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THE ROLE OF INTERMOLECULAR INTERACTIONS IN THE VISCOELASTIC PROPERTIES OF POLYMER MELTS

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SUMMARY: The exact microscopic expression for the stress tensor in polymer liquids contains a tensor product of the the segment position vector with the total, intra- plus inter-chain, force acting on the segment. On the other hand, the widely accepted theory of viscoelasticity of polymer melts [1] is based on the assumption, that contributions from interchain interactions to the viscosity of polymer melts is negligible relative to the effectively intrachain entropic interactions. Starting from the exact Green-Kubo formula for the viscosity, the Rouse dynamic correlation functions, and Newton's second law, we show that the intrachain assumption is inadequate. Rather, the intrachain and interchain forces acting on polymer segments cancel each other largely. The intrachain contribution therefore cannot be dominant as anticipated in the usual treatment [1], or, in other words, the interchain contribution cannot be ignored. The main contribution to viscoelastic properties of polymer melts can only arise from a part of the total stress tensor as already suggested by M.Fixman based on a different argument [2]. It is concluded that the viscosity is of a purely interchain nature, and is determined by the tensor product of the vector connecting the centers-of-mass of neighboring macromolecules on the one hand, and the total force by which macromolecules interact, on the other, just in the case of simple liquids.

THEORY

The polymer variant of the Green/Kubo linear-response formula for the zero-shear viscosity in liquids reads [3,4]

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

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

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

The subscript *n* labels the Kuhn segments within the polymer chain with the number *i*, where $n=1,2,3,\ldots N_s$ and $i=1,2,3,\ldots N_p$. The total number of Kuhn segments per chain is N_s, the total

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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 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 depend term in Eq.2 represents the kinetic contribution to the stress. Neglecting this term as usual leads to the well-known Kramers/Kirkwood relation for the stress,

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

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

$$\vec{F}_{ni}(t) = \vec{F}_{ni}^{\text{intra}}(t) + \vec{F}_{ni}^{\text{inter}}(t). \tag{4}$$

The effective inramolecular force mainly arises from entropy elasticity, and can be written in the continuum limit as 1)

$$\vec{F}_{ni}^{\text{intra}}(t) = \frac{3k_BT}{b^2}\frac{\partial^2\vec{r}_{ni}(t)}{\partial n^2}, \tag{5}$$

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

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

If the many-particle problem of a polymer melt could be solved exactly, the segment accelerations $\vec{a}_{ni}$ were known, and the total force $\vec{F}_{ni}(t)$ 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, $\vec{r}_{ni}$, 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

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

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

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

where the subscripts indicate the normal mode *p* of chain *i*. Inserting 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

$$\eta = \frac{m^2}{k_B T}\frac{N_s^2}{V}\sum_{i,j}\int_0^\infty \Big\langle \Big[X_{0i}^{\alpha}(t)\ddot{X}_{0i}^{\beta}(t) + 2\sum_{p=1}^{N_s-1} X_{pi}^{\alpha}(t)\ddot{X}_{pi}^{\beta}(t) \Big] \Big[X_{0j}^{\alpha}(0)\ddot{X}_{0j}^{\beta}(0) + 2\sum_{p'=1}^{N_s-1} X_{p'j}^{\alpha}(0)\ddot{X}_{p'j}^{\beta}(0) \Big] \Big\rangle dt \qquad (9)$$

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 intermolecular forces in Eq. 4 and considering solely the effective 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)]

$$\eta_{\mathrm{intraforce}} = \frac{c}{36}\zeta N b^2, \qquad (10)$$

where ζ is the friction coefficient of a Kuhn segment, *c* is the Kuhn segment number density. This is an expression very familiar to polymer scientists. Although Eq. (10) contains local friction coefficient arising from interchain interactions, it reflects interchain interactions effects on viscosity only through normal mode dynamics and ignores the second term in right part of Eq.(4). 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 [5)] must therefore be considered to be coincidental.

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

$$\eta_{\mathrm{intracorr}} = \frac{1}{9}\frac{m^2 c\cdot N_s}{k_B T}\int_0^\infty dt \Big\{ \big\langle \vec{X}_0(t)\vec{X}_0(0)\big\rangle \big\langle \ddot{\vec{X}}_0(t)\ddot{\vec{X}}_0(0)\big\rangle + 4\sum_{p=1}^{N_s-1}\big\langle \vec{X}_p(t)\vec{X}_p(0)\big\rangle\big\langle \ddot{\vec{X}}_p(t)\ddot{\vec{X}}_p(0)\big\rangle \Big\}, \qquad (11)$$

where the chain number subscripts are now irrelevant, and have therefore been omitted. The correlation function terms in Eq. 11 can be evaluated using the stationarity relation

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

That is,

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

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

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

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, $\left\langle X_p^2(0)\right\rangle = Nb^2/(2\pi^2 p^2)$.

Inserting Eq. 14 into Eq. 11 now leads to entirely unrealistic results. For example, the first term on the righthand side of Eq. 11 refers to the 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 $\eta \propto L^2 \to \infty$. 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 and has an order of magnitude as neglected kinetic terms. Then, taking into consideration kinetic terms in Eq. (2) corresponding to intra-chain modes, it is possible to see exact cancellation of all contributions into viscosity from internal degrees of freedom of macromolecule.

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-mass of the polymer chains, we consider the center-mass contribution to the stress tensor, Eq. 3,

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

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

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

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

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

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. 2), into Eq. 1 results in the expression for the true zero-shear viscosity of polymers,

$$\eta = \frac{1}{4k_B TV}\sum_{\substack{i \neq j \\ i' \neq j'}}\int_0^{\infty} dt \left\langle \left(X_{0i}^{\alpha}(t) - X_{0i}^{\alpha}(t)\right)F_{ij}^{\beta}(t)\left(X_{0i'}^{\alpha}(0) - X_{0i'}^{\alpha}(0)\right)F_{i'j'}^{\beta}(0)\right\rangle . \tag{18}$$

Equation 18 relates the normal modes of order *p = 0* of two chains *i* and *j* the mutual total forces. It is therefore of an intrinsically intermolecular character and has just the same structure as in the case of simple liquids. 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 $X_{0i}^{\alpha}(t) - X_{0j}^{\beta}(t)$ 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.

Conclusion

Equation 18 tells us that the zero-shear viscosity of concentrated polymer liquids is based on many-chain correlations and interactions and does not contain any contributions from fluctuations of internal degrees of freedom. It seems that this finding is supported by recent computer simulations by [6,7,8] also revealing that the main contribution to stress arises from interchain interactions. Although we are discussing problem based on Rouse model, really our arguments have general nature and Eq. 18 is exact result for any polymer model. We conclude that single-chain formalisms cannot describe viscoelastic phenomena. 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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