{04} = \frac{2\pi}{B}\int_{-1}^{1}\beta^4\frac{d\beta}{\sqrt{(S+P)(S-P)}} \qquad (A20)$$

$$J^{22} = \frac{\pi}{B}\int_{-1}^{1}\beta^2(1-\beta^2)\left[1-\sqrt{\frac{S-P}{S+P}}\right]\frac{d\beta}{P} \qquad (A21)$$

The terms involving square roots can be expressed as elliptic integrals (*13*) of the first (F) and second (E) kind. Thus, if we substitute

$$\delta^2 = \left(\frac{\alpha_x-\alpha_z}{\alpha_x}\right)\beta^2 \qquad (A22)$$

into Equations ($A19$) to ($A21$), the results appear in terms of polynomials and

$$F(\Phi,\kappa) = \int_{o}^{\delta_1}\frac{d\delta}{\sqrt{1-\kappa^2\delta^2}\sqrt{1-\delta^2}} \qquad (A23)$$

$$E(\Phi,\kappa) = \int_{o}^{\delta_1}\frac{\sqrt{1-\kappa^2\delta^2}}{\sqrt{1-\delta^2}}\,d\delta \qquad (A24)$$

where

$$\delta_1 = \sin\Phi = \left(\frac{\alpha_x-\alpha_z}{\alpha_x}\right)^{1/2} \qquad (A25)$$

$$\kappa^2 = \frac{\alpha_x}{\alpha_y}\left(\frac{\alpha_z-\alpha_y}{\alpha_z-\alpha_x}\right) \qquad (A26)$$

The tedious translation into explicit functions of m and the subsequent regrouping are omitted here. Results are displayed in Equations (27) to (34).

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Slip Velocity of Particulate Solids in Vertical Tubes

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An equation using only easily determined physical properties of particles has been developed for calculating the slip velocity of nonspherical particulate solids falling in fluid media in the intermediate flow range where neither the Stokes nor Newton law applies. The variation in Reynolds numbers covered by this work ranged from 12 to 460. Slip velocities calculated from the equation differed from experimental data by an average deviation of only 3.7% when solids of a wide range of diameters (156 to 1,247 microns), densities (71 to 475 lb./cu. ft.), surface shape factors (0.40 to 0.97), and gases of a wide density range (0.01 to 0.31 lb./cu. ft.) were utilized. Thirty-eight different gas-solid systems were studied.

In any system where solids are to fall through or are to be lifted by fluids a knowledge of the slip velocity of the solids is of great importance. At present there is a definite lack of experimental data in the literature for fluid-solid systems. The present work (*2*) in the intermediate or transition region between where the Stokes and Newton laws apply has been carried out to develop an accurate equation for slip velocity calculations for both spherical and nonspherical particles.

THEORY

The slip velocity of a single body falling in a fluid is defined as the constant equilibrium velocity attained by the body when the resistance offered by the viscous medium increases to the point where it is equal to the gravitational acceleration force. If the fluid is also stationary and infinite, the slip velocity equals the terminal velocity.

It has been demonstrated experimentally (*4*) that the resistance φ of a particle in motion involves four quantities: the surface area of the particle A_p, its terminal velocity u_t, and the viscosity μ_f and density ρ_f of the medium through which the particle is flowing. The relationship involved may be expressed by the following equation:

$$\varphi = k_1\,(A_p)^a(u_t)^b(\rho_f)^c(\mu_f)^d \qquad (1)$$

It should be noted that the area used here is the actual surface area of the particle rather than the area of the particle projected on a plane perpendicular to the direction of flow as used by several previous investigators. The actual area was chosen as it is much more readily determined experimentally.

On applying dimensional analysis and substituting the fundamental units of mass M, length L, and time T, this can be expressed as

$$\frac{ML}{T^2} = k_1\,(L^2)^a\left(\frac{L}{T}\right)^b\left(\frac{M}{L^3}\right)^c\left(\frac{M}{LT}\right)^d \qquad (1a)$$

Equating indices of corresponding terms, since the equation must be dimensionally correct, solving for b, and substituting in Equation (1), one obtains

$$\varphi = k_1\,(A_p)^{\frac{b}{2}}(u_t)^b(\rho_f)^{b-1}(\mu_f)^{2-b} \qquad (2)$$

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