

Bead-Spring Polymer Melts

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SYNOPSIS

This analysis of polymer rheology uses conditional probability distributions to describe the phase space dynamics of all macromolecules in a polymer melt. The result is a viscoplastic constitutive equation for the polymer stress. Using conditional probability distributions makes the use of a large number of bead-spring chains in the modeling system possible, but precludes evaluating the intermolecular contribution to the total stress. Both the kinetic and intramolecular contributions are evaluated for a system composed of an arbitrary number of bead-spring chains that interact with one another using molecular dispersion forces. The analysis predicts that the kinetic contribution is isotropic and the intramolecular contribution is viscoplastic. The intermolecular contribution is assumed negligible in comparison to the intramolecular contribution because it results from physical bonds among chains, while the intramolecular contribution results from chemical bonds within a chain.

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INTRODUCTION

Molecular models of polymer melt rheology belong to either of two classes or are a combination of both. The network theories were the first to predict polymer rheology from a molecular viewpoint. To this class belongs such theories as Lodge's rubberlike liquid¹ and the various other adaptations of the classical theory of rubber elasticity.² Appearing later were the phase space kinetic theories, best represented by the work of Curtiss and Bird.³ The most well-known example of a hybrid theory is the "slip link network" model of Doi and Edwards.⁴ Although Curtiss and Bird³ show that the Doi-Edwards model is a limiting case of their theory, its derivation is very different. Tanner⁵ classifies the above-mentioned theories as microstructural to distinguish them from the more empirical theories of continuum mechanics, such as the highly useful K-BKZ theory.^{6,7} With such a diversity of theories, each useful in describing some aspect of polymer rheology, it seems unlikely that a new theory could differ much from those already proposed. This article presents a kinetic theory that shares the fundamental pos-

ulates of statistical mechanics with other kinetic theories, but beyond this little else.

The present work has its origin in previous work of the author that attempted to remedy the flaw in the Rouse-Zimm theories of dilute polymer solutions by providing a mechanism through which the polymer could perturb the solvent.⁸ That work led to a viscoplastic constitutive equation for the polymer material functions in viscometric flow, which is, of course, better suited to describe concentrated solutions and melts. More importantly, it questioned the usefulness of modeling undiluted polymers using single-chain systems.

Ideally, when applying the principles of statistical mechanics, the preferred microscopic system is composed of all of the molecules expected in the macroscopic system. Mathematical difficulties nearly always preclude this. For dilute polymer solutions, using a system containing only one bead-spring chain is realistic because interaction among macromolecules is unlikely. This is not true for undiluted polymers. For them, one must account for the physical bonding among all chains. The theorist's dilemma is to account for the intermolecular interactions expected in undiluted polymers without increasing the mathematical complexity of the model that would render it useless.

Reptation⁹ is one mechanism by which theorists

account for physical bonding among polymer chains and still retain a workable theory. Both the Curtiss–Bird and Doi–Edwards theories use the concept of reptation, but in very different forms. The Curtiss–Bird theory is more similar to the present work.

Curtiss and Bird³ begin their analysis in the most rigorous fashion possible: they model an undiluted polymer using a system containing all chains expected in the polymer. To circumvent the tremendous mathematical difficulty that confronts all kinetic theorists addressing this problem, Curtiss and Bird use a truncation approximation in the form of a tensorial Stokes' law. That is, they reduce the problem from one in the phase space of all the chains to one in the phase space of a single chain by describing the frictional drag experienced by any bead on the chain using Stokes' law in anisotropic form. Their theory also provides for anisotropic Brownian motion of the beads. This landmark accomplishment makes possible describing undiluted polymers with the computational ease once available only for dilute solutions. As with any approximation, it is not perfect, but points in the direction of further progress.

Although a tensorial Stokes' law enables modeling the physical bonds among chains, it does not enable modeling the intermolecular contribution to the total stress. This is because the intermolecular contribution cannot be described using single-chain probability distributions. However, it is believed that the intermolecular contribution is negligible in comparison to the intramolecular contribution because intramolecular forces are far stronger than intermolecular ones.

Describing undiluted polymer using a single-chain system, enhanced with anisotropic Brownian motion and hydrodynamic drag, predicts that both the kinetic and intramolecular contributions can be anisotropic. While anisotropic predictions for the intramolecular contribution are intuitively satisfactory, using anisotropic predictions for the kinetic contribution is less satisfactory. It is unfortunate that intuition is all there is to rely upon regarding this matter. Experiments have never attempted to distinguish among the various contributions to the total stress. While rheologists know that polymer solutions and melts exhibit normal stress anisotropy, it is not known if this results from one, two, or all of the molecular contributions hypothesized to form the measured macroscopic stress.

The author's discomfort with the notion of anisotropic kinetic contributions stems from the belief that, no matter how restricted the motion of any one macromolecule may be, the net motion of all chains should be isotropic unless the space they oc-

cupy has a preferred direction, such as that caused by an external force field. Thus, it seems necessary to consider the impediments to motion of all macromolecules in the polymer to accurately assess the kinetic contribution. As stated before, mathematical difficulties preclude describing the dynamics of all chains using one many-chain probability distribution over the entire phase space. To overcome this, using conditional probability distributions is proposed.

The present analysis describes the dynamics of each chain present in a polymer melt using a conditional probability distribution. Each distribution function is parametrically dependent upon the dynamic state of all other chains. While this approach has the advantage of directly describing all chains present, it is still unable to predict intermolecular contributions to the total stress. Yet, it predicts the kinetic and the intramolecular contributions, and from these some measure of the drawback caused by using single-chain systems.

Wagner and Demarmels¹⁰ state that "viscoelastic stresses in polymer melts are mainly of entropic nature." Any difference between the ability of the current approach and one using a single-chain system to predict the entropy of a polymer melt should therefore be a measure of the relative effectiveness of each approach. The superiority of using a many-chain system becomes evident upon comparison.

The many-chain analysis used in this article also differs from those of single-chain systems because of its ability to simulate molecular-weight distributions. Although polymers usually possess a distribution of molecular weights, theories based on single-chain systems treat polymers as though they were pure substances with a single molecular weight. In essence, such an approach assumes that the polymers' molecular weights are distributed as the Dirac delta distribution. Using a many-chain system removes this restriction and enables simulating any weight distribution.

The Development begins by describing the molecular system and its notation. Having done this, the formulation for the entropy predicted by this system is contrasted with that of a single-chain system. Then, to further distinguish between the two approaches, the manner in which a many-chain system simulates arbitrary molecular weight distributions is demonstrated. After these preliminary expositions, the system's Lagrangian is presented. The Lagrangian is the heart of this analysis. It links the dynamics of each individual chain with all others. The importance of this becomes evident when evaluating the peculiar velocity fields.

The author visualizes a peculiar velocity as a vector field. The peculiar velocity fields describe the peculiar velocity of any bead on any chain anywhere in the real space of the bead. The vector fields are defined using an “internal” Lagrangian formed by all chains in the system. This procedure, using the internal Lagrangian, is similar to the virial theorem of Clausius.¹¹

Equipped with expressions for the peculiar velocities, the theorem of Liouville is supplemented with Lagrangian mechanics to form the governing equation for the phase space distribution function of each bead-spring chain. Then, using the method of moments, the kinetic and intramolecular contributions to the total stress are evaluated. Using linear, conservative forces for definite predictions, these predictions are compared with those of a single-chain analysis.

DEVELOPMENT

The System

The microscopic system consists of N macromolecules. The macromolecules are modeled as linear, bead-spring chains. A lower case *Latin* subscript, e.g., i, j , etc., labels any quantity as belonging to a certain chain. Lower case Greek subscripts index either beads or springs on any chain. The number of beads on chain i is α_i . The mass of any bead on chain i is m_i .

The dynamics of all chains using N single chain conditional probability distributions is described. The phase space distribution (PSD) function of chain i is denoted by f_i . Each PSD describes the dynamics of one chain in its own phase space. The dynamic state of any chain is parametrically dependent upon the state of all other chains.

The position vector of bead μ on chain i is $\mathbf{r}_{\mu i}$. Its velocity is $\dot{\mathbf{r}}_{\mu i}$. The bulk flow velocity is $\mathbf{u}(\mathbf{r})$, where \mathbf{r} is any position in the melt. The peculiar velocity of bead μ on chain i is defined by the difference:

$$\mathbf{v}_{\mu i} = \dot{\mathbf{r}}_{\mu i} - \mathbf{u}(\mathbf{r}_{\mu i}). \quad (1)$$

System Entropy

Wagner and Demarmels¹⁰ emphasize the importance of the entropic nature of viscoelastic stress toward developing a constitutive equation for polymer melts. To assess the effectiveness of modeling with a many-chain system, let us compare its prediction for the entropy with one based on a single-chain system.

When using a single-chain system, the chain represents any of the N chains presumed to exist in the polymer melt. Let α be the number of beads on that chain, and f be its PSD function. Then, the entropy for the entire melt is

$$S = -Nk_B \prod_{\mu=1}^{\alpha} \int_V d^3\mathbf{r}_{\mu} \int_{\Omega} d^3\mathbf{v}_{\mu} f \ln(f) \quad (2)$$

where k_B is Boltzmann's constant, V is the permissible domain of the configuration space of a single bead, and Ω is that for the velocity space.

Let h designate $\ln(f)$, and $\langle \rangle$ designate the phase space average operator. Using this shorthand notation, eq. (2) becomes

$$S = -Nk_B \langle h \rangle. \quad (3)$$

Now, modeling the same polymer melt using a system containing N bead-spring chains each described by a conditional PSD, the entropy becomes:

$$S = -k_B \prod_{i=1}^N \prod_{\mu=1}^{\alpha_i} \int_V d^3\mathbf{r}_{\mu i} \int_{\Omega} d^3\mathbf{v}_{\mu i} \prod_{j=1}^N f_j \ln \left(\prod_{k=1}^N f_k \right) \quad (4)$$

Let h_k designate $\ln(f_k)$ then, using shorthand notation, eq. (4) becomes:

$$S = -k_B \sum_{k=1}^N \langle h_k \rangle \quad (5)$$

Comparing eq. (3) with (5) shows that the entropy predictions for the two approaches are identical only when $\langle h_k \rangle = \langle h \rangle$ for $k = 1, 2, 3, \dots, N$. That is, the two approaches are equivalent, as far as the entropy is concerned, when the dynamic behavior of all chains is the same. One case where this condition is not satisfied is when the polymer melt possesses any molecular weight distribution other than the Dirac delta distribution. Using a many-chain system has the advantage of simulating any molecular weight distribution, and here we see that this influences the prediction for the system's total entropy.

Molecular Weight Distributions

The mass, and therefore the molecular weight, of chain i is $\alpha_i m_i$. Each chain is a distinct species. Although there is only one molecule of species i , both α_i and m_i are arbitrary functions of i . One may vary α_i independently of m_i , but only their product influences the molecular weight distribution. To see

this more clearly, consider the definitions of the number average and weight average molecular weight.

The number average molecular weight for this system is:

$$M_N = \sum_{i=1}^N \alpha_i m_i / N. \quad (6)$$

The weight average is:

$$M_w = \sum_{i=1}^N (\alpha_i m_i)^2 / \left[\sum_{k=1}^N \alpha_k m_k \right]. \quad (7)$$

The ratio of the two is a measure of the polydispersity of the molecular weight distribution:

$$M_w / M_N = N \sum_{i=1}^N (\alpha_i m_i)^2 / \left[\sum_{k=1}^N \alpha_k m_k \right]^2. \quad (8)$$

In eqs. (6), (7), and (8), α_i and m_i always appear as their product with one another. For simulating molecular weight distributions one need only vary the product αm_i as a function of i . However, it may prove useful to vary α_i and m_i independently of one another when simulating other properties of the polymer melt. In those cases it may be useful to vary α_i to describe the polymer's degree of polymerization, and m_i to describe the repeating unit, that is, the monomer.

The Lagrangian

The Lagrangian is the fundamental quantity that links the dynamics of all chains. Although a separate PSD function describes the dynamics for each chain individually, all chains share the same Lagrangian, which describes the system as a whole. The Lagrangian is formed by subtracting the total potential energy of the system from its total kinetic energy. For the many-chain system, it takes the form

$$L = \frac{1}{2} \sum_{i=1}^N \sum_{\mu=1}^{\alpha_i} m_i \dot{\mathbf{r}}_{\mu i} \cdot \dot{\mathbf{r}}_{\mu i} - \Gamma - \Phi - E \quad (9)$$

where Γ is the intermolecular potential, Φ is the intramolecular potential, and E is an external potential.

The intermolecular potential acts among beads on different chains. It has the general functional form

$$\Gamma = \Gamma(\{\mathbf{r}_{\mu i}\}) \quad (10)$$

where the braces signify the set of values contained within.

The intramolecular potential acts between adjacent beads on any one chain. Its functional dependence may be represented as:

$$\Phi = \sum_{i=1}^N \Phi_i(\{\mathbf{r}_{\mu}\}_i) \quad (11)$$

where the subscript i appears outside the braces to indicate the set of values belonging only to chain i .

The external potential corresponds to any energy field that acts on any bead on any chain relative to some external body, that is, a body not contained within the system. Its functional dependence is

$$E = \sum_{i=1}^N E_i = \sum_{i=1}^N \sum_{\mu=1}^{\alpha_i} E_{\mu i}(\mathbf{r}_{\mu i}). \quad (12)$$

That is, the external body acts on any bead independently of all others.

The macroscopic kinetic energy of the system consists solely of that relating to the visible motion of the melt:

$$\frac{1}{2} \sum_{i=1}^N \alpha_i m_i \mathbf{u} \cdot \mathbf{u}. \quad (13)$$

Let E_m represent the macroscopic counterpart to any long-range external potential that acts on the system. Note that only a long-range external potential, such as that caused by gravity, has a macroscopic counterpart. A short-range external potential, such as a wall potential, does not.

Equating the macroscopic counterpart of the Lagrangian with its ensemble average, and using the shorthand notation introduced earlier, yields:

$$\langle L \rangle = \frac{1}{2} \sum_{i=1}^N \alpha_i m_i \mathbf{u} \cdot \mathbf{u} - E_m. \quad (14)$$

Taking the ensemble average of eq. (9) yields:

$$\langle L \rangle = \frac{1}{2} \sum_{i=1}^N \alpha_i m_i \mathbf{u} \cdot \mathbf{u} - E_m + \langle L' \rangle \quad (15)$$

where

$$L' = \frac{1}{2} \sum_{i=1}^N \sum_{\mu=1}^{\alpha_i} m_i \mathbf{v}_{\mu i} \cdot \mathbf{v}_{\mu i} - \Gamma - \Phi. \quad (16)$$

Name L' the system's internal Lagrangian. Subtracting eq. (14) from (15) yields:

$$\langle L' \rangle = 0. \quad (17)$$

Because $\langle \rangle$ signifies an ensemble average over an arbitrary phase space, set $L' = 0$ to satisfy eq. (17). Equating the internal Lagrangian to zero forms a conservation equation that links the kinetic energy of the peculiar velocities with the intra-system potential energy. It defines the peculiar velocity fields.

Peculiar Velocity Fields

A peculiar velocity is a vector field. Because a many-chain system uses all molecules expected in a polymer melt, the author believes that all molecular interactions should be conservative. This suggests that the peculiar velocities are irrotational fields, and therefore derivable from a scalar velocity potential. Let ϕ be the peculiar velocity potential. Then the peculiar velocities are given by:

$$\mathbf{v}_{\mu i} = \partial\phi/\partial\mathbf{r}_{\mu i}. \quad (18)$$

Using (18) in (16), and equating the internal Lagrangian to zero, yields:

$$2(\Gamma + \Phi) = \sum_{i=1}^N \sum_{\mu=1}^{\alpha_i} m_i (\partial\phi/\partial\mathbf{r}_{\mu i})^2. \quad (19)$$

Equation (19) is a nonlinear, first order, partial differential equation for ϕ . Not having an established procedure for solving this nonlinear equation, rewrite it as though it were linear:

$$2(\Gamma + \Phi) = \sum_{i=1}^N \sum_{\mu=1}^{\alpha_i} a_{\mu i} \partial\phi/\partial\mathbf{r}_{\mu i} \quad (20)$$

where

$$a_{\mu i} = m_i \partial\phi/\partial\mathbf{r}_{\mu i}. \quad (21)$$

The method of characteristics, applied to eq. (20), suggests

$$dt = d\mathbf{r}_{\mu i}/a_{\mu i} = d\phi/[2(\Gamma + \Phi)] \quad (22)$$

where t is a parameter measured along a characteristic line. Integrating along the characteristic lines yields:

$$\mathbf{r}_{\mu i} = \int dt a_{\mu i} \quad (23a)$$

$$\phi = 2 \int dt (\Gamma + \Phi). \quad (23b)$$

Now, differentiating (23b) with respect to $\mathbf{r}_{\mu i}$ yields:

$$\partial\phi/\partial\mathbf{r}_{\mu i} = 2(\Gamma + \Phi)\partial t/\partial\mathbf{r}_{\mu i}. \quad (24)$$

Summing eq. (23a) over all μ and i , then inverting, yields the function

$$t = t(\{\mathbf{r}_{\mu i}\}). \quad (25)$$

It follows then, that:

$$dt/d\mathbf{r}_{\mu i} = \alpha_T \partial t/\partial\mathbf{r}_{\mu i} \quad (26)$$

where:

$$\alpha_T = \sum_{j=1}^N \alpha_j \quad (27)$$

is the total number of beads in the system.

Using (26) in (24) yields:

$$\partial\phi/\partial\mathbf{r}_{\mu i} = 2(\Gamma + \Phi)/(\alpha_T a_{\mu i}). \quad (28)$$

Using the definition of the $a_{\mu i}$ in (28) yields:

$$(\partial\phi/\partial\mathbf{r}_{\mu i})^2 = 2(\Gamma + \Phi)/(\alpha_T m_i). \quad (29)$$

Hence, the magnitude of a peculiar velocity is

$$v_{\mu i} = [2(\Gamma + \Phi)/(\alpha_T m_i)]^{1/2}. \quad (30)$$

To obtain an implicit relation for ϕ , integrate (29) with respect to $\mathbf{r}_{\mu i}$ to find

$$\phi = 2/(3\alpha_T m_i) \int d\mathbf{r}_{\mu i} \cdot \partial\mathbf{r}_{\mu i}/\partial\phi (\Gamma + \Phi) + F(\{\mathbf{r}_{\theta j}\}) \quad (31)$$

where $F(\{\mathbf{r}_{\theta j}\})$ is a constant of the integration for θ not equal to μ or j not equal to i . Taking the gradient of (31) yields:

$$\mathbf{v}_{\mu i} \mathbf{v}_{\mu i} = \frac{2}{3} (\Gamma + \Phi)/(\alpha_T m_i) \delta \quad (32)$$

where δ is the unit tensor. Equations (30) and (32) give the necessary information regarding the peculiar velocity fields.

Lagrangian Mechanics and the Liouville Theorem

The basis for this development is the Liouville theorem. Each of the N conditional probability distributions, f_i , satisfies the Liouville equation, each in its own respective phase space:

$$\partial f_i / \partial t = - \sum_{\mu=1}^{\alpha_i} [\partial / \partial \mathbf{r}_{\mu i} \cdot f_i \dot{\mathbf{r}}_{\mu i} + \partial / \partial \dot{\mathbf{r}}_{\mu i} \cdot f_i \ddot{\mathbf{r}}_{\mu i}] \quad (33)$$

for chains $i = 1, 2, 3, \dots, N$, and where t represents time.

Supplement the Liouville equation with Lagrangian mechanics to relate the forces to the accelerations. For each bead there is a Lagrangian equation of motion,

$$d(\partial L / \partial \dot{\mathbf{r}}_{\mu i}) / dt - \partial L / \partial \mathbf{r}_{\mu i} = \mathbf{0}. \quad (34)$$

Using the Lagrangian function of eq. (9) in (34), and assuming that the energy potentials are conservative, yields:

$$m_i \ddot{\mathbf{r}}_{\mu i} = -\partial(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} \quad (35)$$

where

$$\ddot{\mathbf{r}}_{\mu i} = d\dot{\mathbf{r}}_{\mu i} / dt - \frac{1}{2} (\dot{\mathbf{r}}_{\mu i} \cdot \partial \dot{\mathbf{r}}_{\mu i} / \partial \mathbf{r}_{\mu i} + \partial \dot{\mathbf{r}}_{\mu i} / \partial \mathbf{r}_{\mu i} \cdot \dot{\mathbf{r}}_{\mu i}) \quad (36)$$

is reference frame indifferent.

Substituting eq. (35) into (33), and using the definition of the substantial derivative,

$$D/Dt = \partial / \partial t + \sum_{\mu=1}^{\alpha_i} \mathbf{u}(\mathbf{r}_{\mu i}) \cdot \partial / \partial \mathbf{r}_{\mu i} \quad (37)$$

yields the governing equation for the PSD:

$$\begin{aligned} Df_i / Dt = & - \sum_{\mu=1}^{\alpha_i} \partial / \partial \mathbf{r}_{\mu i} \cdot f_i \mathbf{v}_{\mu i} \\ & + 1/m_i \sum_{\mu=1}^{\alpha_i} \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} \\ & \cdot [\partial f_i / \partial \mathbf{v}_{\mu i} + (\partial \mathbf{u} / \partial \mathbf{r}_{\mu i})^{-1} \cdot \partial f_i / \partial \mathbf{r}_{\mu i}]. \quad (38) \end{aligned}$$

Equation (38) is subject to the boundary conditions that f_i is finite on V and Ω , and vanishes outside of them. If one could solve eq. (38), subject to these conditions, one would have the information needed to evaluate any statistical property of the system. Doing so is the most desirable approach, but also formidable. Rather than solve eq. (38) directly, it is

customary to use the method of moments to evaluate those moments of the distribution needed to predict the various contributions to the polymer stress.

Polymer Stress

Describing a many-chain system using N conditional probability distributions precludes evaluating the intermolecular contribution to the total stress. The intermolecular contribution results from physical bonding among the chains, and should, therefore, be negligible in comparison to the intramolecular contribution, which results from chemical bonds within a chain. Analyses based on single-chain systems have always implicitly assumed this. Note that this is not that physical bonds among chains are without effect. While their direct contribution is negligible, the physical bonds modify the kinetic and intramolecular contributions to the total stress. Keeping this in mind, the total stress in the melt is

$$\mathbf{T} = \sigma^{(k)} + \sigma \quad (39)$$

where $\sigma^{(k)}$ is the kinetic contribution and σ is the intramolecular contribution.

The kinetic contribution results from the peculiar motion of the beads. It is defined as

$$\sigma^{(k)} = \sum_{i=1}^N \sum_{\theta=1}^{\alpha_i} \sigma_{\theta i}^{(k)} = \sum_{i=1}^N \sum_{\theta=1}^{\alpha_i} m_i \langle \mathbf{v}_{\theta i} \mathbf{v}_{\theta i} \rangle. \quad (40)$$

By definition, the kinetic contribution must be symmetric.

The intramolecular contribution results from the tension in the springs of the chains as they straddle a plane. It is defined as

$$\sigma = \sum_{i=1}^N \sum_{\theta=1}^{\alpha_i} \sigma'_{\theta i} = \sum_{i=1}^N \sum_{\theta=1}^{\alpha_i} \langle \mathbf{Q}'_{\theta i} \mathbf{F}'_{\theta i} \rangle. \quad (41)$$

The primes indicate a transformation to normal coordinates. $\mathbf{Q}_{\theta i}$ is the spring vector, defined as

$$\mathbf{Q}_{\theta i} = (\mathbf{r}_{(\mu+1)i} - \mathbf{r}_{\mu i}) \delta_{\theta \mu} (1 - \delta_{\mu \alpha_i}) \quad (42)$$

where $\delta_{\theta \mu}$ is Kronecker's delta. $\mathbf{F}_{\theta i}$ is the force directed along the spring. For a conservative intramolecular potential, it is given by

$$\mathbf{F}_{\theta i} = -\partial \Phi / \partial \mathbf{Q}_{\theta i}. \quad (43)$$

Note that, by its definition, the intramolecular contribution need not be symmetric.

Kinetic Contribution

The governing equation for the kinetic contribution is found by evaluating the appropriate moment of (38). Multiplying (38) with

$$m_i \delta(\mathbf{r}_{\theta i} - \mathbf{r}) \mathbf{v}_{\theta i} \mathbf{v}_{\theta i} \prod_{k=1}^N f_k / f_i \quad (44)$$

where $\delta(\mathbf{r}_{\theta i} - \mathbf{r})$ is the Dirac delta distribution, and averaging over the entire phase space, yields

$$\begin{aligned} D\sigma_{\theta i}^{(k)}/Dt &= - \prod_{j=1}^N \prod_{\tau=1}^{\alpha_j} m_i \int_V d^3 \mathbf{r}_{\tau j} \\ &\cdot \int_{\Omega} d^3 \mathbf{v}_{\tau j} \delta(\mathbf{r}_{\theta i} - \mathbf{r}) \mathbf{v}_{\theta i} \mathbf{v}_{\theta i} \prod_{k=1}^N f_k / f_i \sum_{\mu=1}^{\alpha_i} \partial / \partial \mathbf{r}_{\mu i} \cdot f_i \mathbf{v}_{\mu i} \\ &+ \prod_{j=1}^N \prod_{\tau=1}^{\alpha_j} \int_V d^3 \mathbf{r}_{\tau j} \int_{\Omega} d^3 \mathbf{v}_{\tau j} \delta(\mathbf{r}_{\theta i} - \mathbf{r}) \mathbf{v}_{\theta i} \mathbf{v}_{\theta i} \prod_{k=1}^N f_k / \\ &f_i \sum_{\mu=1}^{\alpha_i} \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} \cdot \partial f_i / \partial \mathbf{v}_{\mu i} \\ &+ \prod_{j=1}^N \prod_{\tau=1}^{\alpha_j} \int_V d^3 \mathbf{r}_{\tau j} \int_{\Omega} d^3 \mathbf{v}_{\tau j} \delta(\mathbf{r}_{\theta i} - \mathbf{r}) \mathbf{v}_{\theta i} \mathbf{v}_{\theta i} \prod_{k=1}^N f_k / \\ &f_i \sum_{\mu=1}^{\alpha_i} \partial f_i / \partial \mathbf{r}_{\mu i} \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} : \\ &(\partial \mathbf{u} / \partial \mathbf{r}_{\mu i})^{-1}. \quad (45) \end{aligned}$$

Consider each integration term on the right-hand side (rhs) of (45) separately.

Applying chain-rule differentiation, and using shorthand notation, the first term becomes:

$$m_i \sum_{\mu=1}^{\alpha_i} \langle \langle \mathbf{v}_{\mu i} \cdot \partial(\mathbf{v}_{\theta i} \mathbf{v}_{\theta i}) / \partial \mathbf{r}_{\mu i} \rangle \rangle. \quad (46)$$

Applying chain-rule differentiation to the second term shows that it vanishes because $\Gamma + \Phi + E$ is not a function of the velocities. Chain-rule differentiation applied to the third term yields:

$$\begin{aligned} - \sum_{\mu=1}^{\alpha_i} \langle \langle \mathbf{v}_{\theta i} \mathbf{v}_{\theta i} \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} / \partial \mathbf{r}_{\mu i} \rangle \rangle : \\ (\partial \mathbf{u} / \partial \mathbf{r})^{-1}. \quad (47) \end{aligned}$$

Combining all terms yields:

$$\begin{aligned} D\sigma_{\theta i}^{(k)}/Dt &= m_i \sum_{\mu=1}^{\alpha_i} \langle \langle \mathbf{v}_{\mu i} \cdot \partial(\mathbf{v}_{\theta i} \mathbf{v}_{\theta i}) / \partial \mathbf{r}_{\mu i} \rangle \rangle \\ &- \sum_{\mu=1}^{\alpha_i} \langle \langle \mathbf{v}_{\theta i} \mathbf{v}_{\theta i} \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} / \partial \mathbf{r}_{\mu i} \rangle \rangle : \\ &(\partial \mathbf{u} / \partial \mathbf{r})^{-1}. \quad (48) \end{aligned}$$

When neglecting all density gradients, one must set $E = 0$ on V because an effect of E is to create a density gradient. Use linear forces for both the intra- and intermolecular interactions. Let

$$\partial^2 \Gamma / \partial \mathbf{r}_{\mu i} / \partial \mathbf{r}_{\mu i} = \mathbf{I} \quad (49a)$$

$$\partial^2 \Phi / \partial \mathbf{r}_{\mu i} / \partial \mathbf{r}_{\mu i} = \mathbf{H} \quad (49b)$$

where \mathbf{H} and \mathbf{I} are arbitrary (constant) second-order tensors. Taking \mathbf{H} and \mathbf{I} independent of the indices μ and i implies, without loss of generality, that all springs on all chains obey the same Hooke's law.

Using eqs. (49) in (48) yields

$$\begin{aligned} D\sigma_{\theta i}^{(k)}/Dt + \alpha_i / m_i (\mathbf{I} + \mathbf{H}) : (\partial \mathbf{u} / \partial \mathbf{r})^{-1} \sigma_{\theta i}^{(k)} \\ = m_i \sum_{\mu=1}^{\alpha_i} \langle \langle \mathbf{v}_{\mu i} \cdot \partial(\mathbf{v}_{\theta i} \mathbf{v}_{\theta i}) / \partial \mathbf{r}_{\mu i} \rangle \rangle. \quad (50) \end{aligned}$$

Assuming irrotational peculiar velocity fields, eqs. (30) and (32) show that

$$\begin{aligned} \mathbf{v}_{\mu i} \cdot \partial(\mathbf{v}_{\theta i} \mathbf{v}_{\theta i}) / \partial \mathbf{r}_{\mu i} &= \frac{2}{3} 2^{1/2} / (\alpha_T m_i)^{3/2} (\Gamma + \Phi)^{1/2} \\ &\cdot \partial(\Gamma + \Phi) / \partial \mathbf{r}_{\mu i} \delta. \quad (51) \end{aligned}$$

Using eq. (51) in (50) yields

$$\begin{aligned} D\sigma_{\theta i}^{(k)}/Dt + \alpha_i / m_i (\mathbf{I} + \mathbf{H}) : (\partial \mathbf{u} / \partial \mathbf{r})^{-1} \sigma_{\theta i}^{(k)} \\ = \frac{2}{3} (2 / m_i)^{1/2} / \\ \alpha_T^{3/2} \sum_{\mu=1}^{\alpha_i} \langle \langle (\Gamma + \Phi)^{1/2} \partial(\Gamma + \Phi) / \partial \mathbf{r}_{\mu i} \rangle \rangle \delta. \quad (52) \end{aligned}$$

Equation (52) is the governing equation for the kinetic contribution when using linear forces and irrotational peculiar velocity fields. It predicts that the kinetic contribution to the total stress is isotropic.

Intramolecular Contribution

Configuration Space Distribution

As with the kinetic contribution, the governing equation for the intramolecular contribution is found using the method of moments. However, information regarding the velocity space dynamics is not needed. Therefore, it is customary to average the governing equation for the PSD over the velocity space to form the governing equation for the configuration space distribution (CSD). The intramolecular contribution is then evaluated from moments of the CSD.

Let g_i signify the CSD function for chain i . Define it as

$$g_i = \prod_{j=1}^N \prod_{\theta=1}^{\alpha_j} \int_{\Omega} d^3 \mathbf{v}_{\theta j} f_i. \quad (53)$$

Averaging eq. (38) over the velocity yields:

$$\begin{aligned} Dg_i/Dt = & - \sum_{\mu=1}^{\alpha_i} \prod_{j=1}^N \prod_{\theta=1}^{\alpha_j} \int_{\Omega} d^3 \mathbf{v}_{\theta j} \partial/\partial \mathbf{r}_{\mu i} \cdot f_i \mathbf{v}_{\mu i} \\ & + 1/m_i \sum_{\mu=1}^{\alpha_i} \prod_{j=1}^N \prod_{\theta=1}^{\alpha_j} \int_{\Omega} d^3 \mathbf{v}_{\theta j} \partial(\Gamma + \Phi + E)/ \\ & \partial \mathbf{r}_{\mu i} \cdot \partial f_i / \partial \mathbf{v}_{\mu i} + 1/m_i \sum_{\mu=1}^{\alpha_i} \prod_{j=1}^N \prod_{\theta=1}^{\alpha_j} \int_{\Omega} d^3 \mathbf{v}_{\theta j} \partial f_i / \\ & \partial \mathbf{r}_{\mu i} \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} : (\partial \mathbf{u} / \partial \mathbf{r}_{\mu i})^{-1}. \quad (54) \end{aligned}$$

Consider each integration term on the rhs separately.

Chain-rule differentiation shows that the first term is zero by definition of the peculiar velocity. Applying chain-rule differentiation to the second term shows that it vanishes because $\Gamma + \Phi + E$ is not a function of the peculiar velocities. By definition of the CSD, the third term reduces to

$$1/m_i \sum_{\mu=1}^{\alpha_i} \partial g_i / \partial \mathbf{r}_{\mu i} \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} : (\partial \mathbf{u} / \partial \mathbf{r}_{\mu i})^{-1}. \quad (55)$$

Combining all terms yields:

$$m_i Dg_i/Dt = \sum_{\mu=1}^{\alpha_i} \partial g_i / \partial \mathbf{r}_{\mu i} \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_{\mu i} : (\partial \mathbf{u} / \partial \mathbf{r}_{\mu i})^{-1}. \quad (56)$$

As is customary, transform the independent variables from the set of bead coordinates $\{\mathbf{r}_{\mu i}\}$ to the

set of internal, or spring, coordinates $\{\mathbf{Q}_{\theta i}\}$, $\theta = 1, 2, 3, \dots, \alpha_i - 1$, and the center of mass coordinates, \mathbf{r}_i . The center of mass position vector for chain i is given by

$$\mathbf{r}_i = 1/\alpha_i \sum_{\mu=1}^{\alpha_i} \mathbf{r}_{\mu i}. \quad (57)$$

Transform the bead position vectors to the spring vectors using

$$\mathbf{Q}_{\theta i} = \sum_{\mu=1}^{\alpha_i} B_{\theta \mu} \mathbf{r}_{\mu i}. \quad (58)$$

Transforming variables in (56), and neglecting any density variations in the melt, yields:

$$\begin{aligned} m_i Dg_i/Dt = & \alpha_i \sum_{\theta=1}^{\alpha_i-1} \sum_{\mu=1}^{\alpha_i-1} A_{\theta \mu} \partial g_i / \\ & \partial \mathbf{Q}_{\theta i} \partial(\Gamma + \Phi) / \partial \mathbf{Q}_{\mu i} : (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1} \quad (59) \end{aligned}$$

where:

$$A_{\theta \mu} = \sum_{\tau=1}^{\alpha_i-1} B_{\theta \tau} B_{\mu \tau} \quad (60)$$

is the Rouse matrix of dilute solution theory. Note that one must set $E = 0$ on V when assuming a uniform density.

Method of Moments

Define the configuration space average operator as

$$\langle \rangle = \prod_{j=1}^N \prod_{\epsilon=1}^{\alpha_j} \int_V d^3 \mathbf{Q}_{\epsilon j} \prod_{k=1}^N g_k. \quad (61)$$

Multiplying eq. (59) with

$$\mathbf{Q}_{\tau i} \partial \Phi / \partial \mathbf{Q}_{\tau i} \prod_{k=1}^N g_k / g_i \quad (62)$$

and averaging over the configuration space yields

$$\begin{aligned} m_i D\sigma_{\tau i}/Dt = & \alpha_i \sum_{\theta=1}^{\alpha_i-1} \sum_{\mu=1}^{\alpha_i-1} A_{\theta \mu} \prod_{j=1}^N \prod_{\epsilon=1}^{\alpha_j} \int_V d^3 \mathbf{Q}_{\epsilon j} \mathbf{Q}_{\tau i} \partial \Phi / \\ & \partial \mathbf{Q}_{\tau i} \prod_{k=1}^N g_k \partial \ln(g_i) / \partial \mathbf{Q}_{\theta i} \partial(\Gamma + \Phi) / \partial \mathbf{Q}_{\mu i} : \\ & (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1}. \quad (63) \end{aligned}$$

Applying chain-rule differentiation several times to the integrand of (63), rearranging, and using the operator of (61), yields:

$$m_i D\sigma_{\tau i}/Dt = \alpha_i \sum_{\theta=1}^{\alpha_i-1} \sum_{\mu=1}^{\alpha_i-1} A_{\theta\mu} \cdot \left[\left(\partial\beta_i/\partial Q_{\theta i} - \sum_{k=1}^N \partial\beta_k/\partial Q_{\theta i} \right) \cdot Q_{\tau i} \partial\Phi/\partial Q_{\tau i} \partial(\Gamma + \Phi)/\partial Q_{\mu i} \right. \\ \left. - \partial(Q_{\tau i} \partial\Phi/\partial Q_{\tau i})/\partial Q_{\theta i} \partial(\Gamma + \Phi)/\partial Q_{\mu i} \right. \\ \left. - Q_{\tau i} \partial\Phi/\partial Q_{\tau i} \partial^2(\Gamma + \Phi)/\partial Q_{\theta i} \partial Q_{\mu i} \right] : \\ (\partial u/\partial r_i)^{-1} \quad (64)$$

where β_i is defined as

$$\beta_i = \ln(g_i). \quad (65)$$

Chain Configuration Entropy

Note that β_i is the logarithm of a chain's CSD, while h_i , used to evaluate the system's total entropy, is the logarithm of a chain's PSD. Having first averaged over the velocity space to form g_i , β_i lost all information regarding the velocity space dynamics of chain i . Therefore, while $-k_B \langle h_i \rangle$ can be viewed as one chain's total entropy, $-k_B \beta_i$ must then be viewed as the chain's configuration entropy because the logarithmic and ensemble average operations do not commute.

Transforming independent variables in eq. (64) to normal coordinates, using the orthogonal transformation of the Rouse matrix, yields⁸

$$m_i D\sigma'_{\tau i}/Dt \\ + \sum_{\theta=1}^{\alpha_i-1} a_{\theta} \partial(Q'_{\tau i} \partial\Phi/\partial Q'_{\tau i})/\partial Q'_{\theta i} \partial(\Gamma + \Phi)/\partial Q'_{\theta i} \\ + Q'_{\tau i} \partial\Phi/\partial Q'_{\tau i} \partial^2(\Gamma + \Phi)/\partial Q'_{\theta i} \partial Q'_{\theta i} : (\partial u/\partial r_i)^{-1} \\ = \sum_{\theta=1}^{\alpha_i-1} a_{\theta} \left(\partial\beta_i \partial Q'_{\theta i} - \sum_{k=1}^N \partial\beta_k \partial Q'_{\theta i} \right) Q'_{\tau i} \partial\Phi \\ \partial Q'_{\tau i} \partial(\Gamma + \Phi)/\partial Q'_{\theta i} : (\partial u/\partial r_i)^{-1} \quad (66)$$

where a_{θ} , $\theta = 1, 2, 3, \dots, \alpha_i - 1$, are the eigenvalues

of the Rouse matrix and the primes signify eigenvectors.

From eq. (66), if

$$\partial\beta_k/\partial Q'_{\theta i} = 0 \quad (67)$$

for i not equal to k , then the rhs of (66) vanishes and (66) becomes identical to the governing equation for σ'_{τ} found for a single chain system.⁸ In ref. 8, Γ is the solvent-polymer intermolecular potential instead of the polymer-polymer intermolecular potential that it is here. Equation (67) says that the logarithm of the CSD function for any chain is not a function of the internal coordinates of any other chain. When this restriction is satisfied, as far as the intramolecular contribution is concerned, the analysis effectively reduces to one of modeling with a single chain.

However, the basic premise of this analysis is that the dynamic state of any chain depends upon the state of other chains. Eq. (66) indicates that one must know β_i as a function of the internal coordinates of the other chains. To find the governing equation for β_i , return to eq. (59) and divide it by g_i . In normal form, it becomes

$$m_k D\beta_k/Dt = \sum_{\theta=1}^{\alpha_k-1} a_{\theta} \partial\beta_k/\partial Q'_{\theta k} \partial(\Gamma + \Phi)/\partial Q'_{\theta k} : \\ (\partial u/\partial r_k)^{-1}. \quad (68)$$

Solving (68) for β_k as a function of time and the internal coordinates of all chains is difficult. Fortunately, it is unnecessary because one need not know β_k in its entirety, but only its derivatives with respect to the internal coordinates of other chains. Therefore, follow this procedure:

Rearrange eq. (68) by applying chain-rule differentiation to its rhs. Write the result as

$$m_k D\beta_k/Dt \\ + \beta_k \sum_{\theta=1}^{\alpha_k-1} a_{\theta} \partial^2(\Gamma + \Phi)/\partial Q'_{\theta k} \partial Q'_{\theta k} : (\partial u/\partial r_k)^{-1} \\ = \sum_{\theta=1}^{\alpha_k-1} a_{\theta} \partial[\beta_k \partial(\Gamma + \Phi)/\partial Q'_{\theta k}] / \partial Q'_{\theta k} : \\ (\partial u/\partial r_k)^{-1}. \quad (69)$$

Restrict eq. (69) to a nonequilibrium stationary state. Rearrange and write the result as

$$\beta_k = \sum_{\theta=1}^{\alpha_k-1} a_\theta \partial[\beta_k \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\theta k}] / \partial \mathbf{Q}'_{\theta k} : (\partial \mathbf{u} / \partial \mathbf{r}_k)^{-1} / \left[\sum_{\mu=1}^{\alpha_k-1} a_\mu \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_{\mu k} / \partial \mathbf{Q}'_{\mu k} : (\partial \mathbf{u} / \partial \mathbf{r}_k)^{-1} \right]. \quad (70)$$

Equation (70) is an implicit relation for β_k , which one may solve using the method of direct substitution.

To form an initial guess, recall that at equilibrium

$$\beta_k = -(\Gamma + \Phi) / (N k_B T) \quad (71)$$

where T is the absolute temperature and the factor $1/N$ accounts for the fact that each of the N chains contributes $1/N$ of the total. Therefore, use

$$\beta_k = -c_k(\Gamma + \Phi) / (k_B T) \quad (72)$$

as the initial guess, where c_k is an unknown constant. The reason for using the unknown constant c_k will become clear.

Using (72) in the rhs of eq. (70) yields

$$\beta_k = -c_k / (k_B T) \left[\Gamma + \Phi + \sum_{\theta=1}^{\alpha_k-1} a_\theta \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\theta k} \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\theta k} : (\partial \mathbf{u} / \partial \mathbf{r}_k)^{-1} / \left(\sum_{\mu=1}^{\alpha_k-1} a_\mu \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_{\mu k} / \partial \mathbf{Q}'_{\mu k} : (\partial \mathbf{u} / \partial \mathbf{r}_k)^{-1} \right) \right]. \quad (73)$$

Usually, one continues iterating until the output equals the input. However, only derivatives of β_k are needed, and when using linear forces this one iteration suffices.

Differentiating eq. (73) with respect to $\mathbf{Q}'_{\theta i}$ yields

$$\begin{aligned} \partial \beta_k / \partial \mathbf{Q}'_{\theta i} &= -c_k / (k_B T) \left[\partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\theta i} \right. \\ &+ \partial \left[\sum_{\tau=1}^{\alpha_k-1} a_\tau \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\tau k} \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\tau k} : (\partial \mathbf{u} / \partial \mathbf{r}_k)^{-1} / \left(\sum_{\mu=1}^{\alpha_k-1} a_\mu \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_{\mu k} / \partial \mathbf{Q}'_{\mu k} : (\partial \mathbf{u} / \partial \mathbf{r}_k)^{-1} \right) \right] / \partial \mathbf{Q}'_{\theta i} \left. \right]. \quad (74) \end{aligned}$$

Restrict Γ and Φ to linear forces of the form

$$\partial \Gamma / \partial \mathbf{Q}'_{\theta i} = \mathbf{I} \cdot (\mathbf{Q}'_{\theta i} - \mathbf{b}) \quad (75a)$$

$$\partial \Phi / \partial \mathbf{Q}'_{\theta i} = \mathbf{H} \cdot (\mathbf{Q}'_{\theta i} - \mathbf{d}) \quad (75b)$$

where \mathbf{I} , \mathbf{H} , \mathbf{b} , and \mathbf{d} are constants. Note that \mathbf{I} and \mathbf{H} are not necessarily the same tensors used in (49). Then, using eqs. (75) in (74) yields

$$\partial \beta_k / \partial \mathbf{Q}'_{\theta i} = -c_k / (k_B T) \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\theta i} \quad (76)$$

for i not equal to k . Equation (76) is identical to the result that one finds when differentiating the initial guess. Since one need not evaluate the case where i equals k , because it cancels itself in (66), this one iteration suffices by providing the derivatives that are needed.

The factor c_k shows that one arrives at the result (76) only to within an unknown (constant) factor. Using (76) one finds

$$\begin{aligned} \partial \beta_i / \partial \mathbf{Q}'_{\theta i} &- \sum_{k=1}^N \partial \beta_k / \partial \mathbf{Q}'_{\theta i} \\ &= -1 / (k_B T) \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\theta i} \sum_{k=1}^N (1 - \delta_{ki}) c_k. \quad (77) \end{aligned}$$

The sum of $(1 - \delta_{ki}) c_k$ over all k is just another constant. Let G_i designate it, then

$$\begin{aligned} \partial \beta_i / \partial \mathbf{Q}'_{\theta i} &- \sum_{k=1}^N \partial \beta_k / \partial \mathbf{Q}'_{\theta i} \\ &= -G_i / (k_B T) \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_{\theta i}. \quad (78) \end{aligned}$$

Short of actually solving for β_k in its entirety, G_i is unknown unless one uses the equilibrium values $c_k = 1/N$ to evaluate it. In that case,

$$G_i = (N - 1) / N \quad (79)$$

which for practical purposes is unity because N is a very large number.

Returning to the governing equation for σ'_{ri} , substitute (78), and the linear force relations of (75), into (66) to find

$$\begin{aligned} m_i D \sigma'_{ri} / Dt &+ 2(\alpha_i - 1)(\mathbf{I} + \mathbf{H}) : (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1} \sigma'_{ri} \\ &+ a_r \setminus (\delta \partial \Phi / \partial \mathbf{Q}'_{ri} + \mathbf{Q}'_{ri} \mathbf{H}) \\ &\cdot [\mathbf{I} \cdot (\mathbf{Q}'_{ri} - \mathbf{b}) + \mathbf{H} \cdot (\mathbf{Q}'_{ri} - \mathbf{d})] \setminus : (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1} \end{aligned}$$

$$\begin{aligned}
 &= -G_i/(k_B T) \sum_{\theta=1}^{\alpha_i-1} a_{\theta} \backslash [(\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \\
 &\quad - \mathbf{I} \cdot \mathbf{b} - \mathbf{H} \cdot \mathbf{d}] \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} [(\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \\
 &\quad - \mathbf{I} \cdot \mathbf{b} - \mathbf{H} \cdot \mathbf{d}] \backslash : (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1}. \quad (80)
 \end{aligned}$$

Equation (80) is exact only for linear forces. Its left-hand side poses no problems because it is handled in the same manner as in ref. 8. However, the terms on the rhs are not present in the single-chain analysis of ref. 8, and must now be evaluated.

Rearranging (80) so that only unknown ensemble averages appear on the rhs yields:

$$\begin{aligned}
 &m_i D \sigma'_{\tau i} / Dt + 2(\alpha_i - 1) [(\mathbf{I} + \mathbf{H}) : (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1} \sigma'_{\tau i} \\
 &\quad + G_i / (k_B T) (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \sigma'_{\tau i} (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) : \\
 &\quad (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1}] + a_{\tau} \backslash (\delta \partial \Phi / \partial \mathbf{Q}'_{\tau i} + \mathbf{Q}'_{\tau i} \mathbf{H}) \\
 &\quad \cdot [(\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\tau i} - \mathbf{I} \cdot \mathbf{b} - \mathbf{H} \cdot \mathbf{d}] \backslash : (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1} \\
 &= -G_i / (k_B T) \sum_{\theta=1}^{\alpha_i-1} a_{\theta} [(\mathbf{I} + \mathbf{H}) \\
 &\quad \cdot \backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash \\
 &\quad - (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \backslash \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash \\
 &\quad - (\mathbf{I} + \mathbf{H}) \cdot \backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} \backslash (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d})] \\
 &\quad : (\partial \mathbf{u} / \partial \mathbf{r}_i)^{-1}. \quad (81)
 \end{aligned}$$

Equation (81) contains ensemble averages of three new quantities:

$$\backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash \quad (82a)$$

$$\backslash \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash \quad (82b)$$

$$\backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} \backslash. \quad (82c)$$

Equilibrium Averaging Approximation

All three moments in (82) are of higher order than $\sigma'_{\tau i}$. This is unfortunate because it means that one cannot obtain the governing equations for these ensemble averages, using the method of moments, without introducing even higher order moments. This is the so-called closure problem, the bane of the method of moments. Unable to evaluate the ensemble averages in (82) rigorously, one is forced to approximate.

The three unknown averages result from the dependence of the dynamic state of any chain upon the internal coordinates of other chains. These av-

erages do not appear when a single-chain system is used. The terms represent an improvement upon a single-chain analysis furnished by using a many-chain system. Therefore, even though one must approximate these averages, they still represent an improvement over a single-chain analysis.

Two remedies are to either assume closure approximations, that is, represent higher order moments using known lower order ones, or evaluate the averages using a known probability distribution, such as that of the equilibrium state. A closure approximation is really a constitutive equation. Unless it is based upon experimental observation or theoretical principles, it has no justification other than mathematical expediency. On the other hand, evaluating the ensemble averages using the equilibrium distribution approximates the exact quantities for small departures from equilibrium. Viewing these terms as corrections to the predictive capability of single-chain analyses, equilibrium averaging seems reasonable.

At equilibrium, the CSD function for any chain is proportional to

$$\exp[-(\Gamma + \Phi)/(Nk_B T)]. \quad (83)$$

The linear force relations of (75) yield quadratic potentials of the form

$$\Gamma = \frac{1}{2} \mathbf{I} : \sum_{k=1}^N \sum_{\theta=1}^{\alpha_k-1} (\mathbf{Q}'_{\theta k} - \mathbf{b})(\mathbf{Q}'_{\theta k} - \mathbf{b}) \quad (84a)$$

$$\Phi = \frac{1}{2} \mathbf{H} : \sum_{k=1}^N \sum_{\theta=1}^{\alpha_k-1} (\mathbf{Q}'_{\theta k} - \mathbf{d})(\mathbf{Q}'_{\theta k} - \mathbf{d}) \quad (84b)$$

to within an additive constant. To find the proportionality constant for (83), multiply the N CSD functions together such that

$$\prod_{i=1}^N g_i = N C_{eq} \exp[-(\Gamma + \Phi)/(k_B T)] \quad (85)$$

where C_{eq} is the normalization constant at equilibrium. Define C_{eq} using:

$$\begin{aligned}
 &C_{eq}^{-1} \\
 &= \prod_{j=1}^N \prod_{\epsilon=1}^{\alpha_j-1} \int_{-\infty}^{\infty} d^3 \mathbf{Q}'_{\epsilon j} \exp[-(\Gamma + \Phi)/(k_B T)]. \quad (86)
 \end{aligned}$$

Equation (86) is greatly simplified if all chains have the same number of beads, that is, $\alpha_i = \alpha$ for all i . As noted before, to simulate arbitrary molecular

weight distributions, one need only vary the product αm_i as a function of i . Therefore, giving all chains the same number of beads retains that capability. With this simplification, and using eqs. (84), eq. (86) becomes

$$C_{eq} = \left[\int_{-\infty}^{\infty} d^3 \mathbf{Q} \exp(-I/(2k_B T)) : (\mathbf{Q} - \mathbf{b})(\mathbf{Q} - \mathbf{b}) - \mathbf{H}/(2k_B T) : (\mathbf{Q} - \mathbf{d})(\mathbf{Q} - \mathbf{d}) \right]^{-N\alpha}. \quad (87)$$

The normalization constant C_{eq} must be finite for all values of the force parameters \mathbf{I} , \mathbf{H} , \mathbf{b} , and \mathbf{d} , if it is to be used to evaluate any statistical property. For the integral of (85) to exist, the rate of decay caused by the quadratic terms within the exponential function of the integrand must be greater than the rate of growth of all other terms. This means that there cannot be any bilinear terms of the Cartesian components such as $Q_x Q_y$, $Q_y Q_z$, and $Q_x Q_z$. This places the following constraints on the Cartesian components of \mathbf{I} and \mathbf{H}

$$I_{xy} + H_{xy} + I_{yx} + H_{yx} = 0 \quad (88a)$$

$$I_{yz} + H_{yz} + I_{zy} + H_{zy} = 0 \quad (88b)$$

$$I_{zx} + H_{zx} + I_{xz} + H_{xz} = 0. \quad (88c)$$

These three constraints are one way of saying that the sum $\mathbf{I} + \mathbf{H}$ must be formed by the sum of a diagonal matrix and a skew-symmetric matrix.

Restricting $\mathbf{I} + \mathbf{H}$ with eqs. (88) and integrating (87) yields

$$C_{eq} = (p_x p_y p_z / \pi^3)^{1/2 N\alpha} \exp[N\alpha(s - q_x^2/p_x - q_y^2/p_y - q_z^2/p_z)] \quad (89)$$

where

$$p_x = (I_{xx} + H_{xx})/(2k_B T) \quad (90a)$$

$$p_y = (I_{yy} + H_{yy})/(2k_B T) \quad (90b)$$

$$p_z = (I_{zz} + H_{zz})/(2k_B T) \quad (90c)$$

$$q_x = -[I_{xx} b_x + H_{xx} d_x + (I_{xy} + I_{yx}) b_y + (I_{xz} + I_{zx}) b_z + (H_{xy} + H_{yx}) d_y + (H_{zx} + H_{xz}) d_z]/(2k_B T) \quad (91a)$$

$$q_y = -[I_{yy} b_y + H_{yy} d_y + (I_{xy} + I_{yx}) b_x + (I_{yz} + I_{zy}) b_z + (H_{xy} + H_{yx}) d_x + (H_{yz} + H_{zy}) d_z]/(2k_B T) \quad (91b)$$

$$q_z = -[I_{zz} b_z + H_{zz} d_z + (I_{xz} + I_{zx}) b_x + (I_{yz} + I_{zy}) b_y + (H_{xz} + H_{zx}) d_x + (H_{yz} + H_{zy}) d_y]/(2k_B T) \quad (91c)$$

$$s = (\mathbf{I} : \mathbf{b}\mathbf{b} + \mathbf{H} : \mathbf{d}\mathbf{d})/(2k_B T). \quad (92)$$

Having evaluated the normalization constant, it can now be used in (85) to evaluate the ensemble averages of (82). Rather than evaluating all components of (82), one need only evaluate those components pertinent to the flow field. Assuming homogeneous flow with the gradient

$$\partial \mathbf{u} / \partial \mathbf{r} = \dot{\gamma} \delta_z \delta_x \quad (93)$$

where $\dot{\gamma}$ is the shear rate, requires evaluating only the following components of (82):

$$\backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash : \delta_z \delta_x \quad (94a)$$

$$\backslash \mathbf{Q}'_{\tau i} \partial \phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash : \delta_z \delta_x \quad (94b)$$

$$\backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} \backslash \cdot \delta_x. \quad (94c)$$

Constitutive Equation

To simplify the very lengthy expressions that result from the integrations defining the ensemble averages, use the following notation:

$$\backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash_{eq} : \delta_z \delta_x = N[\delta_{\theta\tau} \mathbf{W}_I + (1 - \delta_{\theta\tau}) \mathbf{W}_{II}] \quad (95a)$$

$$\backslash \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} (\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}'_{\theta i} \backslash_{eq} : \delta_z \delta_x = N[\delta_{\theta\tau} \mathbf{U}_I + (1 - \delta_{\theta\tau}) \mathbf{U}_{II}] \quad (95b)$$

$$\backslash \mathbf{Q}'_{\theta i} \mathbf{Q}'_{\tau i} \partial \Phi / \partial \mathbf{Q}'_{\tau i} \backslash_{eq} \cdot \delta_x = N[\delta_{\theta\tau} \mathbf{J}_I + (1 - \delta_{\theta\tau}) \mathbf{J}_{II}]. \quad (95c)$$

The subscript I on \mathbf{W} , \mathbf{U} , and \mathbf{J} indicates that part which corresponds to the contribution when θ equals τ . Conversely, the subscript II designates the contribution when θ does not equal τ . The subscript eq on the ensemble average operator indicates equilibrium averaging. Note that \mathbf{W} and \mathbf{J} are second-order tensors, but \mathbf{U} is a vector.

Evaluating the ensemble averages using the notation of eqs. (95) for homogeneous flow, and restricting all chains to have the same number of beads, reduces eq. (81) to:

$$\dot{\gamma} m_i D\sigma'_{\tau i} / Dt + 2(\alpha - 1)[(I_{zx} + H_{zx}) \sigma'_{\tau i} + G_i / (k_B T) (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \sigma'_{\tau i} (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) : \delta_z \delta_x]$$

$$\begin{aligned}
 &+ a_r \backslash (\delta \delta \Phi / \delta Q_{ri} + Q_{ri} \mathbf{H}) \\
 &\quad [(\mathbf{I} + \mathbf{H}) \cdot \mathbf{Q}_{ri} - \mathbf{I} \cdot \mathbf{b} - \mathbf{H} \cdot \mathbf{d}] \backslash : \delta_z \delta_x \\
 &= -NG_i / (k_B T) [a_r [(\mathbf{I} + \mathbf{H}) \cdot \mathbf{W}_I \\
 &\quad - (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \mathbf{U}_I - (\mathbf{I} + \mathbf{H}) \cdot \\
 &\quad \mathbf{J}_I (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \cdot \delta_z] + [2(\alpha - 1) - a_r] \\
 &\quad [(\mathbf{I} + \mathbf{H}) \cdot \mathbf{W}_{II} - (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \mathbf{U}_{II} \\
 &\quad - (\mathbf{I} + \mathbf{H}) \cdot \mathbf{J}_{III} (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \cdot \delta_z]] \quad (96)
 \end{aligned}$$

where the elements of the tensors \mathbf{W} and \mathbf{J} and of the vector \mathbf{U} are given in the Appendix.

Equation (96) is similar in form to the prediction of the single chain analysis.⁸ The shear rate multiplies only the time derivative term, thereby predicting viscoplasticity. Consequently, the multi-chain analysis yields constitutive equations of the same character as the single-chain analysis, differing only in that there are more terms containing more physical parameters. As it is the custom in polymer melt rheology to fit the parameters to experimental data, the multi-chain analysis has shown that the use of a single-chain analysis is valid, although it must remain semi-empirical.

CONCLUSIONS

This analysis predicts the rheological behavior of a polymer melt using a microscopic system composed of all the macromolecules expected in the melt. Unlike a single-chain system, using a many chain system enables one to describe molecular weight distributions. As a result, the prediction for the system's entropy differs from that of a single-chain system. The analysis shows that the chain configuration entropy has a marked effect upon the intramolecular contribution to the total stress.

Describing the intramolecular contribution using a many-chain system links the dynamic state of all chains. Specifically, the CSD of any chain depends upon the configuration of all other chains. This link is entropic, resulting from the logarithms of all other CSD functions. Without this coupling, ensemble averages over any one chain suffice to describe the system, and the analysis reduces to that of a single-chain system.

Regardless of the entropic coupling, the analysis predicts a viscoplastic intramolecular contribution just as the single chain system does. Although it was necessary to average three moments in the constitutive equation for the intramolecular contribution

using the equilibrium CSD, doing so has no effect on this fundamental characteristic of the analysis. The prediction of the many-chain system would differ from that of the single-chain system only in the time constants of a transient response and the steady-state values of the material functions. The prediction for viscoplasticity appears to be founded at a more fundamental level.

The prediction for the kinetic contribution to the total stress is little changed in form from that of the single-chain system, but the dynamic state of all chains influences this contribution from any bead on any chain. Each bead affects the motion of all other beads by contributing to form the Lagrangian of the entire system. Yet, for irrotational peculiar velocity fields, the many-chain system predicts that the kinetic contribution is isotropic just as the single-chain system does.

The significant factor deciding the nature of the kinetic contribution appears to be the field structure of the peculiar velocities. Even when using a many-chain system, a complete understanding of the structure of the peculiar velocity fields is lacking. However, using all chains expected in the macroscopic system strongly suggests that the peculiar velocity fields be irrotational.

To the extent that bead-spring chains represent macromolecules, a many-chain system must use only conservative molecular interactions because, otherwise, they would dissipate the energy of all beads until it vanished. That is, one expects the energy of the beads to transform from kinetic to potential energy, and vice versa, but to no other form. Irrotational peculiar velocities are consistent with this notion because a theorem from vector analysis states that the work integral of an irrotational field taken around any closed curve is zero. That is, irrotational peculiar velocity fields have zero circulation, thereby automatically satisfying Kelvin's circulation theorem for all time and guaranteeing that no dissipation occurs.

Unless describing a many-chain system using a single, many-chain probability distribution leads to different results, restricting the peculiar velocities to irrotational fields predicts only isotropic kinetic contributions. As mentioned in previous work,⁸ the kinetic contribution would almost certainly be anisotropic if the peculiar velocity fields possessed a rotational component. To evaluate whether anisotropic kinetic contributions are possible, the issue reduces to whether or not one can include a rotational component for the peculiar velocity fields and still maintain conservative molecular interactions. That is, if one provides for a rotational component

to the peculiar velocity fields, does there exist a theorem or relation that conserves the energy of the beads?

The question remains whether it is necessary, or just sufficient, to restrict the peculiar velocities to irrotational fields to conserve the energy of the beads. According to a well-known theorem in vector analysis, any vector field may be uniquely described as the sum of the gradient of a scalar potential and the curl of a vector potential, if the source densities are zero at infinity. Therefore, in principle, a vector potential may exist, but it could not be defined solely by the internal Lagrangian. At least three other defining relations would have to be found: one for each component of the vector potential. These defining relations must guarantee that the energy of all beads is conserved. However, until it can be shown that these conditions cannot be met, one cannot rule out the possibility of peculiar velocities with a rotational component.

At this time, it is moot to argue for or against predictions of anisotropic kinetic contributions because experiments have yet to distinguish among the various contributions to the total stress. Only predictions for the total stress matter, and even then only the material functions that can be measured. However, this issue is important from a fundamental viewpoint because it can help explain the structure of the peculiar velocity fields. And the peculiar velocities are the *sine qua non* of all kinetic theories.

APPENDIX

Here are the elements of the tensors \mathbf{W} and \mathbf{J} and those of the vector \mathbf{U} that appear in eq. (96). These elements represent the contribution resulting from Lagrangian coupling among the polymer chains. For a single-chain analysis the elements of these quantities are all zero.

$$\begin{aligned}
\mathbf{W}_I = & [H_{xx}(I_{xx} + H_{xx})(\frac{3}{4} + 3q_x^2/p_x + q_x^4/p_x^2)/p_x^2 + (H_{xy}(I_{xy} + H_{xy})(\frac{1}{2} + q_y^2/p_y)/p_y + H_{xz}(I_{zz} + H_{zz})) \\
& \times (\frac{1}{2} + q_z^2/p_z)/p_z)(\frac{1}{2} + q_x^2/p_x)/p_x + (H_{xx}(I_{xy} + H_{xy}) + H_{xy}(I_{xx} + H_{xx}))q_y/p_yq_x/p_x(\frac{3}{2} + q_x^2)/p_x \\
& + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{xx} + H_{xx}))q_y/p_yq_x/p_x(\frac{3}{2} + q_x^2)/p_x + (H_{xx}(I_{zz} + H_{zz}) \\
& + H_{xz}(I_{xx} + H_{xx}))q_x/p_x(\frac{3}{2} + q_x^2)/p_xq_z/p_z + (H_{xy}(I_{zz} + H_{zz}) + H_{xz}(I_{xy} + H_{xy})) \\
& \times (\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_yq_z/p_z + (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z)((I_{xx} + H_{xx})q_x/p_x(\frac{3}{2} + q_x^2)/p_x \\
& + (I_{zy} + H_{zy})(\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_y + (I_{zz} + H_{zz})(\frac{1}{2} + q_x^2/p_x)/p_xq_z/p_z] \delta_x \delta_x \\
& + [H_{xx}(I_{xx} + H_{xx})(\frac{1}{2} + q_x^2/p_x)/p_x(\frac{1}{2} + q_y^2/p_y)/p_y + H_{xy}(I_{xy} + H_{xy})(\frac{3}{4} + 3q_y^2/p_y + q_y^4/p_y^2)/p_y^2 \\
& + H_{xz}(I_{zz} + H_{zz})(\frac{1}{2} + q_y^2/p_y)/p_y(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xx}(I_{xy} + H_{xy}) + H_{xy}(I_{xx} + H_{xx}))q_x/p_xq_y/ \\
& \times p_y(\frac{3}{2} + q_y^2)/p_y + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{xx} + H_{xx}))q_x/p_x(\frac{1}{2} + q_y^2/p_y)/p_yq_z/p_z \\
& + (H_{xy}(I_{zz} + H_{zz}) + H_{xz}(I_{xy} + H_{xy}))q_y/p_y(\frac{3}{2} + q_y^2)/p_yq_z/p_z + (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z) \\
& \times ((I_{xx} + H_{xx})q_x/p_x(\frac{1}{2} + q_y^2/p_y)/p_y + (I_{zy} + H_{zy})q_y/p_y(\frac{3}{2} + q_y^2)/p_y \\
& + (I_{zz} + H_{zz})(\frac{1}{2} + q_y^2/p_y)/p_yq_z/p_z] \delta_y \delta_y + [H_{xx}(I_{xx} + H_{xx})(\frac{1}{2} + q_x^2/p_x)/p_x(\frac{1}{2} + q_z^2/p_z)/p_z \\
& + H_{xy}(I_{xy} + H_{xy})(\frac{1}{2} + q_y^2/p_y)/p_y(\frac{1}{2} + q_z^2/p_z)/p_z + H_{xz}(I_{zz} + H_{zz})(\frac{3}{4} + 3q_z^2/p_z + q_z^4/p_z^2)/p_z^2 \\
& + (H_{xx}(I_{xy} + H_{xy}) + H_{xy}(I_{xx} + H_{xx}))q_x/p_xq_y/p_y(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xx}(I_{zz} + H_{zz}) \\
& + H_{xz}(I_{xy} + H_{xy}))q_x/p_xq_z/p_z(\frac{3}{2} + q_z^2)/p_z + (H_{xy}(I_{zz} + H_{zz}) + (H_{xz}(I_{xy} + H_{xy})))q_y/p_yq_z/p_z(\frac{3}{2} + q_z^2)/p_z \\
& + (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z)((I_{xx} + H_{xx})q_x/p_x(\frac{1}{2} + q_z^2/p_z)/p_z + (I_{zy} + H_{zy})q_y/p_y(\frac{1}{2} + q_z^2/p_z)/p_z \\
& + (I_{zz} + H_{zz})q_z/p_z(\frac{3}{2} + q_z^2)/p_z] \delta_x \delta_z + [H_{xx}(I_{xx} + H_{xx})q_x/p_x(\frac{3}{2} + q_x^2)/p_xq_y/p_y \\
& + H_{xy}(I_{xy} + H_{xy})q_x/p_xq_y/p_y(\frac{3}{2} + q_y^2)/p_y + H_{xz}(I_{zz} + H_{zz})q_x/p_xq_y/p_y(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xx}(I_{xy} + H_{xy}) \\
& + H_{xy}(I_{xx} + H_{xx}))(\frac{1}{2} + q_x^2/p_x)/p_x(\frac{1}{2} + q_y^2/p_y)/p_y + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{xx} + H_{xx})) \\
& \times (\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_yq_z/p_z + (H_{xy}(I_{zz} + H_{zz}) + H_{xz}(I_{xy} + H_{xy}))q_x/p_x(\frac{1}{2} + q_y^2/p_y)/p_yq_z/p_z \\
& + (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z)((I_{xx} + H_{xx})(\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_y + (I_{zy} + H_{zy})q_x/p_x(\frac{1}{2} + q_y^2/p_y)/p_y \\
& + (I_{zz} + H_{zz})q_x/p_xq_y/p_yq_z/p_z] (\delta_x \delta_y + \delta_y \delta_x) + [H_{xx}(I_{xx} + H_{xx})q_x/p_x(\frac{3}{2} + q_x^2)/p_xq_z/p_z
\end{aligned}$$

$$\begin{aligned}
 & + H_{xy}(I_{zy} + H_{zy})q_x/p_xq_y/p_yq_z/p_z + H_{xz}(I_{zz} + H_{zz})q_x/p_xq_z/p_z(\frac{3}{2} + q_z^2)/p_z \\
 & + (H_{xx}(I_{zy} + H_{zy}) + H_{xy}(I_{zx} + H_{zx}))(\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_yq_z/p_z + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{zx} + H_{zx})) \\
 & \times (\frac{1}{2} + q_x^2/p_x)/p_x(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xy}(I_{zz} + H_{zz}) + H_{xz}(I_{zy} + H_{zy}))q_x/p_xq_y/p_y(\frac{1}{2} + q_z^2/p_z)/p_z \\
 & + (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z)((I_{zx} + H_{zx})(\frac{1}{2} + q_x^2/p_x)/p_x + (I_{zy} + H_{zy})q_x/p_xq_y/p_yq_z/p_z(I_{zz} + H_{zz})q_x/ \\
 & p_x(\frac{1}{2} + q_z^2/p_z)/p_z)(\delta_x\delta_z + \delta_z\delta_x) + [H_{xx}(I_{zx} + H_{zx})(\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_yq_z/p_z \\
 & + H_{xy}(I_{zy} + H_{zy})q_y/p_y(\frac{3}{2} + q_y^2)/p_yq_z/p_z + H_{xz}(I_{zz} + H_{zz})q_y/p_yq_z/p_z(\frac{3}{2} + q_z^2)/p_z + (H_{xx}(I_{zy} + H_{zy}) \\
 & + H_{xy}(I_{zx} + H_{zx}))q_x/p_x(\frac{1}{2} + q_y^2/p_y)/p_yq_z/p_z + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{zx} + H_{zx}))q_x/ \\
 & p_xq_y(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xy}(I_{zz} + H_{zz}) + H_{xz}(I_{zy} + H_{zy}))(\frac{1}{2} + q_y^2/p_y)/p_y(\frac{1}{2} + q_z^2/p_z)/p_z \\
 & + (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z)((I_{zx} + H_{zx})q_x/p_xq_y/p_yq_z/p_z + (I_{zy} + H_{zy})(\frac{1}{2} + q_y^2/p_y)/p_yq_z/p_z \\
 & + (I_{zz} + H_{zz})q_y/p_y(\frac{1}{2} + q_z^2/p_z)/p_z](\delta_y\delta_z + \delta_z\delta_y) \quad (97a)
 \end{aligned}$$

$$\begin{aligned}
 W_{II} = & ((I_{zx} + H_{zx})(\frac{1}{2} + q_x^2/p_x)/p_x + (I_{zy} + H_{zy})q_x/p_xq_y/p_y + (I_{zz} + H_{zz})q_x/p_xq_z/p_z)\delta_x \\
 & \times [(H_{xx}(\frac{1}{2} + q_x^2/p_x + d_xq_x)/p_x + H_{xy}q_x/p_x(q_y/p_y + d_y) + H_{xz}q_x/p_x(q_z/p_z + d_z))\delta_x \\
 & + (H_{xx}(q_x/p_x + d_x)q_y/p_y + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_yq_y)/p_y + H_{xz}q_y/p_y(q_z/p_z + d_z))\delta_y \\
 & + (H_{xx}(q_x/p_x + d_x)q_z/p_z + H_{xy}(q_y/p_y + d_y)q_z/p_y + H_{xz}(\frac{1}{2} + q_z^2/p_z + d_zq_z)/p_z)\delta_z] \\
 & + ((I_{zx} + H_{zx})q_x/p_xq_y/p_y + (I_{zy} + H_{zy})(\frac{1}{2} + q_y^2/p_y)/p_y + (I_{zz} + H_{zz})q_y/p_yq_z/p_z)\delta_y \\
 & \times [(H_{xx}(\frac{1}{2} + q_x^2/p_x + d_xq_x)/p_x + H_{xy}q_x/p_x(q_y/p_y + d_y) + H_{xz}q_x/p_x(q_z/p_z + d_z))\delta_x \\
 & + (H_{xx}(q_x/p_x + d_x)q_y/p_y + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_yq_y)/p_y + H_{xz}q_y/p_y(q_z/p_z + d_z))\delta_y \\
 & + (H_{xx}(q_x/p_x + d_x)q_z/p_z + H_{xy}(q_y/p_y + d_y)q_z/p_z + H_{xz}(\frac{1}{2} + q_z^2/p_z + d_zq_z)/p_z)\delta_z] \\
 & + ((I_{zx} + H_{zx})q_x/p_xq_z/p_z + (I_{zy} + H_{zy})q_y/p_yq_z/p_z + (I_{zz} + H_{zz})(\frac{1}{2} + q_z^2/p_z)/p_z)\delta_z[(H_{xx}(\frac{1}{2} + q_x^2/p_x \\
 & + d_xq_x) + H_{xy}q_x/p_x(q_y/p_y + d_y) + H_{xz}q_x/p_x(q_z/p_z + d_z))\delta_x + (H_{xx}(q_x/p_x + d_x)q_y/p_y \\
 & + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_yq_y)/p_y + H_{xz}q_y/p_y(q_z/p_z + d_z))\delta_y + (H_{xx}(q_x/p_x + d_x)q_z/p_z \\
 & + H_{xy}(q_y/p_y + d_y)q_z/p_z + H_{xz}(\frac{1}{2} + q_z^2/p_z + d_zq_z)/p_z)\delta_z] \quad (97b)
 \end{aligned}$$

$$\begin{aligned}
 U_I = & -[H_{xx}(I_{zx} + H_{zx})q_x/p_x(\frac{3}{2} + q_x^2)/p_x + H_{xy}(I_{zy} + H_{zy})q_x/p_x(\frac{1}{2} + q_y^2/p_y)/p_y \\
 & + H_{xz}(I_{zz} + H_{zz})q_x/p_x(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xx}(I_{zy} + H_{zy}) + H_{xy}(I_{zx} + H_{zx}))(\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_y \\
 & + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{zx} + H_{zx}))(\frac{1}{2} + q_x^2/p_x)/p_xq_z/p_z + (H_{xy}(I_{zz} + H_{zz}) \\
 & + H_{xz}(I_{zy} + H_{zy})q_x/p_xq_y/p_yq_z/p_z - (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z)((I_{zx} + H_{zx})(\frac{1}{2} + q_x^2/p_x)/p_x \\
 & + (I_{zy} + H_{zy})q_x/p_xq_y/p_y + (I_{zz} + H_{zz})q_x/p_xq_z/p_z)]\delta_x - [H_{xx}(I_{zx} + H_{zx})(\frac{1}{2} + q_x^2/p_x)/p_xq_y/p_y \\
 & + H_{xy}(I_{zy} + H_{zy})q_y/p_y(\frac{3}{2} + q_y^2)/p_y + H_{xz}(I_{zz} + H_{zz})q_y/p_y(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xx}(I_{zy} + H_{zy}) \\
 & + H_{xy}(I_{zx} + H_{zx}))q_x/p_x(\frac{1}{2} + q_y^2/p_y)/p_y + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{zx} + H_{zx}))q_x/p_xq_y/p_yq_z/p_z \\
 & + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{zy} + H_{zy}))(\frac{1}{2} + q_y^2/p_y)/p_yq_z/p_z - (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z) \\
 & \times ((I_{zx} + H_{zx})q_x/p_xq_y/p_y + (I_{zy} + H_{zy})(\frac{1}{2} + q_y^2/p_y)/p_y + (I_{zz} + H_{zz})q_y/p_yq_z/p_z)]\delta_y \\
 & - [H_{xx}(I_{zx} + H_{zx})(\frac{1}{2} + q_x^2/p_x)/p_xq_z/p_z + H_{xy}(I_{zy} + H_{zy})(\frac{1}{2} + q_y^2/p_y)/p_yq_z/p_z \\
 & + H_{xz}(I_{zz} + H_{zz})q_z/p_z(\frac{3}{2} + q_z^2)/p_z + (H_{xx}(I_{zy} + H_{zy}) + H_{xy}(I_{zx} + H_{zx}))q_x/p_xq_y/p_yq_z/p_z \\
 & + (H_{xx}(I_{zz} + H_{zz}) + H_{xz}(I_{zx} + H_{zx}))q_x/p_x(\frac{1}{2} + q_z^2/p_z)/p_z + (H_{xy}(I_{zz} + H_{zz}) \\
 & + H_{xz}(I_{zy} + H_{zy}))q_y/p_y(\frac{1}{2} + q_z^2/p_z)/p_z - (H_{xx}d_x + H_{xy}d_y + H_{xz}d_z) \\
 & \times ((I_{zx} + H_{zx})q_x/p_xq_z/p_z + (I_{zy} + H_{zy})q_y/p_yq_z/p_z + (I_{zz} + H_{zz})(\frac{1}{2} + q_z^2/p_z)/p_z)]\delta_z \quad (98a)
 \end{aligned}$$

$$\begin{aligned}
U_{II} = & -(q_x/p_x(I_{2x} + H_{2x}) + q_y/p_y(I_{2y} + H_{2y}) + q_z/p_z(I_{2z} + H_{2z}))[(H_{xx}(\frac{1}{2} + q_x^2/p_x + d_x q_x)/p_x \\
& + H_{xy}q_x/p_x(q_y/p_y + d_y) + H_{xz}q_x/p_x(q_z/p_z + d_z))\delta_x + (H_{xx}(q_x/p_x + d_x)q_y/p_y \\
& + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_y q_y)/p_y + H_{xz}q_y/p_y(q_z/p_z + d_z))\delta_y + (H_{xx}(q_x/p_x + d_x)q_z/p_z \\
& + H_{xy}(q_y/p_y + d_y)q_z/p_z + H_{xz}(\frac{1}{2} + q_z^2/p_z + d_z q_z)/p_z)\delta_z] \quad (98b)
\end{aligned}$$

$$\begin{aligned}
J_I = & -[H_{xx}(q_x/p_x(\frac{3}{2} + q_x^2)/p_x + d_x(\frac{1}{2} + q_x^2/p_x)/p_x) + (\frac{1}{2} + q_x^2/p_x)/p_x(H_{xy}(q_y/p_y + d_y) \\
& + H_{xz}(q_z/p_z + d_z))]\delta_x\delta_x - (\frac{1}{2} + q_x^2/p_x)/p_x(H_{xy}(q_y/p_y + d_y) + H_{xz}(q_z/p_z + d_z)) \\
& + H_{xy}(q_y/p_y(\frac{3}{2} + q_y^2)/p_y + d_y(\frac{1}{2} + q_y^2/p_y)/p_y)]\delta_y\delta_y - [(\frac{1}{2} + q_z^2/p_z)/p_z(H_{xx}(q_x/p_x + d_x) \\
& + H_{xy}(q_y/p_y + d_y)) + H_{xz}(q_z/p_z(\frac{3}{2} + q_z^2)/p_z + d_z(\frac{1}{2} + q_z^2/p_z)/p_z)]\delta_z\delta_z \\
& - [H_{xx}(\frac{1}{2} + q_x^2/p_x + d_x q_x)/p_x q_y/p_y + H_{xy}q_x/p_x(\frac{1}{2} + q_y^2/p_y + d_y q_y)/p_y + H_{xz}q_x/p_x q_y/p_y(q_z/p_z + d_z)] \\
& \times (\delta_x\delta_y + \delta_y\delta_x) - [H_{xx}(\frac{1}{2} + q_x^2/p_x + d_x q_x)/p_x q_z/p_z + H_{xy}q_x/p_x(q_y/p_y + d_y)q_z/p_z \\
& + H_{xz}q_x/p_x(\frac{1}{2} + q_z^2/p_z + d_z q_z)/p_z](\delta_x\delta_z + \delta_z\delta_x) - [H_{xx}(q_x/p_x + d_x)q_y/p_y q_z/p_z \\
& + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_y q_y)/p_y q_z/p_z + H_{xz}q_y/p_y(\frac{1}{2} + q_z^2/p_z + d_z q_z)/p_z](\delta_y\delta_z + \delta_z\delta_y) \quad (99a)
\end{aligned}$$

$$\begin{aligned}
J_{II} = & -q_x/p_x[H_{xx}(\frac{1}{2} + q_x^2/p_x + d_x q_x)/p_x + q_x/p_x(H_{xy}(q_y/p_y + d_y) + H_{xz}(q_z/p_z + d_z))]\delta_x\delta_x \\
& - q_y/p_y[(H_{xx}(q_x/p_x + d_x) + H_{xz}(q_z/p_z + d_z))q_y/p_y + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_y q_y)/p_y]\delta_y\delta_y \\
& - q_z/p_z[(H_{xx}(q_x/p_x + d_x) + H_{xy}(q_y/p_y + d_y))q_z/p_z + H_{xz}(\frac{1}{2} + q_z^2/p_z + d_z q_z)/p_z]\delta_z\delta_z \\
& - q_x/p_x[(H_{xx}(q_x/p_x + d_x) + H_{xz}(q_z/p_z + d_z))q_y/p_y + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_y q_y)/p_y]\delta_x\delta_y \\
& - q_y/p_y[H_{xy}(q_y/p_y + d_y) + H_{xz}(q_z/p_z + d_z)]q_x/p_x + H_{xx}(\frac{1}{2} + q_x^2/p_x + d_x q_x)/p_x]\delta_y\delta_x \\
& - [H_{xx}(\frac{1}{2} + q_x^2/p_x + d_x q_x)/p_x q_z/p_z + H_{xy}q_x/p_x(q_y/p_y + d_y)q_z/p_z + H_{xz}q_x/p_x(\frac{1}{2} + q_z^2/p_z + d_z q_z)/p_z]\delta_z\delta_x \\
& - [(H_{xx}(q_x/p_x + d_x) + H_{xy}(q_y/p_y + d_y))q_z/p_z + H_{xz}(\frac{1}{2} + q_z^2/p_z + d_z q_z)](q_x/p_x\delta_x\delta_z + q_y/p_y\delta_y\delta_z) \\
& - q_z/p_z[(H_{xx}(q_x/p_x + d_x) + H_{xz}(q_z/p_z + d_z))q_y/p_y + H_{xy}(\frac{1}{2} + q_y^2/p_y + d_y q_y)/p_y]\delta_z\delta_y. \quad (99b)
\end{aligned}$$

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