

Bead-Spring Macromolecules: The Kinetic Contribution to the Total Stress

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SYNOPSIS

Using complete phase space distributions, this analysis predicts an isotropic kinetic contribution to the total stress for both the solvent and polymer. The solvent's contribution depends on the polymer's intramolecular potential energy, as well as the intermolecular potential between the solvent and polymer. The analysis questions whether single molecule distributions are capable of investigating the possibility of anisotropic kinetic distributions. The analysis uses the peculiar velocity fields in lieu of modeling molecular collisions.

INTRODUCTION

In kinetic theory analyses of polymer solutions the information regarding the velocity space distribution is usually lost by averaging the phase space distribution over the velocity space to form the configuration space distribution function. Losing this information requires assuming that the velocities of the beads forming the polymer chain are distributed over all possible values according to the Maxwellian velocity distribution. This is the so-called equilibration in momentum space assumption.

This assumption is necessary only if we fail to retain the information regarding the velocity space distribution by choosing to work with a configuration space analysis. In our previous study,¹ we chose to work solely with the configuration space because doing so simplified the analysis considerably. In this article we retain the information regarding the velocity space and work directly with the phase space distributions to compute the kinetic contribution to the total stress in flows of polymer solutions.

The information provided by the velocity space distribution is needed to compute the kinetic contribution because it is defined by the ensemble average over the velocity dyadic product. Using the Maxwellian velocity distribution, only isotropic contributions are predicted. These are the predictions for the equilibrium state of the fluid. To eval-

uate the possibility of anisotropic kinetic contributions requires retaining the information about the nonequilibrium behavior of the velocity space distribution.

For describing the rheological behavior of concentrated polymer solutions and polymer melts, nonequilibrium velocity space distributions appear necessary. The concept of reptation,² used for describing this behavior, requires a nonequilibrium velocity space distribution. Many different kinetic theories considered the possibility of anisotropic kinetic contributions arising from various proposed nonequilibrium velocity space distributions. What they have in common is that they use a single molecule distribution function to describe the behavior of one macromolecule.

Using single molecule distributions, the reptation models^{3,4} and the encapsulated dumbbell models^{5,6} account for the macromolecule's restricted movement by assigning a preferred directionality to space. This is a useful procedure that enables one to account for physical bonding among macromolecules. As far as the kinetic contribution is concerned, however, it seems to overlook that, no matter how restricted the movements of any one particular macromolecule, the net motion of all molecules should be isotropic because space is isotropic. This is a fundamental difficulty we face when we use single molecule distributions.

The enormous complications that arise when using many molecule, or even pair, distribution functions preclude their usefulness for modeling the

rheological behavior of polymer solutions and melts. Although using them may be the only way to accurately assess whether anisotropic kinetic contributions are fact or fiction, we should be able to investigate the assumptions needed to create anisotropic kinetic contributions using single molecule distributions.

As stated in our previous study,¹ our approach is to model a polymer solution using two conditional single molecule probability distributions. We suggested that this approach may be useful for describing concentrated polymer solutions.⁷ The basis for this suggestion was that the intramolecular contribution from the polymer to the total stress should dominate any intermolecular contributions. Intermolecular contributions require using pair distribution functions for their development and cannot be predicted using single molecule distributions no matter how many are used. Since we suggest using our approach for evaluating concentrated polymer solutions and also polymer melts, which should correspond to our so-called theta condition,⁷ we now evaluate the kinetic contribution without using the Maxwellian velocity distribution.

Working directly with the phase space distributions in our approach poses few new mathematical difficulties, but a conceptual difficulty of significant proportions. Our approach transforms the myriad of unknown molecular peregrinations and encounters into an unknown vector field: the peculiar velocity. In the kinetic theory of gases, scientists modeled each molecular encounter as an individual event, requiring restrictive assumptions regarding the feasibility of an encounter. These assumptions, such as Boltzmann's molecular disorder assumption,⁸ were not only necessary from a calculational viewpoint but were vital for visualizing the molecular interactions. Our approach ignores each molecular encounter as an individual event, but rather views all molecular interactions as developing the peculiar velocity fields. Thus, our approach spares us from having to model a molecular collision. However, we have not overcome this ignorance but have only postponed having to satisfy it.

To identify the peculiar velocity fields we assume that they are irrotational. This assumption can be compared to Boltzmann's molecular disorder assumption,⁸ which is equivalent to assuming that the peculiar velocity fields are isotropic and homogeneous. We place no other restrictions on the fields. Although we believe that physical considerations warrant assuming that a peculiar velocity is also a solenoidal field, we do not because doing so precludes using linear molecular forces. Certainly the actual

molecular forces are nonlinear, but the ease of calculation that using linear forces affords us prevents our precluding their use.

DEVELOPMENT

The Peculiar Velocity Fields

To identify the peculiar velocity fields we consider the Lagrangian function for our system. Our system consists of one point mass solvent molecule and one macromolecule, modeled by a linear bead-spring assembly containing α beads. The Lagrangian function is defined as the excess of the kinetic energy, K , over the potential energy, U ,

$$L = K - U \quad (1)$$

We consider the macroscopic manifestation of the Lagrangian function. The macroscopic counterpart is found by averaging the ensemble of microscopic systems over the joint solvent-polymer phase space,

$$\langle\langle L \rangle\rangle = \langle\langle K \rangle\rangle - \langle\langle U \rangle\rangle \quad (2)$$

The double pair of angle brackets and backward slashes, without subscripts, denotes the joint phase space average. We use it in its normalized form such that $\langle\langle 1 \rangle\rangle = 1$.

The polymer solution flows with a bulk velocity $\mathbf{u} = \mathbf{u}(\mathbf{r})$, where \mathbf{r} is the macroscopic position field. The macroscopic kinetic energy of the polymer solution consists wholly of this visible motion. Let m_s denote the mass of the solvent molecule and let m_p denote the mass of a bead; then the macroscopic kinetic energy of the system is

$$\langle\langle K \rangle\rangle = \frac{1}{2}(m_s + \alpha m_p)\mathbf{u} \cdot \mathbf{u} \quad (3)$$

The macroscopic counterpart to the microscopic potential energy can result only from an external potential. That is, no intrasystem potential energy will result in a macroscopic potential energy. Let E_m signify the macroscopic counterpart of the microscopic external potential energy, E . Note that although E may exist, E_m does not necessarily exist. For example, if E is a wall potential, E_m does not exist. Generally speaking, only long-range external forces, such as that due to gravity, will establish E_m .

Putting the macroscopic kinetic and potential energies together yields the macroscopic Lagrangian as

$$\langle\langle L \rangle\rangle = \frac{1}{2}(m_s + \alpha m_p)\mathbf{u} \cdot \mathbf{u} - E_m \quad (4)$$

The Lagrangian function for our system in terms of the microscopic variables is

$$L = \frac{1}{2} m_s \dot{\mathbf{r}}_s \cdot \dot{\mathbf{r}}_s + \frac{1}{2} m_p \sum_{\mu=1}^{\infty} \dot{\mathbf{r}}_{\mu} \cdot \dot{\mathbf{r}}_{\mu} - \Gamma - \Phi - E \quad (5)$$

where $\dot{\mathbf{r}}_s$ is the velocity of the solvent molecule and $\dot{\mathbf{r}}_{\mu}$ is the velocity of bead μ ; Γ is the intermolecular potential between the solvent and all of the beads on the polymer chain; Φ is the intramolecular potential between adjacent beads on the chain.

We define the peculiar velocity for a particle by subtracting the bulk velocity from the particle's velocity:

$$\mathbf{v}_s = \dot{\mathbf{r}}_s - \mathbf{u}(\mathbf{r}_s) \quad (6a)$$

$$\mathbf{v}_{\mu} = \dot{\mathbf{r}}_{\mu} - \mathbf{u}(\mathbf{r}_{\mu}) \quad (6b)$$

where the bulk velocity is evaluated at the location of the particle. We simplify the notation by letting \mathbf{u}_s signify $\mathbf{u}(\mathbf{r}_s)$ and \mathbf{u}_{μ} signify $\mathbf{u}(\mathbf{r}_{\mu})$. Then, using Eqs. (6) in (5) yields

$$L = \frac{1}{2} m_s \mathbf{u}_s \cdot \mathbf{u}_s + \frac{1}{2} m_p \sum_{\mu=1}^{\infty} \mathbf{u}_{\mu} \cdot \mathbf{u}_{\mu} + m_s \mathbf{v}_s \cdot \mathbf{u}_s + m_p \sum_{\mu=1}^{\infty} \mathbf{v}_{\mu} \cdot \mathbf{u}_{\mu} - E + L' \quad (7)$$

where we have let

$$L' = \frac{1}{2} m_s \mathbf{v}_s \cdot \mathbf{v}_s + \frac{1}{2} m_p \sum_{\mu=1}^{\infty} \mathbf{v}_{\mu} \cdot \mathbf{v}_{\mu} - \Gamma - \Phi \quad (8)$$

Averaging Eq. (7) over the joint solvent-polymer phase space yields

$$\langle\langle L \rangle\rangle = \frac{1}{2} (m_s + \alpha m_p) \mathbf{u} \cdot \mathbf{u} - E_m + \langle\langle L' \rangle\rangle \quad (9)$$

Subtracting Eq. (4) from (9) yields

$$\langle\langle L' \rangle\rangle = 0 \quad (10)$$

The argument of the ensemble average in Eq. (10) is the integrand of an integral over an arbitrary phase space. To satisfy Eq. (10) we evaluate the conditions for which the integrand vanishes. Hence, we have

$$\frac{1}{2} m_s \mathbf{v}_s \cdot \mathbf{v}_s - \frac{1}{2} m_p \sum_{\mu=1}^{\infty} \mathbf{v}_{\mu} \cdot \mathbf{v}_{\mu} - \Gamma - \Phi = 0 \quad (11)$$

We assume that the peculiar velocity fields are derivable from a gradient of a scalar function, i.e., a peculiar velocity is an irrotational field. Let ϕ denote this velocity potential, then

$$\mathbf{v}_s = \frac{\partial \phi}{\partial \mathbf{r}_s} \quad (12a)$$

$$\mathbf{v}_{\mu} = \frac{\partial \phi}{\partial \mathbf{r}_{\mu}} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (12b)$$

Using Eqs. (12) in (11) yields our governing equation for the peculiar velocity potential:

$$2(\Gamma + \Phi) = m_s \left(\frac{\partial \phi}{\partial \mathbf{r}_s} \right)^2 + m_p \sum_{\mu=1}^{\infty} \left(\frac{\partial \phi}{\partial \mathbf{r}_{\mu}} \right)^2 \quad (13)$$

This equation is an $\alpha + 1$ -dimensional, nonlinear, first-order, partial differential equation for ϕ . Since there are no systematic procedures for solving such an equation, let us rewrite Eq. (13) as if it were a linear equation:

$$2(\Gamma + \Phi) = a_s \frac{\partial \phi}{\partial \mathbf{r}_s} + \sum_{\mu=1}^{\infty} a_{\mu} \frac{\partial \phi}{\partial \mathbf{r}_{\mu}} \quad (14a)$$

where

$$a_s = m_s \frac{\partial \phi}{\partial \mathbf{r}_s} \quad (14b)$$

$$a_{\mu} = m_{\mu} \frac{\partial \phi}{\partial \mathbf{r}_{\mu}} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (14c)$$

Applying the method of characteristics to this pseudo-linear equation tells us

$$dt = \frac{d\phi}{2(\Gamma + \Phi)} = \frac{dr_s}{a_s} = \frac{dr_{\mu}}{a_{\mu}} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (15)$$

where t is a parameter. Equations (15) are $\alpha + 2$ ordinary differential equations that integrate to

$$r_s = \int dt a_s \equiv r_s(t) \quad (16a)$$

$$r_{\mu} = \int dt a_{\mu} \equiv r_{\mu}(t) \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (16b)$$

$$\phi = 2 \int dt (\Gamma + \Phi) \quad (16c)$$

Differentiating Eq. (16c) with respect to r_s and r_{μ} yields

$$\frac{\partial \phi}{\partial r_s} = \frac{2 \partial \left[\int dt (\Gamma + \Phi) \right]}{\partial r_s} \quad (17a)$$

$$\frac{\partial \phi}{\partial r_\mu} = \frac{2 \partial \left[\int dt (\Gamma + \Phi) \right]}{\partial r_\mu} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (17b)$$

We rewrite these as

$$\frac{\partial \phi}{\partial r_s} = \frac{2 \partial t}{\partial r_s} \frac{\partial \left[\int dt (\Gamma + \Phi) \right]}{\partial t} \quad (18a)$$

$$\frac{\partial \phi}{\partial r_\mu} = \frac{2 \partial t}{\partial r_\mu} \frac{\partial \left[\int dt (\Gamma + \Phi) \right]}{\partial t} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (18b)$$

These reduce to

$$\frac{\partial \phi}{\partial r_s} = \frac{2 \partial t}{\partial r_s} (\Gamma + \Phi) \quad (19a)$$

$$\frac{\partial \phi}{\partial r_\mu} = \frac{2 \partial t}{\partial r_\mu} (\Gamma + \Phi) \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (19b)$$

To evaluate the partial derivatives $\partial t / \partial r_s$ and $\partial t / \partial r_\mu$, $\mu = 1, 2, 3, \dots, \alpha$, we add the $\alpha + 1$ equations [16(a) and (b)]. Inverting the equation formed by the sum of these equations yields the function

$$t = t(r_s, r_1, r_2, r_3, \dots, r_\alpha) \quad (20)$$

From this it is easy to show that

$$\frac{dt}{dr_s} = (\alpha + 1) \frac{\partial t}{\partial r_s} \quad (21a)$$

$$\frac{dt}{dr_\mu} = (\alpha + 1) \frac{\partial t}{\partial r_\mu} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (21b)$$

Using Eqs. (15) and (21) in (19) yields

$$\frac{\partial \phi}{\partial r_s} = \frac{2(\Gamma + \Phi)}{(\alpha + 1)a_s} \quad (22a)$$

$$\frac{\partial \phi}{\partial r_\mu} = \frac{2(\Gamma + \Phi)}{(\alpha + 1)a_\mu} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (22b)$$

Now substituting the definitions for a_s and a_μ yields

$$v_s = \frac{\partial \phi}{\partial r_s} = \left[\frac{2(\Gamma + \Phi)}{(\alpha + 1)m_s} \right]^{1/2} \quad (23a)$$

$$v_\mu = \frac{\partial \phi}{\partial r_\mu} = \left[\frac{2(\Gamma + \Phi)}{(\alpha + 1)m_\mu} \right]^{1/2} \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (23b)$$

Direct substitution of Eqs. (23) into (13) shows that they satisfy it.

Integrating Eqs. (22) yields the implicit relations

$$\phi = \frac{2/3}{(\alpha + 1)m_s} \int \frac{d\mathbf{r}_s \cdot \partial \mathbf{r}_s}{\partial \phi} (\Gamma + \Phi) + C_s(\{r_\mu\}) \quad (24a)$$

$$\phi = \frac{2/3}{(\alpha + 1)m_p} \int \frac{d\mathbf{r}_\mu \cdot \partial \mathbf{r}_\mu}{\partial \phi} (\Gamma + \Phi) + C_\mu(r_s, \{r_\theta\}), \quad \theta \neq \mu \quad (24b)$$

where C_s and C_μ are constants of the integrations. Evaluating the gradients of Eqs. (24) yields

$$\mathbf{v}_s \mathbf{v}_s = \frac{\partial \phi}{\partial r_s} \frac{\partial \phi}{\partial r_s} = \frac{2(\Gamma + \Phi)}{(\alpha + 1)m_s} \delta \quad (25a)$$

$$\mathbf{v}_\mu \mathbf{v}_\mu = \frac{\partial \phi}{\partial r_\mu} \frac{\partial \phi}{\partial r_\mu} = \frac{2(\Gamma + \Phi)}{(\alpha + 1)m_p} \delta \quad \text{for } \mu = 1, 2, 3, \dots, \alpha \quad (25b)$$

where δ is the unit tensor. Equations (23) and (25) tell us all that we need to know about the peculiar velocity fields.

The Solvent's Kinetic Contribution

Having modeled the solvent with a single point mass, its properties are akin to those of an ideal gas. As stated in our previous study,¹ we do not use ideal gas properties for the solvent but rather substitute the appropriate liquid viscosity and density. The issue of evaluating the solvent's kinetic contribution would be moot if not for the fact that the presence of the polymer molecule perturbs the motion of the solvent molecule. Because of this, and the possibility that it may create an anisotropic kinetic contribution, we evaluate the solvent's contribution for fluid flow.

We define the solvent's contribution as

$$\sigma^{(s)} = m_s \int_V d^3 \mathbf{r}_s \times \int_\Omega d^3 \mathbf{v}_s \delta(\mathbf{r}_s - \mathbf{r}) \mathbf{v}_s \mathbf{v}_s \langle f_s \rangle_p \quad (26)$$

where V is the domain of the configuration space for a single particle and Ω is that for the velocity space. The delta function allows for a spatial variation of the stress. The pair of angle brackets nested in the pair of backward slashes with the subscript p indicates that its argument, the solvent's phase space distribution function f_s , is averaged over the polymer phase space. We rewrite Eq. (26) in more compact form as

$$\sigma^{(s)} = m_s \langle \langle \langle \mathbf{v}_s \mathbf{v}_s \rangle \rangle \rangle \quad (27)$$

To establish the governing equation for $\sigma^{(s)}$, we use the theorem of Liouville. It tells us that f_s is conserved by

$$\frac{\partial f_s}{\partial t} = -\frac{\partial}{\partial \mathbf{r}_s} \cdot f_s \dot{\mathbf{r}}_s - \frac{\partial}{\partial \dot{\mathbf{r}}_s} \cdot f_s \ddot{\mathbf{r}}_s \quad (28)$$

where $\ddot{\mathbf{r}}_s$ represents the acceleration of the solvent molecule. Lagrangian mechanics yields the force balance

$$m_s \ddot{\mathbf{r}}_s = -\frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \quad (29)$$

where $\dot{\mathbf{r}}_s$ is reference frame indifferent. Γ and E are conservative. Combining this force balance with the continuity equation for f_s , and assuming that the bulk flow is incompressible, yields

$$\begin{aligned} \frac{Df_s}{Dt} &= \frac{-\partial}{\partial \mathbf{r}_s} \cdot f_s \mathbf{v}_s + \frac{1}{m_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \\ &\cdot \left[\frac{\partial f_s}{\partial \mathbf{v}_s} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \cdot \frac{\partial f_s}{\partial \mathbf{r}_s} \right] \quad (30) \end{aligned}$$

where we have used the definition of the substantial derivative and the peculiar velocity.

Multiplying Eq. (30) by $\delta(\mathbf{r}_s - \mathbf{r}) m_s \mathbf{v}_s \mathbf{v}_s f_p$ and averaging over the joint solvent-polymer phase space yields

$$\frac{D\sigma^{(s)}}{Dt} = -m_s \int_V d^3 \mathbf{r}_s \int_\Omega d^3 \mathbf{v}_s \delta(\mathbf{r}_s - \mathbf{r}) \mathbf{v}_s \mathbf{v}_s$$

$$\begin{aligned} &\left\langle \left\langle \frac{\partial}{\partial \mathbf{r}_s} \cdot f_s \mathbf{v}_s \right\rangle \right\rangle_p \int_V d^3 \mathbf{r}_s \\ &\times \int_\Omega d^3 \mathbf{v}_s \delta(\mathbf{r}_s - \mathbf{r}) \mathbf{v}_s \mathbf{v}_s \end{aligned}$$

$$\begin{aligned} &\left\langle \left\langle \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \cdot \frac{\partial f_s}{\partial \mathbf{v}_s} \right\rangle \right\rangle_p \\ &+ \int_V d^3 \mathbf{r}_s \int_\Omega d^3 \mathbf{v}_s \delta(\mathbf{r}_s - \mathbf{r}) \mathbf{v}_s \mathbf{v}_s \\ &\left\langle \left\langle \frac{\partial f_s}{\partial \mathbf{r}_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \right\rangle \right\rangle_p : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \quad (31) \end{aligned}$$

We evaluate the three terms on the right-hand side (RHS) of (31) separately.

Applying chain rule differentiation to the integrand of the first term yields

$$\begin{aligned} &-m_s \int_V d^3 \mathbf{r}_s \int_\Omega d^3 \mathbf{v}_s \delta(\mathbf{r}_s - \mathbf{r}) \mathbf{v}_s \mathbf{v}_s \left\langle \left\langle \frac{\partial}{\partial \mathbf{r}_s} \cdot f_s \mathbf{v}_s \right\rangle \right\rangle_p \\ &= m_s \left\langle \left\langle \left\langle \left\langle \mathbf{v}_s \cdot \frac{\partial(\mathbf{v}_s \mathbf{v}_s)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle \quad (32) \end{aligned}$$

Doing the same to the second term shows that it vanishes because we have assumed that Γ and E are conservative.

Applying chain rule differentiation twice to the integrand of the third term yields

$$\begin{aligned} &\int_V d^3 \mathbf{r}_s \int_\Omega d^3 \mathbf{v}_s \delta(\mathbf{r}_s - \mathbf{r}) \mathbf{v}_s \mathbf{v}_s \\ &\left\langle \left\langle \frac{\partial f_s}{\partial \mathbf{r}_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \right\rangle \right\rangle_p : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \\ &= -\left\langle \left\langle \left\langle \left\langle \frac{\partial(\mathbf{v}_s \mathbf{v}_s)}{\partial \mathbf{r}_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle \\ &\quad + \mathbf{v}_s \mathbf{v}_s \frac{\partial^2(\Gamma + E)}{\partial \mathbf{r}_s \partial \mathbf{r}_s} \left\langle \left\langle \left\langle \left\langle \frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \quad (33) \end{aligned}$$

Note that

$$\begin{aligned} &\left\langle \left\langle \left\langle \left\langle \frac{\partial(\mathbf{v}_s \mathbf{v}_s)}{\partial \mathbf{r}_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle \\ &= \left\langle \left\langle \left\langle \left\langle \mathbf{v}_s \frac{\partial \mathbf{v}_s}{\partial \mathbf{r}_s} \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle \\ &\quad + \left\langle \left\langle \left\langle \left\langle \frac{\partial \mathbf{v}_s}{\partial \mathbf{r}_s} \mathbf{v}_s \frac{\partial(\Gamma + E)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle = 0 \quad (34) \end{aligned}$$

because ensemble averages over odd powers of the peculiar velocity are zero. Hence, the third term on the RHS of (31) reduces to

$$-\left\langle \left\langle \left\langle \left\langle \mathbf{v}_s \mathbf{v}_s \frac{\partial^2(\Gamma + E)}{\partial \mathbf{r}_s \partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}_s} \right)^{-1} \quad (35)$$

Combining all terms yields our constitutive equation for $\sigma^{(s)}$:

$$\frac{D\sigma^{(s)}}{Dt} = m_s \left\langle \left\langle \left\langle \mathbf{v}_s \cdot \frac{\partial(\mathbf{v}_s \mathbf{v}_s)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle - \left\langle \left\langle \left\langle \frac{\mathbf{v}_s \mathbf{v}_s \partial^2(\Gamma + E)}{\partial \mathbf{r}_s \partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \quad (36)$$

We simplify by neglecting all concentration gradients. Therefore, $E = 0$ on V . For linear forces, we let

$$\frac{\partial^2 \Gamma}{\partial \mathbf{r}_s \partial \mathbf{r}_s} = \mathbf{I} \quad (37)$$

where \mathbf{I} is some arbitrary (constant) second-order tensor. These two assumptions reduce Eq. (36) to

$$\frac{D\sigma^{(s)}}{Dt} + \frac{1}{m_s} \mathbf{I} : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \sigma^{(s)} = m_s \left\langle \left\langle \left\langle \mathbf{v}_s \cdot \frac{\partial(\mathbf{v}_s \mathbf{v}_s)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle \quad (38)$$

To progress further, we must know the peculiar velocity field.

Assuming that a peculiar velocity is an irrotational field, the RHS of Eq. (38) becomes

$$m_s \left\langle \left\langle \left\langle \mathbf{v}_s \cdot \frac{\partial(\mathbf{v}_s \mathbf{v}_s)}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle = \frac{1}{3} \left(\frac{2}{\alpha + 1} \right)^{3/2} \left\langle \left\langle \left\langle \left(\frac{\Gamma + \Phi}{m_s} \right)^{1/2} \frac{\partial \Gamma}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle \delta \quad (39)$$

Using this in Eq. (38) transforms the constitutive equation for $\sigma^{(s)}$ to

$$\frac{D\sigma^{(s)}}{Dt} + \frac{1}{m_s} \mathbf{I} : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \sigma^{(s)} = \frac{1}{3} \left(\frac{2}{\alpha + 1} \right)^{3/2} \left\langle \left\langle \left\langle \left(\frac{\Gamma + \Phi}{m_s} \right)^{1/2} \frac{\partial \Gamma}{\partial \mathbf{r}_s} \right\rangle \right\rangle \right\rangle \delta \quad (40)$$

This contribution to the total stress is isotropic and, therefore, irrelevant. However, it shows clearly how the polymer perturbs the solvent and how this perturbation manifests itself in macroscopic terms. It is interesting to see that the polymer's intramolecular potential Φ , as well as the intermolecular

potential Γ , affects the solvent's contribution to the total stress.

The Polymer's Kinetic Contribution

The analysis for the polymer's kinetic contribution is nearly identical to that for the solvent. The only difference is that we account for the motion of each of the α beads. We define the polymer's kinetic contribution as

$$\sigma^{(k)} = m_p \prod_{\mu=1}^{\alpha} \int_V d^3 \mathbf{r}_{\mu} \int_{\Omega} d^3 \mathbf{v}_{\mu} \times \sum_{\theta=1}^{\alpha} \delta(\mathbf{r}_{\theta} - \mathbf{r}) \mathbf{v}_{\theta} \mathbf{v}_{\theta} \langle f_p \rangle_s \quad (41)$$

where the pair of angle brackets nested within the backward slashes carrying the subscript s denotes the ensemble average over the solvent phase space. Writing Eq. (41) in compact notation yields

$$\sigma^{(k)} = \sum_{\theta=1}^{\alpha} \sigma_{\theta}^{(k)} = m_p \sum_{\theta=1}^{\alpha} \langle \langle \mathbf{v}_{\theta} \mathbf{v}_{\theta} \rangle \rangle \quad (42)$$

Proceeding in the same manner as for the solvent, we use the theorem of Liouville to define the continuity equation for the polymer's phase space distribution function, f_p ,

$$\frac{\partial f_p}{\partial t} = - \sum_{\tau=1}^{\alpha} \left[\frac{\partial}{\partial \mathbf{r}_{\tau}} \cdot f_p \dot{\mathbf{r}}_{\tau} + \frac{\partial}{\partial \dot{\mathbf{r}}_{\tau}} \cdot f_p \ddot{\mathbf{r}}_{\tau} \right] \quad (43)$$

where $\ddot{\mathbf{r}}_{\tau}$ is the acceleration of bead τ . A force balance on bead τ yields

$$m_p \ddot{\mathbf{r}}_{\tau} = \frac{-\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_{\tau}} \quad (44)$$

because all of the molecular potentials are conservative. Combining the force balance on bead τ with the continuity equation for f_p , and assuming that the bulk flow is incompressible, yields

$$\frac{Df_p}{Dt} = - \sum_{\tau=1}^{\alpha} \frac{\partial}{\partial \mathbf{r}_{\tau}} \cdot f_p \mathbf{v}_{\tau} + \frac{1}{m_p} \sum_{\tau=1}^{\alpha} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_{\tau}} \cdot \left[\frac{\partial f_p}{\partial \mathbf{v}_{\tau}} + \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \cdot \frac{\partial f_p}{\partial \mathbf{r}_{\tau}} \right] \quad (45)$$

where we have used the definition for the substantial derivative and the peculiar velocity.

Multiplying Eq. (45) by $\delta(\mathbf{r}_\theta - \mathbf{r})m_p\mathbf{v}_\theta\mathbf{v}_\theta f_s$ and averaging over the joint solvent-polymer phase space yields

$$\begin{aligned} \frac{D\sigma_\theta^{(k)}}{Dt} &= -m_p \prod_{\mu=1}^{\alpha} \int_V d^3\mathbf{r}_\mu \int_\Omega d^3\mathbf{v}_\mu \delta(\mathbf{r}_\theta - \mathbf{r}) \mathbf{v}_\theta \mathbf{v}_\theta \\ &\quad \times \sum_{\tau=1}^{\alpha} \left\langle \left\langle \frac{\partial}{\partial \mathbf{r}_\tau} \cdot f_p \mathbf{v}_\tau \right\rangle \right\rangle_s \\ &\quad + \prod_{\mu=1}^{\alpha} \int_V d^3\mathbf{r}_\mu \int_\Omega d^3\mathbf{v}_\mu \delta(\mathbf{r}_\theta - \mathbf{r}) \mathbf{v}_\theta \mathbf{v}_\theta \sum_{\tau=1}^{\alpha} \\ &\quad \left\langle \left\langle \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_\tau} \cdot \frac{\partial f_p}{\partial \mathbf{v}_\tau} \right\rangle \right\rangle_s \\ &\quad + \prod_{\mu=1}^{\alpha} \int_V d^3\mathbf{r}_\mu \int_\Omega d^3\mathbf{v}_\mu \delta(\mathbf{r}_\theta - \mathbf{r}) \mathbf{v}_\theta \mathbf{v}_\theta \\ &\quad \times \sum_{\tau=1}^{\alpha} \left\langle \left\langle \frac{\partial f_p}{\partial \mathbf{r}_\tau} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_\tau} \right\rangle \right\rangle_s : \\ &\quad \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \end{aligned} \quad (46)$$

We consider each term separately.

Handling for the first term on the RHS of (46) is nearly the same as for the solvent. From the integrand of the first term we have

$$\begin{aligned} \mathbf{v}_\theta \mathbf{v}_\theta \left\langle \left\langle \frac{\partial}{\partial \mathbf{r}_\tau} \cdot f_p \mathbf{v}_\tau \right\rangle \right\rangle_s \\ = \left\langle \left\langle \frac{\partial}{\partial \mathbf{r}_\tau} \cdot (f_p \mathbf{v}_\tau \mathbf{v}_\theta \mathbf{v}_\theta) - f_p \mathbf{v}_\tau \cdot \frac{\partial(\mathbf{v}_\theta \mathbf{v}_\theta)}{\partial \mathbf{r}_\tau} \right\rangle \right\rangle_s \end{aligned} \quad (47)$$

Taking the ensemble average of (47) over the polymer phase space shows that the first term on the RHS of (47) vanishes because f_p vanishes at the boundary of V . Hence, the first term on the RHS of (46) reduces to

$$m_p \sum_{\tau=1}^{\alpha} \left\langle \left\langle \left\langle \left\langle \mathbf{v}_\tau \cdot \frac{\partial(\mathbf{v}_\theta \mathbf{v}_\theta)}{\partial \mathbf{r}_\tau} \right\rangle \right\rangle \right\rangle \quad (48)$$

The second term on the RHS of (46) vanishes for the same reason that its corresponding term for the solvent does, i.e., because Γ , Φ , and E are not functions of the peculiar velocity.

From the third term on the RHS of (46) we have

$$\begin{aligned} \mathbf{v}_\theta \mathbf{v}_\theta \left\langle \left\langle \frac{\partial f_p}{\partial \mathbf{r}_\tau} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_\tau} \right\rangle \right\rangle_s \\ = \left\langle \left\langle \frac{\partial(\mathbf{v}_\theta \mathbf{v}_\theta f_p \partial(\Gamma + \Phi + E)/\partial \mathbf{r}_\tau)}{\partial \mathbf{r}_\tau} \right. \right. \\ \left. \left. - f_p \frac{\partial(\mathbf{v}_\theta \mathbf{v}_\theta)}{\partial \mathbf{r}_\tau} \frac{\partial(\Gamma + \Phi + E)}{\partial \mathbf{r}_\tau} \right. \right. \\ \left. \left. - f_p \mathbf{v}_\theta \mathbf{v}_\theta \frac{\partial^2(\Gamma + \Phi + E)}{\partial \mathbf{r}_\mu \partial \mathbf{r}_\mu} \right\rangle \right\rangle_s \end{aligned} \quad (49)$$

Averaging (49) over the polymer phase space shows that the third term on the RHS of (46) reduces to

$$\begin{aligned} - \sum_{\tau=1}^{\alpha} \left\langle \left\langle \left\langle \left\langle \mathbf{v}_\theta \mathbf{v}_\theta \frac{\partial^2(\Gamma + \Phi + E)}{\partial \mathbf{r}_\tau \partial \mathbf{r}_\tau} \right\rangle \right\rangle \right\rangle : \\ \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \end{aligned} \quad (50)$$

Combining the expressions for all of the terms of (46) transforms it to

$$\begin{aligned} \frac{D\sigma_\theta^{(k)}}{Dt} &= m_p \sum_{\mu=1}^{\alpha} \left\langle \left\langle \left\langle \left\langle \mathbf{v}_\mu \cdot \frac{\partial(\mathbf{v}_\theta \mathbf{v}_\theta)}{\partial \mathbf{r}_\mu} \right\rangle \right\rangle \right\rangle \\ &\quad - \sum_{\mu=1}^{\alpha} \left\langle \left\langle \left\langle \left\langle \mathbf{v}_\theta \mathbf{v}_\theta \frac{\partial^2(\Gamma + \Phi + E)}{\partial \mathbf{r}_\mu \partial \mathbf{r}_\mu} \right\rangle \right\rangle \right\rangle : \\ &\quad \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \end{aligned} \quad (51)$$

This is our constitutive equation for the polymer's kinetic contribution from bead θ , $\theta = 1, 2, 3, \dots, \alpha$.

In the absence of all concentration gradients, we set $E = 0$ on V . For linear forces we use (37) and let

$$\frac{\partial^2 \Phi}{\partial \mathbf{r}_\mu \partial \mathbf{r}_\mu} = \mathbf{H} \quad (52)$$

where \mathbf{H} is an arbitrary (constant) second-order tensor. Using these assumptions in (51) transforms it to

$$\begin{aligned} \frac{D\sigma_\theta^{(k)}}{Dt} + \frac{\alpha}{m_p} (\mathbf{I} + \mathbf{H}) : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \sigma_\theta^{(k)} \\ = m_p \sum_{\mu=1}^{\alpha} \left\langle \left\langle \left\langle \left\langle \mathbf{v}_\mu \cdot \frac{\partial(\mathbf{v}_\theta \mathbf{v}_\theta)}{\partial \mathbf{r}_\mu} \right\rangle \right\rangle \right\rangle \end{aligned} \quad (53)$$

To evaluate Eq. (53) further requires knowledge of the peculiar velocity fields.

Assuming that a peculiar velocity is an irrotational field transforms Eq. (53) to

$$\begin{aligned} \frac{D\sigma_{\theta}^{(k)}}{Dt} + \frac{\alpha}{m_p} (\mathbf{I} + \mathbf{H}) : \left(\frac{\partial \mathbf{u}}{\partial \mathbf{r}} \right)^{-1} \sigma_{\theta}^{(k)} \\ = \frac{1}{3} \left(\frac{2}{(\alpha + 1)} \right)^{3/2} \sum_{\mu=1}^{\alpha} \\ \left\langle \left\langle \left(\frac{\Gamma + \Phi}{m_p} \right)^{1/2} \frac{\partial(\Gamma + E)}{\partial r_{\mu}} \right\rangle \right\rangle \delta \quad (54) \end{aligned}$$

Just as it was for the solvent, this kinetic contribution is isotropic. The contribution from bead θ is affected by the position of the solvent molecule as well as that for all of the other beads. In addition to this, the kinetic contribution from bead θ is affected by the magnitude of the forces acting on all of the other beads. Unlike the corresponding intramolecular contribution evaluated in our previous study,⁷ it is not viscoplastic.

CONCLUSIONS

This analysis shows that both the solvent's and the polymer's kinetic contribution is isotropic when linear forces are used and when the peculiar velocity is evaluated as an irrotational field. Using nonlinear molecular forces or rotational peculiar velocity fields may change these predictions, but physical considerations lead us to believe that they ought not. Using nonlinear forces would complicate the analysis considerably and may force us to use a closure approximation. However, their use should not change the isotropy prediction. Using peculiar velocity fields with a rotational component would almost certainly lead to anisotropic predictions; however, it seems reasonable that a peculiar velocity field is irrotational.

We need greater insight into the nature of the peculiar velocity field to rule out the possibility for predicting anisotropic kinetic contributions using this approach. That insight may require greater labor than the system merits. The fundamental difficulty is that our system consists solely of one solvent molecule and one macromolecule. While it may be too difficult to use a microscopic system consisting of two macromolecules described by a pair distribution function, it may prove worthwhile to describe such a system using two conditional single molecule probability distributions. Such an approach is hampered by the inability to predict intermolecular contributions to the total stress, but these should be negligible compared to the intramolecular contributions. Although this approach would not be decisive in testing the hypothesis of whether anisotropic kinetic contributions are fact or fiction, it may prove convincing.

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