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Effect of Nematic Interaction on the Rouse Dynamics

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ABSTRACT: The dynamics of Rouse chains that interact with each other by a nematic potential is formulated. The formulation leads to a unique expression for the stress tensor and resolves the controversy on the stress expression. The relaxation modulus for the linear viscoelasticity agrees with that given in the previous paper (Watanabe et al. *Macromolecules*). It is shown that the effect of the nematic interaction is small for the rheological properties but significant for the orientation of polymer segments.

1. Introduction

Various experiments done recently[1,2] suggested that there is a specific interaction in polymer melts, called the nematic interaction, which tends to orient the neighboring polymer segments in melts toward the same direction. Such an orientational coupling has been known to exist for rubbers for a long time,[3–6] but its importance for polymers melts has been realized only recently.[7]

If the nematic interaction exists in polymer melts, it would require a modification of the conventional theories. For example, the theory of viscoelasticity should be modified since the stress in polymer melts is related to the chain orientation,[8,9] which is affected by the nematic interaction. Such modification has been done for the reptation dynamics by Merrill et al.[7] and Doi et al.[10]

On the other hand, it is also important to study the effect of the nematic interaction on the Rouse dynamics since (i) the dynamics of short polymers in melts is described by the Rouse model and (ii) even for long polymers, the dynamics is described by the Rouse model on a short time scale.[8] In the previous paper,[11] an equation of motion for the Rouse chain with nematic interaction was proposed. It was shown that the effect of the nematic interaction is large for the optical properties but small for the viscoelastic properties, particularly in the long-time behavior.

In the previous paper,[11] however, the basic equation was derived on a rather intuitive basis. In this paper, we give a more refined formulation for the nematic interaction for the Rouse dynamics based on the general kinetic theory. For linear viscoelasticity, this formulation leads to a relaxation modulus identical with the previous one.[11] An advantage of this formulation is that the expression for the stress tensor can be derived without any additional assumptions. This also resolves the previous controversy on the expression for the stress tensor in the reptation dynamics.[7,10]

2. Free Energy of the Rouse Chain with Nematic Interaction

To handle the nematic interaction, we need a model that describes the local structure of the polymer molecule. Here, for simplicity, we use the model of a freely jointed chain, but the theory can be developed for a more realistic model.

Consider a freely jointed chain consisting of N_0 segments of length b_0. Let $\mathbf{u}_i$ ($i = 1, 2, ..., N_0$) be the unit vector in the direction of the ith segment. The orientational tensor of the ith segment is defined by

$$q_{i\alpha\beta} = \langle u_{i\alpha}u_{i\beta} - {}^1/{}_3\delta_{\alpha\beta}\rangle \tag{1}$$

The average of $q_{i\alpha\beta}$ for all segments in the system is denoted by $q_{\alpha\beta}$:

$$q_{\alpha\beta} = \sum_{\substack{\text{all segments}\\ \text{in the system}}} q_{i\alpha\beta}/(\text{number of segments in the system}) \tag{2}$$

To express the nematic interaction, we use the following mean field potential (Maier–Saupe potential) as is usually done in the theory of liquid crystals:[12]

$$U_{\mathrm{NI}} = -\sum_i E q_{\alpha\beta}(u_{i\alpha}u_{i\beta} - {}^1/{}_3\delta_{\alpha\beta}) \tag{3}$$

This potential becomes minimum when $\mathbf{u}_i$ is in the average direction of the surrounding medium. The parameter E denotes the strength of the nematic interaction.

Now it is generally believed that if the dynamics of a chain is determined locally, its behavior on a large length scale can be described by the Rouse model. To relate the freely jointed chain with the Rouse model, we select N segments evenly along the chain at every $N_{\mathrm{R}} = N_0/N$ segments and represent the conformation of the chain by the position vector of the N selected segments $\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N$. The part bound by the nth and $(n + 1)$th selected segments is called the nth Rouse submolecule.

To derive an equation of motion, we need the free energy of the chain for fixed $\{\mathbf{R}_n\}$. This is the sum of the free energy of each submolecule, the nth one of which is given by

$$A_{\mathrm{sub}}(\mathbf{r}_n) = -k_{\mathrm{B}}T \ln \int \mathrm{d}\{\mathbf{u}_i\} \exp\left(-\frac{U(\{\mathbf{u}_i\})}{k_{\mathrm{B}}T}\right)\delta(\mathbf{r}_n - b_0\sum_i \mathbf{u}_i) \tag{4}$$

where

$$\mathbf{r}_n = \mathbf{R}_{n+1} - \mathbf{R}_n$$

is the vector joining the ends of the submolecule, U is the energy of the segments, and the index i runs over all the bonds in the submolecule.

The energy U consists of two parts: (i) the energy associated with the internal rotation of segments and (ii) the energy associated with the nematic interaction, U_{NI} (eq 3). (The excluded volume interaction can be neglected

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in the mean field approximation.) For the freely jointed chain, U consists of U_{NI} only. In this case, Jarry and Monnerie[5] showed[13]

$$A_{\mathrm{sub}}(\mathbf{r}_n) = \frac{3k_{\mathrm{B}}T}{2b^2}(\delta_{\alpha\beta} - \epsilon_0 q_{\alpha\beta})r_{n\alpha}r_{n\beta} + \text{constant} \qquad (5)$$

where

$$b^2 = N_{\mathrm{R}}b_0^{\,2} \qquad (6)$$

is the mean square end-to-end distance of the submolecule and

$$\epsilon_0 = \frac{2E}{5k_{\mathrm{B}}T} \qquad (7)$$

is a dimensionless parameter representing the nematic interaction. Also, the orientational tensor of a *segment* is calculated to be[5]

$$q_{i\alpha\beta} = \frac{\int \mathrm{d}\{\mathbf{u}_j\} \exp\left(-\frac{U_{\mathrm{NI}}}{k_{\mathrm{B}}T}\right)\delta(\mathbf{r}_n - b_0\sum_j \mathbf{u}_j)(u_{i\alpha}u_{i\beta} - {}^1\!/_3\delta_{\alpha\beta})}{\int \mathrm{d}\{\mathbf{u}_j\} \exp\left(-\frac{U_{\mathrm{NI}}}{k_{\mathrm{B}}T}\right)\delta(\mathbf{r}_n - b_0\sum_j \mathbf{u}_j)}$$

$$= \frac{3}{5N_{\mathrm{R}}b^2}\langle r_{n\alpha}r_{n\beta} - {}^1\!/_3 r_n^{\,2}\delta_{\alpha\beta}\rangle + {}^1\!/_3\epsilon_0 q_{\alpha\beta} \qquad (8)$$

Let the orientational tensor of the nth *submolecule* be defined by

$$S_{n\alpha\beta} \equiv \frac{3}{b^2}\langle r_{n\alpha}r_{n\beta} - {}^1\!/_3 r_n^{\,2}\delta_{\alpha\beta}\rangle \qquad (9)$$

The average of $S_{n\alpha\beta}$ for all the submolecules in the system is denoted by $S_{\alpha\beta}$. It then follows from eqs 2 and 8 that

$$q_{\alpha\beta} = \frac{1}{5N_{\mathrm{R}}}S_{\alpha\beta} + {}^1\!/_3\epsilon_0 q_{\alpha\beta} \qquad (10)$$

or

$$q_{\alpha\beta} = \frac{1}{5N_{\mathrm{R}}}\frac{1}{1 - {}^1\!/_3\epsilon_0}S_{\alpha\beta} \qquad (11)$$

Thus eq 5 is written as

$$A_{\mathrm{sub}}(\mathbf{r}_n) = \frac{3k_{\mathrm{B}}T}{2b^2}(\delta_{\alpha\beta} - \epsilon S_{\alpha\beta})r_{n\alpha}r_{n\beta} + \text{constant} \qquad (12)$$

where

$$\epsilon = \frac{1}{5N_{\mathrm{R}}}\frac{\epsilon_0}{1 - {}^1\!/_3\epsilon_0} \qquad (13)$$

The free energy of the Rouse chain in a matrix with an orientation $S_{\alpha\beta}$ is given by

$$A_{\mathrm{chain}} = \frac{3k_{\mathrm{B}}T}{2b^2}\sum_{n=1}^{N}(\mathbf{r}_n^{\,2} - \epsilon S_{\alpha\beta}r_{n\alpha}r_{n\beta}) \qquad (14)$$

The first term in the parentheses is the intramolecular entropic contribution, and the second term represents the nematic interaction.

3. Equation of Motion

We now consider the dynamics of the Rouse chain in the macroscopic flow field

$$v_\alpha(\mathbf{r},t) = \kappa_{\alpha\beta}(t)r_\beta \qquad (15)$$

Given the free energy, the equation of motion for the Rouse chain is derived as[8]

$$\zeta\left(\frac{\partial R_{n\alpha}}{\partial t} - \kappa_{\alpha\beta}R_{n\beta}\right) = -\frac{\partial A_{\mathrm{chain}}}{\partial R_{n\alpha}} + f_{n\alpha} \qquad (16)$$

where ζ is the friction constant of a submolecule, and $\mathbf{f}_n(t)$ is the random force characterized by

$$\langle f_{n\alpha}(t)f_{m\beta}(t')\rangle = 2\zeta k_{\mathrm{B}}T\delta_{nm}\delta_{\alpha\beta}\delta(t - t') \qquad (17)$$

Equations 14 and 16 give

$$\zeta\left(\frac{\partial R_{n\alpha}}{\partial t} - \kappa_{\alpha\beta}R_{n\beta}\right) = \frac{3k_{\mathrm{B}}T}{b^2}(\delta_{\alpha\beta} - \epsilon S_{\alpha\beta})(R_{n+1\beta} - 2R_{n\beta} + R_{n-1\beta}) + f_{n\alpha} \qquad (18)$$

This form of the equation of motion is identical with that given in ref 11.[14]

To handle the Rouse equation, it is convenient to use the normal coordinate

$$\mathbf{X}_p(t) = \frac{1}{N}\sum_{n=0}^{N}\cos\left(\frac{p\pi n}{N}\right)\mathbf{R}_n(t) \qquad (p = 0, 1, 2, ...) \qquad (19)$$

Then eq 18 is rewritten as

$$\zeta_p\left(\frac{\partial}{\partial t}X_{p\alpha} - \kappa_{\alpha\beta}X_{p\beta}\right) = -k_p(\delta_{\alpha\beta} - \epsilon S_{\alpha\beta})X_{p\beta} + f_{p\alpha} \qquad (20)$$

where

$$\zeta_p = 2N\zeta; \qquad k_p = \frac{24Nk_{\mathrm{B}}T}{b^2}\sin^2\left(\frac{p\pi}{2N}\right);$$

$$f_{p\alpha} = 2\sum_{n=0}^{N}\cos\left(\frac{p\pi n}{N}\right)f_{n\alpha} \qquad (p = 1, 2, ...) \qquad (21)$$

From eq 20, the equation for the second moment can be derived by the same procedure described in ref 8, p 112.

$$\zeta_p\left(\frac{\partial}{\partial t}\langle X_{p\alpha}X_{p\beta}\rangle - \kappa_{\alpha\mu}\langle X_{p\mu}X_{p\beta}\rangle - \kappa_{\beta\mu}\langle X_{p\mu}X_{p\alpha}\rangle\right) = 2k_{\mathrm{B}}T\delta_{\alpha\beta} - k_p(2\langle X_{p\alpha}X_{p\beta}\rangle - \epsilon S_{\alpha\mu}\langle X_{p\mu}X_{p\beta}\rangle - \epsilon S_{\beta\mu}\langle \chi_{p\mu}X_{p\alpha}\rangle) \qquad (22)$$

Equation 22 involves an unknown quantity $S_{\alpha\beta}(t)$, which is determined self-consistently. For example, for a monodisperse system, $S_{\alpha\beta}(t)$ is given by

$$S_{\alpha\beta} = \frac{1}{N}\sum_{n=1}^{N}S_{n\alpha\beta} = \frac{3}{Nb^2}\sum_{n=1}^{N}\langle r_{n\alpha}r_{n\beta} - {}^1\!/_3\delta_{\alpha\beta}\mathbf{r}_n^{\,2}\rangle \qquad (23)$$

or in terms of the normal coordinates

$$S_{\alpha\beta} = \frac{1}{Nk_{\mathrm{B}}T}\sum_{p=1}^{N}k_p\langle X_{p\alpha}X_{p\beta} - {}^1\!/_3\delta_{\alpha\beta}X_p^{\,2}\rangle \qquad (24)$$

Equations 22 and 24 give a complete set of equations for $S_{\alpha\beta}$ and $\langle X_{p\alpha}X_{p\beta}\rangle$.

4. Stress Tensor

The expression for the stress tensor is obtained by the procedure described in ref 8. Let A_{tot} be the free energy of the system per unit volume. Consider a macroscopic deformation that displaces a point at $\mathbf{r}$ as

$$r_\alpha \rightarrow r_\alpha + \delta\epsilon_{\alpha\beta}r_\beta \qquad (25)$$

and let δA_{tot} be the change of A_{tot} under this deformation;

then the stress tensor $\sigma_{\alpha\beta}$ is given by

$$\delta A_{\text{tot}} = \sigma_{\alpha\beta}\delta\epsilon_{\alpha\beta} \tag{26}$$

In the mean field approximation, the free energy per unit volume is given by

$$A_{\text{tot}} = n_{\text{chain}}\langle A_{\text{chain}}\rangle - A_{\text{NI}} \tag{27}$$

where n_{chain} is the number of Rouse chains in unit volume and A_{NI} is the energy of the nematic interaction; the term A_{NI} is needed to compensate for the double counting of the interaction energy. In particular, for a monodisperse system, A_{NI} is given by

$$A_{\text{NI}} = -\frac{3}{2b^2}k_{\text{B}}Tn_{\text{chain}}\sum_{n=1}^{N}\frac{1}{2}\epsilon S_{\alpha\beta}\langle r_{n\alpha}r_{n\beta}\rangle = -\frac{1}{4}k_{\text{B}}TN_{\text{tot}}\epsilon S_{\alpha\beta}^2 \tag{28}$$

where $N_{\text{tot}} = Nn_{\text{chain}}$ is the number of Rouse submolecules in unit volume. Thus

$$A_{\text{tot}} = \frac{1}{2}k_{\text{B}}TN_{\text{tot}}\left(\frac{3}{Nb^2}\sum_{n=1}^{N}\langle \mathbf{r}_n^2\rangle - \frac{1}{2}\epsilon S_{\alpha\beta}^2\right) \tag{29}$$

Under the hypothetical deformation (25), each submolecule is deformed affinely; i.e., $R_{n\alpha} \rightarrow R_{n\alpha} + \delta\epsilon_{\alpha\beta}R_{n\beta}$ or $r_{n\alpha} \rightarrow r_{n\alpha} + \delta\epsilon_{\alpha\beta}r_{n\beta}$. Thus

$$\delta A_{\text{tot}} = k_{\text{B}}TN_{\text{tot}}[\delta\epsilon_{\alpha\beta}(S_{\alpha\beta} + l\delta_{\alpha\beta}) - {}^1/_2\epsilon S_{\alpha\beta}\delta S_{\alpha\beta}] \tag{30}$$

where

$$l = \frac{1}{Nb^2}\sum_{n=1}^{N}\langle \mathbf{r}_n^2\rangle \tag{31}$$

On the other hand, from eq 23, we have

$$\delta S_{\alpha\beta} = \delta\epsilon_{\alpha\mu}(S_{\beta\mu} + l\delta_{\beta\mu}) + \delta\epsilon_{\beta\mu}(S_{\alpha\mu} + l\delta_{\alpha\mu}) - {}^2/_3\delta_{\alpha\beta}\delta\epsilon_{\mu\nu}(S_{\mu\nu} + l\delta_{\mu\nu}) \tag{32}$$

Equation 30 then gives

$$\delta A_{\text{tot}} = k_{\text{B}}TN_{\text{tot}}\delta\epsilon_{\alpha\beta}[(S_{\alpha\beta} + l\delta_{\alpha\beta}) - \epsilon(S_{\alpha\mu}S_{\beta\mu} + lS_{\alpha\beta})] \tag{33}$$

whence the stress tensor is obtained as

$$\sigma_{\alpha\beta} = k_{\text{B}}TN_{\text{tot}}[S_{\alpha\beta} - \epsilon(S_{\alpha\mu}S_{\beta\mu} + lS_{\alpha\beta})] \tag{34}$$

5. Linear Viscoelasticity for a Monodisperse System

Now let us examine the linear viscoelasticity of the system using the above formulation. Consider the shear flow:

$$\kappa_{\alpha\beta}(t) = \begin{cases} \dot\gamma(t) & \text{if } \alpha = x \text{ and } \beta = y \\ 0 & \text{otherwise} \end{cases} \tag{35}$$

In this case, only the xy (and yx) components of the tensors $\langle X_{p\alpha}X_{p\beta}\rangle$ and $S_{\alpha\beta}$ are of the order of $\dot\gamma$; the rest components may be set to the equilibrium value:

$$\langle X_{p\alpha}X_{p\beta}\rangle = \frac{k_{\text{B}}T}{k_p}\delta_{\alpha\beta},\quad S_{\alpha\beta} = 0,\quad l = 1 \quad \text{at equilibrium} \tag{36}$$

Hence eq 22 gives

$$\zeta_p\frac{\partial}{\partial t}\left(\langle X_{px}X_{py}\rangle - \frac{k_{\text{B}}T}{k_p}\dot\gamma\right) = -2k_p\langle X_{px}X_{py}\rangle + 2\epsilon k_{\text{B}}TS_{xy} \tag{37}$$

which is solved as

$$\langle X_{px}X_{py}\rangle = \frac{k_{\text{B}}T}{k_p}\int_{-\infty}^{t}\mathrm{d}t'\,\exp[-(t-t')/\tau_p]\left[\dot\gamma(t') + \frac{\epsilon}{\tau_p}S_{xy}(t')\right] \tag{38}$$

where

$$\tau_p = \zeta_p/2k_p \tag{39}$$

Equations 24 and 38 lead to an integral equation for $S_{xy}(t)$:

$$S_{xy}(t) = \int_{-\infty}^{t}\mathrm{d}t'\left[\mu_0(t-t')\dot\gamma(t') + \epsilon\left(\frac{\partial}{\partial t'}\mu_0(t-t')\right)S_{xy}(t')\right] \tag{40}$$

where

$$\mu_0(t) = \frac{1}{N}\sum_{p=1}^{N}\exp(-t/\tau_p) \tag{41}$$

Since $S_{xy}(t)$ is a linear functional of $\dot\gamma(t)$, the solution of eq 40 can be written as

$$S_{xy}(t) = \int_{-\infty}^{t}\mathrm{d}t'\,\mu(t-t')\dot\gamma(t') \tag{42}$$

where the memory kernel $\mu(t)$ is the solution of the integral equation:

$$\mu(t) = \mu_0(t) + \epsilon\int_{0}^{t}\mathrm{d}t'\left[\frac{\partial}{\partial t'}\mu_0(t-t')\right]\mu(t') \tag{43}$$

(This equation is obtained from eq 40 by putting $\dot\gamma(t)$ equal to $\delta(t)$.)

From eq 34, the shear stress is given by

$$\sigma_{xy}(t) = k_{\text{B}}TN_{\text{tot}}(1-\epsilon)S_{xy}(t) \tag{44}$$

$$= k_{\text{B}}TN_{\text{tot}}(1-\epsilon)\int_{-\infty}^{t}\mathrm{d}t'\mu(t-t')\dot\gamma(t') \tag{45}$$

Thus the relaxation modulus $G_{\text{NI}}(t)$ for the Rouse chain with the nematic interaction is obtained as

$$G_{\text{NI}}(t) = k_{\text{B}}TN_{\text{tot}}(1-\epsilon)\mu(t) \tag{46}$$

This result agrees completely with that in ref 11. The equation for $\mu(t)$ in ref 11 is superficially different from eq 43, but the equivalence can be shown as follows. From eqs 41 and 43, it follows

$$\mu_0(0) = \mu(0) = 1 \tag{47}$$

By integration by parts

$$\int_{0}^{t}\mathrm{d}t'\left[\frac{\partial}{\partial t'}\mu_0(t-t')\right]\mu(t') = \mu(t) - \mu_0(t) - \int_{0}^{t}\mathrm{d}t'\,\mu_0(t-t')\frac{\partial}{\partial t'}\mu(t')$$

Equation 43 is then rewritten as

$$\mu(t) = \mu_0(t) - \frac{\epsilon}{1-\epsilon}\int_{0}^{t}\mathrm{d}t'\,\mu_0(t-t')\frac{\partial}{\partial t'}\mu(t') \tag{48}$$

which agrees with eq 25 in ref 11.

If there is no nematic interaction, the relaxation modulus is given by

$$G_{\text{R}}(t) = k_{\text{B}}TN_{\text{tot}}\mu_0(t) \tag{49}$$

Given $\mu_0(t)$, we can solve eq 43 for $\mu(t)$ numerically. The result of the numerical calculation is schematically shown in Figure 1, where $G_{\text{NI}}(t)$ is compared with $G_{\text{R}}(t)$. Notice that (i) at $t = 0$, $G_{\text{NI}}(t)$ is smaller than $G_{\text{R}}(t)$ by a factor $(1 - \epsilon)$ but (ii) as t increases, $G_{\text{NI}}(t)$ approaches $G_{\text{R}}(t)$ quickly.

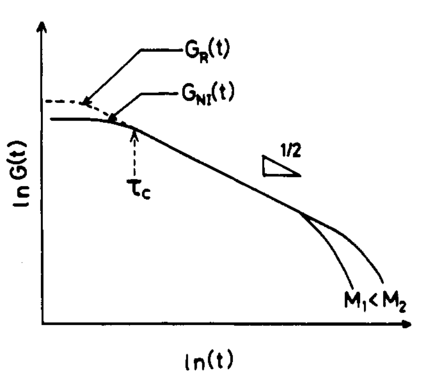

Figure 1. Relaxation modulus of the Rouse model with the nematic interaction, $G_{NI}(t)$ (the solid line), is compared with the conventional relaxation modulus without the nematic interaction, $G_R(t)$ (dashed line). The long-time behavior changes as the molecular weight changes from M_1 to M_2, but the short-time behavior is independent of the molecular weight.

The first point is obvious from eq 47. It is consistent with the result of the theory of liquid crystalline polymers that the initial relaxation modulus decreases if there is the nematic interaction (see ref 8, p 366).

The second point is seen as follows. Since $\mu_0(t)$ is proportional to $t^{-1/2}$,[8] the integral in eq 43 is dominated by the contribution near $t' \simeq t$ and may be approximated as

$$\int_0^t \mathrm{d}t' \left[\frac{\partial}{\partial t'}\mu_0(t-t')\right]\mu(t') \approx \mu(t)\int_0^t \mathrm{d}t' \left[\frac{\partial}{\partial t'}\mu_0(t-t')\right] = \mu(t)(1-\mu_0(t)) \quad (50)$$

Hence eq 43 is solved as

$$\mu(t) \approx \frac{\mu_0(t)}{1-\epsilon(1-\mu_0(t))} \quad (51)$$

Thus when $\mu_0(t) \ll 1$, $\mu(t)$ is larger than $\mu_0(t)$ by a factor $1/(1-\epsilon)$. This cancels with the front factor $(1-\epsilon)$ in the stress expression, so that $G_{NI}(t)$ and $G_R(t)$ agree with each other precisely.

Equation 51 is valid for t larger than a certain characteristic time τ_c, but it is also valid at $t = 0$. Thus eq 51 is expected to be a good approximation over the entire time region.

The above result resolves the previous controversy whether one should have a factor $(1-\epsilon)$ in the expression for the stress tensor. The present formulation shows that there is such a factor and supports the argument in ref 7. On the other hand, if one considers the dynamics, the factor in the stress expression cancels precisely with the factor arising from the dynamics, and the nematic interaction plays no role in the rheological properties on a long time scale. Thus the argument in ref 10 is valid also. Actually, the question whether one should have the factor $(1-\epsilon)$ in the stress expression is an ill-posed problem because the answer depends on the time scale for which the model equation is proposed. Therefore there is no essential difference in the final results in refs 7 and 11. The present paper showed that the effect of the nematic interaction on the rheological properties can be neglected in the regime where reptation motion is dominant (since the characteristic relaxation time of the chain between the entanglement point is considered to be much longer than τ_c).

That the rheological properties of the Rouse chains on the long time scale are unaffected by the nematic interaction can be shown more directly. Notice that the parameter ϵ depends on the size of the Rouse submolecule N_R. On the long time scale, one can choose a larger submolecule consisting of, say, N_R' segments. The rheological properties are unaffected by this renormalization of the submolecules, but the nematic interaction parameter ϵ' becomes smaller. Thus on the long time scale, the effect of the nematic interaction is neglected.

6. Linear Viscoelasticity of a Polymer Blend

The above theory can be easily generalized to a mixture of Rouse chains with different molecular weights. Let ϕ_A and ϕ_B be the volume fraction of each component. In this section, the quantities of each component are distinguished by the subscripts A and B; for example, N_A is the number of submolecules in the A chain. The free energy of the A chain is written as

$$A_{\mathrm{A\,chain}} = \frac{3k_BT}{2b^2}\sum_{n=0}^{N_A}(\delta_{\alpha\beta} - \epsilon S_{\alpha\beta})r_{\mathrm{A}n\alpha}r_{\mathrm{A}n\beta} \quad (52)$$

where $S_{\alpha\beta}$ is the overall orientational tensor of the submolecule and is given by the volume average of the tensor of each component:

$$S_{\alpha\beta} = \phi_A S_{\mathrm{A}\alpha\beta} + \phi_B S_{\mathrm{B}\alpha\beta} \quad (53)$$

where

$$S_{\mathrm{A}\alpha\beta} = \frac{3}{N_A b^2}\sum_{n=1}^{N_A}\langle r_{\mathrm{A}n\alpha}r_{\mathrm{A}n\beta} - {}^1/_3\delta_{\alpha\beta}\mathbf{r}_{\mathrm{A}n}{}^2\rangle \quad (54)$$

For this definition of $S_{\alpha\beta}$, the equation of motion for each component is given by the same equation as eq 18, and the stress is again given by eq 34.

In the case of linear viscoelasticity, the memory function for each component satisfies

$$\mu_A(t) = \mu_{A0}(t) + \epsilon\int_0^t \mathrm{d}t' \left[\frac{\partial}{\partial t'}\mu_0(t-t')\right]\mu_A(t') \quad (55)$$

where

$$\mu_0(t) = \phi_A\mu_{A0}(t) + \phi_B\mu_{B0}(t) \quad (56)$$

and $\mu_{A0}(t)$ is the relaxation function of component A without the nematic interaction. From eqs 55 and 56, it follows that $\mu(t) \equiv \phi_A\mu_A(t) + \phi_B\mu_B(t)$ satisfies precisely the same equation as eq 43, and the relaxation modulus is again given by eq 46, the only distinction being that $\mu_0(t)$ is given by eq 56. Thus the comments given for the monodisperse case holds for polymer blends also. In particular, the total stress is not affected by the nematic interaction on the long time scale.

7. Conclusion

In this paper, the Rouse dynamics with the nematic interaction is formulated. From the expression of the free energy, the equation of motion and the expression for the stress tensor are derived straightforwardly. As an example, the relaxation modulus in linear viscoelasticity is calculated, and this agrees with that given in the previous paper.[11] Thus the formulation in this paper includes that in the previous paper for small shear strain as a special case.

One of the main conclusions in the previous and this work is that the rheological properties on the long time scale are very insensitive to the nematic interaction. This insensitivity has been known in the theory of rubber elasticity.[3-5] It has been shown that the effect of the nematic interaction on the modulus of the rubber is of the order of $1/N_x$, where N_x is the number of segments between the cross-links. Although this result is for the equlibrium situation, it can be translated to the nonequilibrium situation: one expects that the effect of the nematic interaction on the relaxation modulus is of the order of $1/N_{\mathrm{relax}}(t)$, where $N_{\mathrm{relax}}(t)$ is the number of submolecules relaxed at time t. Thus one can anticipate that the nematic interaction is negligible on the long time scale. The present formulation demonstrated quantitatively that this anticipation is correct.

Although the nematic interaction becomes negligible in the rheological properties on the long scale, it should be mentioned that the effect is significant for the orientation of segments. Indeed, the nematic interaction gives the factor $1/(1 - \epsilon_0/3)$ on the orientation of segments (see eq 11), and this factor is independent of time.

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(13) In eq 5, terms of order ϵ^{02} are neglected. Therefore, the argument in this paper is correct only up to the order of ϵ_0. On the other hand, we may regard eq 12 as a kind of model Hamiltonian; then the calculation is correct to all orders of ϵ_0.

(14) Although the form of the equation of motion is the same as in ref 11, the definition of the orientational tensor is slightly different. In ref 11, the orientational order parameter was given by $\Gamma' = (3/b^2)\langle r_\alpha r_\beta - {}^1/_3 b^2 \delta_{\alpha\beta}\rangle$, while it is given by $S_{\alpha\beta} = (3/b^2)\langle r_\alpha r_\beta - {}^1/_3 \mathbf{r}^2 \delta_{\alpha\beta}\rangle$ in the present paper. The distinction arises from a difference in the modeling of the nematic interaction: in ref 11, both the length and the direction of submolecules are coupled with the matrix, while in the present paper, only the direction of the submolecule is coupled with the matrix. This difference in the model of the nematic interaction has no effects in the regime of linear viscoelasticity.