

THE INTRA AND INTERMOLECULAR BASIS OF THE ZERO-SHEAR VISCOSITY IN UNENTANGLED POLYMERS

N.Fatkullin¹⁾, R.Kimmich

*Universität Ulm, Sektion Kernresonanzspektroskopie
89069 Ulm, Germany*

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A general expression for the zero-shear viscosity in unentangled polymers is derived grounded on chain pair correlations of normal modes and mutual interaction forces.

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It is widely believed that the zero-shear viscosity of concentrated polymer liquids below the critical molecular mass can be treated solely based on intramolecular forces and normal modes. A typical result of this approach is the linear molecular-mass dependence of the viscosity, a finding that is often identified with Rouse chain dynamics [1]. In this communication, we show that the neglect of interchain forces and of interchain normal-mode correlations is not compatible with basic physical laws. The coincidence of the linear molecular-mass dependence of the viscosity apparently predicted by the Rouse model with experimental findings may suggest tempting conclusions. However, in the light of the present discussion, this conformity is coincidental and not representative for the real nature of chain dynamics.

The polymer variant of the Green/Kubo linear-response formula for the zero-shear viscosity in liquids reads [2, 3]

$$\eta = \frac{V}{k_B T} \int_0^{\infty} \langle \sigma^{\alpha\beta}(t) \sigma^{\alpha\beta}(0) \rangle dt, \quad (1)$$

where V is the sample volume, k_B is Boltzmann's constant, T is the absolute temperature, $\sigma^{\alpha\beta}(t)$ is an off-diagonal element of the stress tensor given by

$$\sigma^{\alpha\beta}(t) = -\frac{1}{V} \sum_{i=1}^{N_p} \sum_{n=1}^{N_s} \left[m v_{ni}^{\alpha}(t) v_{ni}^{\beta}(t) + r_{ni}^{\alpha}(t) F_{ni}^{\beta}(t) \right]. \quad (2)$$

The subscript n labels the Kuhn segments within the polymer chain with the number i , where $n = 1, 2, 3, \dots, N_s$ and $i = 1, 2, 3, \dots, N_p$. The total number of Kuhn segments per chain is N_s , the total number of polymer chains in the sample is N_p . The quantities $r_{ni}^{\alpha}(t)$ and $v_{ni}^{\alpha}(t)$ are the α components of the position and velocity vectors, respectively, of the n^{th} segment in the i^{th} chain at time t . Analogously, $F_{ni}^{\beta}(t)$ is the β component of the total force vector exerted on the n^{th} segment in the i^{th} chain owing to interactions with all other segments. The velocity dependent term in Eq. (2) represents the kinetic contribution to the stress. Neglecting this term as usual leads to the well-known Kramers/Kirkwood

¹⁾ On leave from Kazan State University, Department of Physics, Kazan 420008, Russia/Tatarstan

relation for the stress,

$$\sigma^{\alpha\beta}(t) = -\frac{1}{V} \sum_{i=1}^{N_p} \sum_{n=1}^{N_s} r_{ni}^{\alpha}(t) F_{ni}^{\beta}(t). \quad (3)$$

The total force acting on segment n of chain i may be analyzed into intra and interchain contributions,

$$\mathbf{F}_{ni}(t) = \mathbf{F}_{ni}^{intra}(t) + \mathbf{F}_{ni}^{inter}(t). \quad (4)$$

The intramolecular force mainly arises from entropy elasticity, and can be written in the continuum limit as^[1]

$$\mathbf{F}_{ni}^{intra}(t) = \frac{3k_B T}{b^2} \frac{\partial^2 \mathbf{r}_{ni}(t)}{\partial n^2}, \quad (5)$$

where b is the Kuhn segment length. Newton's second law now tells us that the total force acting on segment n of chain i is related to the segment acceleration according to

$$m \mathbf{a}_{ni} \equiv m \frac{d^2}{dt^2} \mathbf{r}_{ni} = \mathbf{F}_{ni}(t). \quad (6)$$

If the many-particle problem of a polymer melt could be solved exactly, the segment accelerations \mathbf{a}_{ni} were known, and the total force $\mathbf{F}_{ni}(t)$ could be determined via Eq. (6). That is, the stress tensor, Eq. (3), and the viscosity, Eq. 1, could then be calculated exactly. In reality, we are restricted to approximations.

We therefore proceed in the following way. The solutions of semi phenomenological equations of motion such as the Rouse equation provide the time dependence of the segment position vector, \mathbf{r}_{ni} , so that the accelerations and, hence, the total force vectors, Eq. (6), can be derived. Using Eqs. (3) and (6) we can rewrite Eq. (1) in the form

$$\eta = \frac{m^2}{k_B T} \frac{1}{V} \sum_{i,n;j,o} \int_0^{\infty} \left\langle r_{ni}^{\alpha}(t) \ddot{r}_{ni}^{\beta}(t) r_{oj}^{\alpha}(0) \ddot{r}_{oj}^{\beta}(0) \right\rangle dt. \quad (7)$$

The position vector of the n^{th} segment is expressed in the usual normal-mode representation,

$$\mathbf{r}_{ni}(t) = \mathbf{X}_{i0}(t) + 2 \sum_{p=1}^{N_s-1} \mathbf{X}_{ip}(t) \cos\left(\frac{\pi n p}{N_s}\right), \quad (8)$$

where the subscripts indicate the normal mode p of chain i . Eq. (8) into Eq. (7), and summing up over all segments, i. e., the sum terms with the subscripts n and o for the segments of the chains i and j , respectively, gives

$$\begin{aligned} \eta = & \frac{m^2}{k_B T} \frac{1}{V} \sum_{i,j} \int_0^{\infty} \left\langle \left[X_{0i}^{\alpha}(t) \ddot{X}_{0i}^{\beta}(t) + 2N_s \sum_{p=1}^{N_s-1} X_{pi}^{\alpha}(t) \ddot{X}_{pi}^{\beta}(t) \right] \times \right. \\ & \left. \times \left[X_{0j}^{\alpha}(0) \ddot{X}_{0j}^{\beta}(0) + 2N_s \sum_{p'=1}^{N_s-1} X_{p'j}^{\alpha}(0) \ddot{X}_{p'j}^{\beta}(0) \right] \right\rangle dt. \end{aligned} \quad (9)$$

Apart from the uncritical approximations mentioned so far, the result Eq. 9 is exact. It obviously correlates normal modes of single chains as well as of pairs of chains i, j . Let us now discuss three levels of treatments of different physical relevance and accuracy.

Treatment 1. Ignoring all intermolecular correlations implied in Eq. (1), and all intermolecular forces in Eq. (4) and considering solely the intrachain force given by Eq. (5) leads to a fictitious result that is usually believed to represent the Rouse version of the shear viscosity[1],

$$\eta_{intraforce} = \frac{1}{36} \frac{\zeta}{b} N_s, \quad (10)$$

where ζ is the friction coefficient of a Kuhn segment. This is an expression very familiar to polymer scientists. However, there is no physical justification to replace the total force on a segment by just the intramolecular entropy elasticity contribution. The coincidence of the chain length dependence suggested by Eq. (10) with experimental data measured in polymer melts below the critical molecular weight [4] must therefore be considered to be coincidental. The neglect of inertial forces in the Rouse equation of motion does not justify to do so in evaluating the Green/Kubo formula given in Eq. (1). Inertial forces are small relative to the other force terms in that equation, and therefore do not matter very much for the intrachain relaxation modes to be derived in the frame of the Rouse model. However, the Green/Kubo formula given in Eq. (1) is explicitly based on the total force acting on a segment. Seeking an approximate solution of an equation of motion and deriving an expression for the stress tensor are two different things which should not be intermingled. The neglect of the total force in the evaluation of the Green/Kubo formula would simply mean that the viscosity takes the value zero. According to Newton's second law, the total force on a particle is equal to the inertial force. Vanishing total force therefore would mean constant velocity in contradiction to viscous behavior.

Treatment 2. A somewhat more consistent attempt is to ignore all interchain correlations, but to take all forces acting on a segment into account via Newton's second law. With this strategy, Eq. (9) becomes

$$\begin{aligned} \eta_{intracorr.} &= \frac{m^2}{k_B T} \frac{N_p}{V} \int_0^\infty dt \left\{ \langle X_0^\alpha(t) X_0^\alpha(0) \rangle \langle \ddot{X}_0^\beta(t) \ddot{X}_0^\beta(0) \rangle + \right. \\ &\quad \left. + 4N_s^2 \sum_{p=1}^{N_s-1} \langle X_p^\alpha(t) X_p^\alpha(0) \rangle \langle \ddot{X}_p^\beta(t) \ddot{X}_p^\beta(0) \rangle \right\} = \\ &= \frac{1}{9} \frac{m^2 c}{k_B T N_s} \int_0^\infty dt \left\{ \langle \mathbf{X}_0(t) \mathbf{X}_0(0) \rangle \langle \ddot{\mathbf{X}}_0(t) \ddot{\mathbf{X}}_0(0) \rangle + \right. \\ &\quad \left. + 4N_s^2 \sum_{p=1}^{N_s-1} \langle \mathbf{X}_p(t) \mathbf{X}_p(0) \rangle \langle \ddot{\mathbf{X}}_p(t) \ddot{\mathbf{X}}_p(0) \rangle \right\}, \quad (11) \end{aligned}$$

where the chain number subscripts are now irrelevant, and have therefore been omitted. The quantity $c \equiv N_p N_s / V = \text{const}$ is the Kuhn segment number density. The correlation function terms in Eq. (11) can be evaluated using the stationarity relation

$$\langle \dot{A}(t) B(0) \rangle = - \langle A(t) \dot{B}(0) \rangle. \quad (12)$$

That is,

$$\langle \ddot{\mathbf{X}}_p(t) \cdot \ddot{\mathbf{X}}_p(0) \rangle = \left\langle \frac{d^4}{dt^4} \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \right\rangle = \frac{d^4}{dt^4} \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle. \quad (13)$$

Inserting the well-known Rouse normal-mode solutions[1] gives

$$\langle \ddot{\mathbf{X}}_p(t) \cdot \ddot{\mathbf{X}}_p(0) \rangle = \left(\frac{1}{\tau_p} \right)^4 \langle X_p^2(0) \rangle \exp \left\{ -\frac{t}{\tau_p} \right\}. \quad (14)$$

The relaxation time of the normal mode p is given by $\tau_p = \tau_s N^2 / p^2$, where $\tau_s = \zeta b^2 / (3\pi^2) k_B T$ is the Rouse relaxation time of a Kuhn segment. Furthermore, $\langle X_p^2(0) \rangle = N b^2 / (2\pi^2 p^2)$.

Inserting Eq. (14) into Eq. (11) now leads to entirely unrealistic results. For example, the first term on the righthand side of Eq. (11), that is the zeroth mode, refers to the absolute position of the center of mass of a chain. Designating the linear dimension of the sample with L and considering the thermodynamic limit, this suggests $\eta \propto L^2 \rightarrow \infty$. The origin of this singularity is that the treatment is restricted to single-chain mode correlations. It is readily conceivable that the viscous behaviour is generally based on motions of molecules relative to each other. That is, intermolecular interactions, and in the case of polymers, intermolecular mode correlations are therefore crucial. The neglect of intermolecular phenomena is not permissible.

It is also of interest to note that, calculating the contribution of all intra-chain modes to the viscosity analogously to treatment 1, leads to an expression independent of the molecular mass in contrast to Eq. (10) resulting from treatment 1. Practically this contribution is safely negligible because the effects of intra and intermolecular forces on the Rouse dynamics tend to compensate each other.

Treatment 3. A correct result for the zero-shear viscosity can only be expected if all interactions and all mode correlations are accounted for. That is, Eq. (9) must be examined in full. This in particular refers to the two-chain mode correlations implied in this equation. As the zero-shear viscosity is determined by motions of the centers-of-mass of the polymer chains, we consider the center-of-mass contribution to the stress tensor, Eq. (3),

$$\sigma_{cm}^{\alpha\beta}(t) = -\frac{1}{V} \sum_{i=1}^{N_p} \sum_{n=1}^{N_s} X_{ni}^{\alpha}(t) F_{ni}^{\beta}(t), \quad (15)$$

in terms of the normal-mode representation Eq. (8). The total force exerted on chain i from all other chains is

$$\mathbf{F}_i(t) = \sum_{n,i;o,j} \mathbf{F}_{n,i;o,j}(t) \quad (j \neq i), \quad (16)$$

where $\mathbf{F}_{n,i;o,j}(t)$ is the force exerted by segment o of chain $j \neq i$ on segment n of chain i . Using Newton's third law, $\mathbf{F}_{n,i;o,j}(t) = -\mathbf{F}_{o,j;n,i}(t)$, and summing up over all segments n and o converts Eq. (15) into

$$\sigma_{cm}^{\alpha\beta}(t) = -\frac{1}{2V} \sum_{i \neq j} (X_{0i}^{\alpha}(t) - X_{0j}^{\alpha}(t)) F_{ij}^{\beta}(t), \quad (17)$$

where $F_{ij}^{\beta}(t)$ is the total force exerted on chain j by chain i . Inserting Eq. (17), which was first established in Ref. [5], into Eq. (1) results in the expression for the true zero-shear viscosity of polymers,

$$\eta = \frac{1}{4k_B T V} \sum_{i \neq j} \int_0^{\infty} dt \langle (X_{0i}^{\alpha}(t) - X_{0j}^{\alpha}(t)) F_{ij}^{\beta}(t) (X_{0i}^{\alpha}(0) - X_{0j}^{\alpha}(0)) F_{ij}^{\beta}(0) \rangle. \quad (18)$$

Eq. (18) relates the normal modes of order $p = 0$ of two chains i and j and the mutual total forces. It is therefore of an intrinsically intermolecular character. Its further evaluation requires the knowledge of interchain mode correlations and forces for which no theoretical treatment is available so far. However, it is obvious that the singularity that has appeared in treatment 2 does not occur anymore: This expression now depends on the difference of the zeroth order normal modes $X_{0i}^\alpha(t) - X_{0j}^\alpha(t)$ rather than on the normal modes $X_{0i}^\alpha(t)$ themselves in treatment 2. That is, the absolute position of the center of mass does not enter anymore.

Eq. (18) tells us that the zero-shear viscosity of concentrated polymer liquids is based on many-chain correlations and interactions even for molecular masses below the critical value, $M < M_c$. This finding is supported by recent computer simulations by Loriot and Weiner [6–8] also revealing that the main contribution to stress arises from interchain interactions. We conclude that single-chain formalisms cannot describe viscoelastic phenomena. That is, even for relatively simple systems such as unentangled polymers and contrary to the impression one gets from the literature, we are far from a satisfactory theoretical description of viscous behaviour.

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