

Bead-Spring Macromolecules that Perturb the Solvent

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Synopsis

A dispersion force based interaction between the solvent and the beads of a bead-spring model macromolecule is used to couple the motion of the solvent and polymer in dilute solution flows. The polymer exerts a force on the solvent equal and opposite to the force that the solvent exerts on it. The friction coefficient approximation of the Rouse-Zimm theories is eliminated. Both the solvent and polymer are subject to ensemble averaging over their respective phase space. A constitutive equation for the polymer stress is presented. By appropriate selection of the interaction potential between the solvent and the polymer, any normal stress difference can be predicted.

INTRODUCTION

Bead-spring model macromolecules, both free-draining¹ and non-free-draining,² are often used to predict the rheological behavior of dilute polymer solutions. The analysis using these models requires knowledge of the flow field acting on the bead-spring assemblies. However, the flow field is part of the information sought when using these models. Problems in which knowledge of the solution is needed to solve the problem often lead to iterative solution techniques in which the answer is guessed and used as an input to produce a (hopefully) improved estimate. In our case, this procedure requires that the velocity field be computed using the polymer stress field and vice versa until a self-consistent velocity field is obtained.³ Although this is purely a mathematical technique, and should be independent of the equations being solved, it has drawn attention to the fact that both the free-draining and the non-free-draining models possess no mechanism by which the solvent can feel the polymer stress field.

Lodge⁴ has pointed to the consequences of using such models to compute the free recovery of a liquid after it has undergone a specified flow history. He has indicated that the models may be useful as "stress calculators," but should not be considered to yield constitutive equations. Lodge has suggested a reexamination of these mean field models in an effort to retain a mechanism by which the solvent can feel the polymer stress. This article presents one way of retaining such a mechanism.

Kinetic theory models of polymer solutions that do not neglect the force of the beads of the macromolecular model on the solvent do exist. These are the most general models in which both the solvent and the polymer are not treated as a continuum but are both subject to ensemble averaging. These phase space kinetic theories are exhaustively presented in Bird et al.⁵ Unfortunately, such theories are intractable without the adoption of several assumptions. It is these

assumptions that have reduced the general theories to those of Rouse and Zimm and have simultaneously removed any means by which the solvent can feel the polymer stress.

The friction coefficient approximation, described in Bird et al., leads to the modeling of the hydrodynamic force of the solvent on a bead of the polymer chain as being proportional to the velocity of the bead relative to the bulk flow velocity. The solvent is thereby treated as a continuum with the basis for the friction coefficient being Stokes drag law. This assumption is crucial and paves the way for a host of others that then produce a tractable model. It is the friction coefficient approximation that requires modification if we are to retain a mechanism by which the solvent feels the polymer.

Curtiss⁶ has resurrected the time-smoothing statistical mechanics treatment of Kirkwood. In doing so he reconsiders the Stokes law type models and thereby modifies the expression for the hydrodynamic force that involves the pair configuration space distribution. However, the friction coefficient approximation is retained in his analysis. The effect of time smoothing does not modify the expressions involving the single-molecule distributions. We consider only single-molecule distributions.

In the following analysis, we eliminate the friction coefficient approximation by considering the interaction between the solvent and the polymer to be the consequence of dispersion forces. The resulting complication is that we need to consider ensemble averages over the solvent as well as the polymer. The resulting benefit is that the polymer exerts a force equal and opposite to that which the solvent exerts on it. We consider a system composed of a single solvent molecule interacting with a single polymer molecule. The analysis addresses the system with two conditional probability distributions.

DEVELOPMENT

The Solvent

The solvent molecule is considered to be a featureless point mass whose state is described by the single-molecule phase space distribution f_s . The conservation of all phase points for the solvent is maintained by

$$\frac{\partial f_s}{\partial t} = -\frac{\partial}{\partial \mathbf{r}_s} \cdot (\dot{\mathbf{r}}_s f_s) - \frac{\partial}{\partial \dot{\mathbf{r}}_s} \cdot (\ddot{\mathbf{r}}_s f_s) \quad (1)$$

where \mathbf{r}_s is the position vector of the single solvent molecule under consideration, t is the time, and the superscript dots signify differentiation with respect to time. We have chosen to use Lagrangian rather than Hamiltonian phase space.

The forces acting on the solvent molecule are identified by the force balance

$$m_s \ddot{\mathbf{r}}_s = -\frac{\partial \Gamma}{\partial \mathbf{r}_s} - \frac{\partial E}{\partial \mathbf{r}_s} \quad (2)$$

where m_s is the mass of a solvent molecule. The interaction potential Γ is a dispersion force based attraction and/or repulsion between the solvent and the

beads of the polymer chain. The Γ is assumed to be a function of the position of the solvent molecule under consideration and of the positions of all the beads within the polymer molecule under consideration. Most importantly, it is conservative and, therefore, not a function of velocity coordinates.

The potential E accounts for the interaction of the system with either long- or short-range external forces. An example of a long-range force is gravity. A solid boundary or wall interaction results in a short-range force. In the vicinity of a wall, the solvent molecules experience dispersion forces exerted by the atoms within the wall. We expect any modification of the solvent density or viscosity caused by the wall to exist within a boundary layer of a size several orders of magnitude smaller than that for the polymer. Therefore, the dependence of E on \mathbf{r}_s can usually be neglected.

By modeling the solvent with a single-molecule distribution, we neglect the interaction between any one solvent molecule and all the others. We are in essence modeling the solvent as if it were an ideal gas. We accept this simplification because we emphasize the interaction between the solvent and the polymer. By design, the solvent density and viscosity can be made pure constants with no attempt made to evaluate them from molecular properties. They remain free parameters to be specified by liquid values if the need arises.

We define the peculiar velocity for the solvent, \mathbf{v}_s , as the velocity of the solvent molecule relative to the bulk flow velocity,

$$\mathbf{v}_s = \dot{\mathbf{r}}_s - \mathbf{u}(\mathbf{r}_s) \quad (3)$$

where \mathbf{u} is the bulk (i.e., solution) velocity. We rearrange the force balance to obtain an expression for the acceleration of the solvent molecule. Using the expression for the molecule's acceleration and peculiar velocity in the conservation equation for f_s yields

$$\frac{\partial f_s}{\partial t} = -\frac{\partial}{\partial \mathbf{r}_s} \cdot f_s(\mathbf{v}_s + \mathbf{u}) + \frac{1}{m_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \cdot \left(\frac{\partial f_s}{\partial \mathbf{v}_s} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} \right) \quad (4a)$$

where we have also used

$$\frac{\partial f_s}{\partial \mathbf{u}} = \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} \quad (4b)$$

We assume that the peculiar velocity is a solenoidal field. This assumption is similar to, but less restrictive than, the "stosszahlansatz" or the molecular chaos assumption of Boltzmann.⁷ If we assume the stosszahlansatz instead, the peculiar velocity is then uncorrelated with position and consequently a solenoidal field. The second assumption we make is that the flow is incompressible. Making use of these assumptions yields,

$$\frac{\partial f_s}{\partial t} = -(\mathbf{v}_s + \mathbf{u}) \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} + \frac{1}{m_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \cdot \left(\frac{\partial f_s}{\partial \mathbf{v}_s} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} \right) \quad (5)$$

When we evaluate f_s at a stationary state, to make certain that it is invariant with respect to a Galilean transformation, we must use the substantial derivative. The substantial derivative for f_s is

$$\frac{df_s}{dt} = \frac{\partial f_s}{\partial t} + \mathbf{u}(\mathbf{r}_s) \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} \quad (6a)$$

Using the substantial derivative in eq. (5) yields

$$\frac{df_s}{dt} = -\mathbf{v}_s \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} + \frac{1}{m_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \cdot \left(\frac{\partial f_s}{\partial \mathbf{v}_s} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} \right) \quad (6b)$$

Equations (6) are the governing equations for f_s . We now simplify by averaging over the velocity space of the solvent molecule.

We define the real space distribution for the solvent as

$$g_s(\mathbf{r}_s, t; \{\mathbf{r}_\mu\}) = \int_{\Omega} d^3\mathbf{v}_s f_s(\mathbf{r}_s, \mathbf{v}_s, t; \{\mathbf{r}_\mu\}) \quad (7)$$

where $\{\mathbf{r}_\mu\}$ denotes the set of position vectors for the beads of the polymer chain. The semicolon preceding the braces indicates that this is parametric dependence. The integration is performed over Ω , which signifies the volume of the velocity space for a single particle.

To find the governing equation for g_s , we integrate the governing equation for f_s over Ω . Averaging eq. (6b) over Ω yields

$$m_s \frac{dg_s}{dt} = \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \cdot \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \cdot \frac{\partial g_s}{\partial \mathbf{r}_s} \quad (8)$$

To complete the average over the entire phase space for the solvent, we define an operator for averaging over real space. We denote this operator with a pair of backward slashes and define it as

$$\backslash \backslash_s = \int_V d^3\mathbf{r}_s g_s(\mathbf{r}_s, t; \{\mathbf{r}_\mu\}). \quad (9)$$

where V designates the volume of real space for a single particle.

The ensemble averages provide a means for evaluating a normalization constant for either f_s or g_s . However, the parametric dependence of both f_s and g_s on the bead positions means that any normalization constant will also have this dependence. The normalization will therefore require a joint solvent-polymer or total mass average. In the absence of polymer, the normalization constraint is

$$N_s = \backslash \backslash_s \quad (10a)$$

where N_s is the total number of solvent molecules in the volume V . If we further restrict the analysis by neglecting any wall or external potential, then g_s is a constant with the value

$$g_s = \frac{N_s}{V} \quad (10b)$$

Both f_s and g_s are conditional probability distributions. The dependence of the interaction potential Γ on the positions of the beads within a polymer molecule makes the probability of finding a solvent molecule at a particular location conditional upon finding the beads at certain other specified locations. We model the polymer in the same manner as we have done for the solvent. As we shall show in the next section, the phase space distribution for the polymer will have a parametric dependence on the position of the solvent molecule.

The Polymer

The state of a single polymer molecule is described by the phase space distribution f_p . We model the macromolecule as a linear assembly of α identical beads connected by $\alpha - 1$ identical springs. The conservation of all phase points is maintained by the continuity equation for f_p ,

$$\frac{\partial f_p}{\partial t} = - \sum_{\mu=1}^{\alpha} \left(\frac{\partial}{\partial \mathbf{r}_{\mu}} \cdot (\dot{\mathbf{r}}_{\mu} f_p) + \frac{\partial}{\partial \dot{\mathbf{r}}_{\mu}} \cdot (\ddot{\mathbf{r}}_{\mu} f_p) \right) \quad (11)$$

where \mathbf{r}_{μ} is the position vector for the μ th bead.

The forces acting on the beads are identified with the force balance on a bead,

$$m_p \ddot{\mathbf{r}}_{\mu} = - \frac{\partial E}{\partial \mathbf{r}_{\mu}} - \frac{\partial \Gamma}{\partial \mathbf{r}_{\mu}} - \frac{\partial \Phi}{\partial \mathbf{r}_{\mu}} \quad (12a)$$

where m_p is the mass of a bead. The potential E , introduced in the presentation for the solvent, represents the interaction between the system and a wall or external potential. The sum of interactions of each bead with the wall yields the total interaction of the macromolecule with the wall; hence,

$$E(\{\mathbf{r}_{\mu}\}, \mathbf{r}_s) = E_s(\mathbf{r}_s) + \sum_{\mu=1}^{\alpha} E_{\mu}(\mathbf{r}_{\mu}) \quad (12b)$$

The potential Γ , also introduced in the presentation for the solvent, is the sum of the interactions of the solvent with each bead:

$$\Gamma(\{\mathbf{r}_{\mu}\}, \mathbf{r}_s) = \sum_{\mu=1}^{\alpha} \Gamma_{\mu}(\mathbf{r}_{\mu}, \mathbf{r}_s) \quad (12c)$$

The potential Φ represents the total interaction of all the beads on the chain caused by each bead interacting with its nearest neighbors by means of the springs. All three potentials are conservative.

We define the peculiar velocity for the μ th bead as

$$\mathbf{v}_\mu = \dot{\mathbf{r}}_\mu - \mathbf{u}(\mathbf{r}_\mu) \quad (13)$$

We substitute the expression for the peculiar velocity and the acceleration of a bead into the continuity equation for f_p to yield

$$\frac{\partial f_p}{\partial t} = - \sum_{\mu=1}^{\alpha} \left[(\mathbf{v}_s + \mathbf{u}) \cdot \frac{\partial f_p}{\partial \mathbf{r}_\mu} - \frac{1}{m_p} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_\mu} \cdot \left(\frac{\partial f_p}{\partial \mathbf{v}_\mu} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_\mu} \right)^{-1} \cdot \frac{\partial f_p}{\partial \mathbf{r}_\mu} \right) \right] \quad (14)$$

where we have assumed incompressible flow and that the peculiar velocity for each bead is a solenoidal field.

The substantial derivative for f_p is

$$\frac{df_p}{dt} = \frac{\partial f_p}{\partial t} + \sum_{\mu=1}^{\alpha} \mathbf{u}(\mathbf{r}_\mu) \cdot \frac{\partial f_p}{\partial \mathbf{r}_\mu} \quad (15a)$$

We use the substantial derivative for f_p in eq. (14) to find

$$\frac{df_p}{dt} = - \sum_{\mu=1}^{\alpha} \left[\mathbf{v}_s \cdot \frac{\partial f_p}{\partial \mathbf{r}_\mu} - \frac{1}{m_p} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_\mu} \cdot \left(\frac{\partial f_p}{\partial \mathbf{v}_\mu} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_\mu} \right)^{-1} \cdot \frac{\partial f_p}{\partial \mathbf{r}_\mu} \right) \right] \quad (15b)$$

Equations (15) are the governing equations for f_p . We now simplify by averaging over the velocity space of all the beads.

We define the polymer configuration space distribution in the same manner by which we defined the solvent real space distribution. The configuration space distribution is defined as

$$g_p(\{\mathbf{r}_\mu\}, t; \mathbf{r}_s) = \prod_{\mu=1}^{\alpha} \int_{\Omega} d^3\mathbf{v}_\mu f_s(\{\mathbf{r}_\mu\}, \{\mathbf{v}_\mu\}, t; \mathbf{r}_s) \quad (16a)$$

To find the governing equation for g_p , we integrate the governing equation for f_p over Ω for each bead. After integrating we find

$$m_p \frac{dg_p}{dt} = \sum_{\mu=1}^{\alpha} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_\mu} \cdot \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_\mu} \right)^{-1} \cdot \frac{\partial g_p}{\partial \mathbf{r}_\mu} \quad (16b)$$

We cast eq. (16b) into a more useful form. We transform from the variables $\{\mathbf{r}_\mu\}$, where $\mu = 1, 2, 3, \dots, \alpha$, to the variables \mathbf{r}_c and $\{\mathbf{Q}_i\}$ where $i = 1, 2, 3, \dots, \alpha - 1$. The variable \mathbf{r}_c is the position vector for the center of mass of the bead-spring assembly. It is defined as

$$\mathbf{r}_c = \frac{1}{\alpha} \sum_{\mu=1}^{\alpha} \mathbf{r}_{\mu} \quad (17a)$$

The variables \mathbf{Q}_i are the spring vectors or internal coordinates of the macromolecule. They are defined by

$$\mathbf{Q}_i = (\mathbf{r}_{\mu+1} - \mathbf{r}_{\mu}) \delta_{i\mu} (1 - \delta_{\mu\alpha}) \quad (17b)$$

where $\delta_{i\mu}$ is Kronecker's delta. The transformation from the \mathbf{r}_{μ} to the \mathbf{Q}_i is expressed by the matrix $B_{i\mu}$; thus

$$\mathbf{Q}_i = \sum_{\mu=1}^{\alpha} B_{i\mu} \mathbf{r}_{\mu} \quad (17c)$$

where

$$B_{i\mu} = \delta_{(i+1)\mu} - \delta_{i\mu} \quad (17d)$$

Using this transformation, the gradients become

$$\frac{\partial g_p}{\partial \mathbf{r}_{\mu}} = \frac{1}{\alpha} \frac{\partial g_p}{\partial \mathbf{r}_c} + \sum_{i=1}^{\alpha-1} B_{i\mu} \frac{\partial g_p}{\partial \mathbf{Q}_i} \quad (18a)$$

$$\frac{\partial(\Gamma + E)}{\partial \mathbf{r}_{\mu}} = \frac{1}{\alpha} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_c} + \sum_{j=1}^{\alpha-1} B_{j\mu} \frac{\partial(\Gamma + E)}{\partial \mathbf{Q}_j} \quad (18b)$$

$$\frac{\partial \Phi}{\partial \mathbf{r}_{\mu}} = \sum_{j=1}^{\alpha-1} B_{j\mu} \frac{\partial \Phi}{\partial \mathbf{Q}_j} \quad (18c)$$

$$\frac{\partial \mathbf{u}}{\partial \mathbf{r}_{\mu}} = \frac{1}{\alpha} \frac{\partial \mathbf{u}}{\partial \mathbf{r}_c} \quad (18d)$$

Substituting the expressions for the gradients shown in eqs. (18) into eq. (16b) yields

$$m_p \frac{dg_p}{dt} = \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_c} \cdot \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_c} \right)^{-1} \cdot \frac{\partial g_p}{\partial \mathbf{r}_c} + \alpha \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} A_{ij} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{Q}_j} \cdot \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_c} \right)^{-1} \cdot \frac{\partial g_p}{\partial \mathbf{Q}_i} \quad (19)$$

where we have used

$$\sum_{\mu=1}^{\alpha} B_{j\mu} = 0 \quad (20a)$$

The matrix A_{ij} is defined by

$$A_{ij} = \sum_{\mu=1}^{\alpha} B_{i\mu} B_{j\mu} \quad (20b)$$

This is the Rouse matrix.

The average over the internal coordinates of the bead–spring assembly occurs far more often than the average over the entire configuration space. For this reason we define the operator

$$\langle \rangle_p = \prod_{i=1}^{\alpha-1} \int d^3\mathbf{Q}_i \quad (21)$$

Since the polymer cannot exist in solution without the solvent, any normalization constraint for the polymer must include an average over the solvent as well. We shall define such a joint solvent–polymer ensemble average in the next section. We use this ensemble average to define the intramolecular contribution to the stress tensor.

The Stress Tensor

The total stress in the fluid, \mathbf{T} , is the sum of the solvent and polymer contributions. The solvent contribution is the familiar isotropic pressure plus the Newtonian deviatoric stress. The polymer contribution is the sum of an isotropic kinetic contribution, $\sigma^{(K)}\delta$ where δ is the unit tensor, and the intramolecular contribution due to the tension in the springs, σ .

At first glance, it would appear that there should exist an explicit contribution to the total stress from the solvent–polymer intermolecular interaction. However, such a contribution requires formulation with the pair distribution, f_{ps} . Since the distributions f_s and f_p are not statistically independent (i.e., they are conditional distributions, not marginal distributions), f_{ps} does not equal the product of f_p and f_s . Although the intermolecular interaction cannot appear explicitly with this formulation, it does contribute to the total stress implicitly by the modification it causes in σ .

The total stress tensor is given by

$$\mathbf{T} = -P_s\delta + \eta_s\dot{\gamma} + \sigma^{(K)}\delta + \sigma \quad (22a)$$

where P_s is the solvent pressure and η_s is the solvent viscosity. $\dot{\gamma}$ is twice the rate of strain dyadic tensor;

$$\dot{\gamma} = \frac{\partial \mathbf{u}}{\partial \mathbf{r}} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^T \quad (22b)$$

where the superscript T denotes the transpose. The kinetic contribution from the polymer is

$$\sigma^{(K)} = -2n_p kT \tag{23}$$

where n_p is the polymer number density, k is Boltzmann's constant, and T is the absolute temperature.

The intramolecular contribution from the polymer is the quantity of interest since in this formulation only it can predict non-Newtonian behavior. It is expressed by

$$\sigma(\mathbf{r}) = \sum_{\mu=1}^{\alpha} \int_0^1 d\beta \mathbf{R}_{\mu} \frac{\partial \Phi}{\partial \mathbf{r}_{\mu}} g_p(\mathbf{r}_c = \mathbf{r} - \beta \mathbf{R}_{\mu}, \{\mathbf{Q}_i\}, t; \mathbf{r}_s) \tag{24a}$$

where \mathbf{R}_{μ} is the position of bead μ relative to the center of mass for the macromolecule; thus

$$\mathbf{R}_{\mu} = \mathbf{r}_{\mu} - \mathbf{r}_c \tag{24b}$$

If we neglect all concentration gradients within the fluid, the expression for the intramolecular contribution to the stress tensor is greatly simplified. In this case the potential E must vanish since its effect is to create a concentration gradient. As a result of neglecting all concentration gradients, the fluid stress must be homogeneous even though it may be anisotropic. Then, the intramolecular contribution becomes

$$\sigma = \sum_{j=1}^{\alpha-1} \mathbf{Q}_j \frac{\partial \Phi}{\partial \mathbf{Q}_j} g_p(\{\mathbf{Q}_i\}, t; \mathbf{r}_s) \tag{25}$$

From eqs. (24a) and (25) we see that the definition of the solvent-polymer ensemble average should be

$$\langle \langle \langle \langle \rangle \rangle \rangle \rangle = \langle \langle g_p \rangle \rangle \tag{26a}$$

The normalization constraint for the solvent-polymer system is then

$$N_s N_p = \langle \langle 1 \rangle \rangle \tag{26b}$$

where N_p is the number of polymer molecules in the solution. Written with the ensemble average symbols, eq. (25) becomes

$$\sigma = \sum_{j=1}^{\alpha-1} \langle \langle \mathbf{Q}_j \frac{\partial \Phi}{\partial \mathbf{Q}_j} \rangle \rangle \tag{26c}$$

To evaluate σ , we return to the governing equation for g_p . If we neglect all concentration gradients, eq. (19) reduces to

$$m_p \frac{d g_p}{dt} = \alpha \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} A_{ij} \frac{\partial(\Gamma + \Phi)}{\partial \mathbf{Q}_j} \cdot \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \cdot \frac{\partial g_p}{\partial \mathbf{Q}_i} \tag{27}$$

where we have dropped the subscript c on \mathbf{r}_c . In the absence of a concentration gradient, g_s is constant and has the value given by eq. (10b). The position \mathbf{r}_c therefore becomes indistinguishable from an arbitrary position in the fluid.

We multiply eq. (27) by g_s and average over real space for the solvent. Then rearranging the vector multiplications yields

$$m_p \frac{d \langle g_p \rangle_s}{dt} = \alpha \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} : \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} A_{ij} \langle \frac{\partial g_p}{\partial \mathbf{Q}_i} \frac{\partial (\Gamma + \Phi)}{\partial \mathbf{Q}_j} \rangle_s \quad (28)$$

We multiply eq. (28) by $\mathbf{Q}_k \partial \Phi / \partial \mathbf{Q}_k$; apply chain rule to the argument of the solvent average; then, average over the internal coordinates of the polymer. After some rearrangement, eq. (28) becomes

$$m_p \frac{d \langle \langle \mathbf{Q}_k \partial \Phi / \partial \mathbf{Q}_k \rangle \rangle}{dt} + \alpha \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} : \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} A_{ij} \langle \langle \frac{\partial (\Gamma + \Phi)}{\partial \mathbf{Q}_j} \frac{\partial (\mathbf{Q}_k \partial \Phi / \partial \mathbf{Q}_k)}{\partial \mathbf{Q}_i} + \frac{\partial^2 (\Gamma + \Phi)}{\partial \mathbf{Q}_i \partial \mathbf{Q}_j} \mathbf{Q}_k \frac{\partial \Phi}{\partial \mathbf{Q}_k} \rangle \rangle = 0 \quad (29)$$

We apply an orthogonal transformation to the matrix A_{ij} to decompose it into its normal modes. If we let a_k denote the eigenvalues of A_{ij} , then we have the transformation

$$\sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} A'_{ki} A_{ij} A'_{jl}{}^T = \frac{a_k}{\alpha} \delta_{kl} \quad (30a)$$

The transforming matrix A'_{ij} is given by

$$A'_{kl} = \sum_{\mu=1}^{\alpha} B'_{\mu k} B'_{\mu l} \quad (30b)$$

where the matrix $B'_{\mu k}$ is

$$B'_{\mu k} = \{ (k - \alpha) / \alpha \text{ for } \mu < k; k / \alpha \text{ for } \mu > k \} \quad (30c)$$

The eigenvectors of the matrix A_{ij} are

$$\mathbf{Q}'_k = \sum_{j=1}^{\alpha-1} A'_{kj} \mathbf{Q}_j \quad (30d)$$

Transforming eq. (29) yields

$$m_p \frac{d \langle \langle \mathbf{Q}'_k \partial \Phi / \partial \mathbf{Q}'_k \rangle \rangle}{dt} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} : \sum_{i=1}^{\alpha-1} a_i \langle \langle \frac{\partial (\Gamma + \Phi)}{\partial \mathbf{Q}'_i} \frac{\partial (\mathbf{Q}'_k \partial \Phi / \partial \mathbf{Q}'_k)}{\partial \mathbf{Q}'_i} + \frac{\partial^2 (\Gamma + \Phi)}{\partial \mathbf{Q}'_i \partial \mathbf{Q}'_i} \mathbf{Q}'_k \frac{\partial \Phi}{\partial \mathbf{Q}'_k} \rangle \rangle = 0 \quad (31)$$

We let

$$\sigma'_k = \mathbf{Q}'_k \frac{\partial \Phi}{\partial \mathbf{Q}'_k} \quad (32a)$$

then eq. (31) becomes

$$m_p \frac{d\sigma'_k}{dt} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} : \sum_{i=1}^{\alpha-1} a_i \frac{\partial(\Gamma + \Phi)}{\partial \mathbf{Q}'_i} \frac{\partial(\mathbf{Q}'_k \partial \Phi / \partial \mathbf{Q}'_k)}{\partial \mathbf{Q}'_i} + \frac{\partial^2(\Gamma + \Phi)}{\partial \mathbf{Q}'_i \partial \mathbf{Q}'_i} \mathbf{Q}'_k \frac{\partial \Phi}{\partial \mathbf{Q}'_k} = 0 \quad (32b)$$

and so

$$\sigma = \sum_{k=1}^{\alpha-1} \sigma'_k \quad (32c)$$

Equations (32) present the rheological constitutive equation for this model.

An Example

In the development so far, the inter- and intramolecular potentials have been arbitrary. These potentials must be specified to make explicit the consequences of the rheological constitutive equation. As an example, we assume Hookean force laws for both the inter- and intramolecular interactions; thus

$$\frac{\partial \Phi}{\partial \mathbf{Q}'_i} = H \mathbf{Q}'_i \quad (33a)$$

$$\frac{\partial \Gamma}{\partial \mathbf{Q}'_i} = L \mathbf{Q}'_i \quad (33b)$$

Note that $\partial \Gamma / \partial \mathbf{Q}'_i$ is just the component of the intermolecular force along \mathbf{Q}'_i .

A Hookean force law for the intramolecular interaction is a fair approximation. This is evident from the success of the Rouse model. The value of the Hooke law constant H can be evaluated from measurements of the radius of gyration of the macromolecule. A Hookean force law for the intermolecular interaction between the solvent and the beads of the macromolecular chain is not as good. We can estimate the value of the Hooke law constant L by assuming an empirical potential, e.g., a Lennard-Jones potential.

The value of L can be found by expanding a Lennard-Jones potential in its Taylor series about the location of the energy well. Truncating the series after the quadratic term and discarding the irrelevant constant term yields the harmonic approximation to the potential. Differentiation of the truncated potential would then yield a Hookean force law. The estimate of L would then be expressed in terms of the energy and length parameters for the Lennard-Jones potential.

Upon close examination of the constitutive equation (32b), we see that the most important feature concerning the intermolecular potential is not whether it yields a linear or nonlinear force, but whether it is isotropic or not. The intermolecular force law given by eq. (33b) is isotropic. If we were to assume that the solvent-potential interaction occurs in, say, only the flow or velocity gradient directions, then very different predictions would result. For the present, we use the isotropic potentials of eq. (33).

Substituting eqs. (33) into eq. (32b) yields

$$m_p \frac{d\sigma'_k}{dt} + (L + H) \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} : (a_k \sigma'_k \delta + 2(\alpha - 1) \delta \sigma'_k) \\ = -a_k (L + H) \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} : H \backslash \backslash \mathbf{Q}'_k \delta \mathbf{Q}'_k \backslash \backslash \quad (34)$$

Equation (34) shows the effect of assuming isotropic interaction potentials. To see how this couples with the directionality of the flow field, we consider homogeneous flow:

$$\frac{\partial \mathbf{u}}{\partial \mathbf{r}} = \dot{\gamma} \delta_z \delta_x \quad (35)$$

where δ_z is the unit vector in the z direction and $\dot{\gamma}$ is the shear rate. If we also consider the flow to be steady, then eq. (34) becomes

$$2(\alpha - 1) \sigma'_k + a_k (\sigma'_{xz})_k \delta + a_k H \backslash \backslash X'_k \delta_z \mathbf{Q}'_k \backslash \backslash = 0 \quad (36)$$

where $(\sigma'_{xz})_k$ is the xz component of σ'_k and X'_k is the x component of \mathbf{Q}'_k . From eq. (36) we find

$$\sigma_{xx} - \sigma_{zz} = \frac{1}{2(\alpha - 1)} \sum_{k=1}^{\alpha-1} a_k (\sigma'_{xz})_k \quad (37a)$$

$$\sigma_{zz} - \sigma_{yy} = \frac{-1}{2(\alpha - 1)} \sum_{k=1}^{\alpha-1} a_k (\sigma'_{xz})_k \quad (37b)$$

So we see that, for linear, isotropic potentials in homogeneous flow, the analysis predicts a second normal stress difference equal to the negative of the first.

CONCLUSIONS

By modeling the interaction between the solvent and the polymer with an intermolecular potential based on dispersion forces, this analysis has shown that the polymer exerts a force on the solvent equal and opposite to that exerted by the solvent on it. The most important feature of the intermolecular potential is its symmetry. The directionality of the dispersion forces couples with that of the flow to determine the normal stress differences and their relation to the

shear stress. The freedom to select any empirically useful intermolecular potential enables this analysis to predict any normal stress difference desired.

This analysis can proceed from either the full phase space or the configuration space of the polymer. In this article, we worked with the polymer configuration space to define the stress within a flow. Alternatively, one could work directly with the phase space distributions and define the stress tensor with moments over the peculiar velocities. In addition, by not averaging over the velocity space portion of the phase space, one would retain the information needed to predict the bulk flow velocity directly from the molecular velocities. However, working directly with the phase space distributions is more difficult. For the purpose of developing a bead-spring model of a macromolecule that perturbs the solvent, working with the polymer configuration space is sufficient.

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