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# Effect of Nematic Interaction in the Orientational Relaxation of Polymer Melts

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The motion in concentrated polymer systems is described by the reptation model which assumes that each polymer slithers through a tube made of other polymers.[1] In the conventional model, it is assumed that the relaxation of each polymer is independent of the other polymers: thus, when a polymer moves out of a tube, it adopts an equilibrium conformation irrespective of the state of the other polymers. However, various experiments done recently have shown that there is certain cooperativity in the orientational relaxation. For example, Erman et al.[2] and Kornfield et al.[3] measured the orientational relaxation of a short polymer in a blend of long and short polymers and found that as long as the whole system is not in equilibrium short polymers remain oriented. Essentially the same result was obtained by Osaki et al.[4] for block copolymers and by Inoue[5] for polymer blends.

Erman et al.[2] explained the effect by "nematic interaction" which forces neighboring polymer segments to orient in the same direction. The existence of such interaction has been established in the study of stress optical coefficients for rubbers.[6-8]

Recently Merrill et al.[9] published a theory which accounts for the nematic interaction for reptating polymers. They assumed that, when a part of a polymer moves out of a tube, it takes an equilibrium conformation in a nematic field, thus being oriented as long as the surrounding polymers are oriented. This model leads to a novel boundary value problem for orientational relaxation, which they solved in an elegant manner. However, from a physical viewpoint, their model is not quite consistent with the earlier theory of nematic interaction for rubbers.[8] In this note, we propose a different model that accounts for the nematic interaction in a more conventional way.

For convenience of demonstration, we shall model the entanglements with slip links[10] and assume that the polymer is a freely jointed chain with constant bond length, $b$. However, the final conclusions is insensitive to the details of the model.

Consider a part of a polymer that passes through two slip links fixed in space with separation $r$. According to ref 10, the average number of polymer segments (or bonds) contained between the slip links is

$$n = ar/b^2 \tag{1}$$

where $a$ is the mean distance between the slip links (or mean entanglement spacing). The orientational distribution of the polymer segments between the slip links can be described in the same way as that for cross-linked networks.[7,8]

Let $i$ be a bond between the slip links, and $\mathbf{u}_i$ be the unit vector parallel to it. The orientational order parameter tensor $q_{i\alpha\beta}$ for the $i$th bond is defined by

$$q_{i\alpha\beta} = \left\langle u_{i\alpha}u_{i\beta} - \frac{1}{3}\delta_{\alpha\beta}\right\rangle \tag{2}$$

This is determined by two factors: one is the constraint imposed by the slip links, and the other is the nematic interaction. The latter is accounted for by a nematic field which is described by a mean field potential for the bond vector, $\mathbf{u}_i$,

$$U_{\mathrm{NI}} = -E\left(u_{i\alpha}u_{i\beta} - \frac{1}{3}\delta_{\alpha\beta}\right)\bar{q}_{\alpha\beta} \tag{3}$$

where $E$ denotes the strength of the nematic interaction, and $\bar{q}_{\alpha\beta}$ is the average of $q_{i\alpha\beta}$ for all bonds:

$$\bar{q}_{\alpha\beta} = \sum_{\text{all bonds in the system}} q_{i\alpha\beta}/\text{number of bonds}$$

The equilibrium distribution of $\mathbf{u}_i$ is then determined by the nematic field, $U_{\mathrm{NI}}$, and the constraint that the polymer has to pass through the slip links, from which one can calculate $q_{i\alpha\beta}$. This problem was essentially solved by Jarry and Monnerie,[8] who showed that if the order parameter is small, $q_{i\alpha\beta}$ is given by

$$q_{i\alpha\beta} = \frac{3r^2}{5n^2b^2}\left(v_\alpha v_\beta - \frac{1}{3}\delta_{\alpha\beta}\right) + \frac{2E}{15k_{\mathrm{B}}T}\bar{q}_{\alpha\beta} \tag{4}$$

where $\mathbf{v}$ is a unit vector parallel to the vector joining the slip links. The first term represents the effect of slip-link constraints, and the second term represents the nematic field.

The tensor $q_{i\alpha\beta}$ is related to birefringence. Since each bond contributes to birefringence additively, the total contribution to the birefringence from the part between the slip links is proportional to

$$\sum_{i=1}^{n} q_{i\alpha\beta} = nq_{i\alpha\beta} = \frac{r}{a}\left(\frac{3}{5}\left(v_\alpha v_\beta - \frac{1}{3}\delta_{\alpha\beta}\right) + \frac{2E}{15k_{\mathrm{B}}T}\frac{a^2}{b^2}\bar{q}_{\alpha\beta}\right) \tag{5}$$

On the other hand, it can be shown that the stress, which is derived from the change of the free energy caused by a hypothetical displacement of slip links, is independent of the nematic field: the contribution to the stress tensor from a polymer chain with the end-to-end vector $rv$ is given by [8]

$$\Delta\sigma_{\alpha\beta} = \frac{3k_{\mathrm{B}}T}{nb^2}r^2\left(v_\alpha v_\beta - \frac{1}{3}\delta_{\alpha\beta}\right) = 3k_{\mathrm{B}}T\frac{r}{a}\left(v_\alpha v_\beta - \frac{1}{3}\delta_{\alpha\beta}\right) \tag{6}$$

We shall now consider a melt of monodisperse polymers. A primitive chain is defined by the set of line segments connecting the slip links that confine a polymer. A point on a primitive chain is denoted by the contour length $s$ measured from the end of the primitive chain: thus $\mathbf{v}(s,t)$ denotes the unit vector tangent to the primitive chain at point $s$.

Let $S_{\alpha\beta}(s,t)$ be the orientational order parameter of the primitive chain at the point $s$:

$$S_{\alpha\beta}(s,t) = \left\langle v_\alpha(s,t)v_\beta(s,t) - \frac{1}{3}\delta_{\alpha\beta}\right\rangle \tag{7}$$

Then the total stress is given by (note that, according to eq 6, the stress is proportional to the contour length of the primitive chain)

$$\sigma_{\alpha\beta} = 3k_{\mathrm{B}}T\nu\frac{1}{a}\int_0^L \mathrm{d}s\, S_{\alpha\beta}(s,t) \tag{8}$$

where $\nu$ is the number of polymers in unit volume, and $L$

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is the contour length of the primitive chain. With the definition

$$\bar{S}_{\alpha\beta}(t) = \frac{1}{L}\int_0^L \mathrm{d}s\; S_{\alpha\beta}(s,t) \tag{9}$$

eq 8 is rewritten as

$$\sigma_{\alpha\beta} = 3k_{\mathrm{B}}T\nu\frac{L}{a}\bar{S}_{\alpha\beta}(t) \tag{10}$$

To discuss the birefringence, we define the tensor

$$q_{\alpha\beta}(s,t) = \langle q_{i\alpha\beta}\rangle \tag{11}$$

where $i$ is the polymer segment at point $s$ of the primitive chain, and the average is taken for the conformation of the primitive chain, i.e., for $\mathbf{v}(s,t)$. The refractive index tensor $\Delta n_{\alpha\beta}$ is proportional to[1]

$$\sum_i \langle q_{i\alpha\beta}\rangle = \nu\frac{a}{b^2}\int_0^L \mathrm{d}s\; q_{\alpha\beta}(s,t) \tag{12}$$

The factor $a/b^2$ accounts for the number of bonds per unit contour length of the primitive chain (see eq 1). For convenience, we introduce a tensor

$$Q_{\alpha\beta}(s,t) = \frac{5a^2}{3b^2}q_{\alpha\beta}(s,t) \tag{13}$$

The tensor $Q_{\alpha\beta}(s,t)$ corresponds to the sum of $q_{i\alpha\beta}$ for a part of the primitive chain with contour length $a$. The factor $5/3$ is used to simplify subsequent equations. The refractive index tensor $\Delta n_{\alpha\beta}$ is proportional to the integral of $Q_{\alpha\beta}(s,t)$ along $s$:

$$\Delta n_{\alpha\beta} \propto \nu\frac{1}{a}\int_0^L \mathrm{d}s\; Q_{\alpha\beta}(s,t) = \nu\frac{L}{a}\bar{Q}_{\alpha\beta}(s,t) \tag{14}$$

where

$$\bar{Q}_{\alpha\beta}(t) \equiv \frac{1}{L}\int_0^L \mathrm{d}s\; Q_{\alpha\beta}(s,t) \tag{15}$$

The average $\bar{q}_{\alpha\beta}$ is given by (see eq 11)

$$\bar{q}_{\alpha\beta} = \frac{3}{5}\frac{b^2}{a^2}\bar{Q}_{\alpha\beta} \tag{16}$$

With these definitions, it follows from eq 5 that

$$Q_{\alpha\beta}(s,t) = S_{\alpha\beta}(s,t) + \epsilon\bar{Q}_{\alpha\beta}(t) \tag{17}$$

where $\epsilon = 2E/15k_{\mathrm{B}}T$. Equation 17 is essentially the same as those derived in the previous theories for the nematic interaction in rubbers,[8] except that in the present theory, for uncross-linked systems, the topological constraint $S_{\alpha\beta}(s,t)$ varies with $s$ and $t$.

The distinction of our model and that of Merrill et al.[9] is now clear. Merrill et al. do not discriminate between $S_{\alpha\beta}$ and $Q_{\alpha\beta}$ and account for the nematic interaction through the boundary condition at the chain end, while we expect that the nematic interaction would alter the orientational order parameter for the internal segments just as it does for rubbers. Thus, there are two order parameters, $S_{\alpha\beta}$ and $Q_{\alpha\beta}$: the former represents the order parameter of the primitive chain (or tube), and the latter represents the actual polymer segments.

In our model, it is $S_{\alpha\beta}(s,t)$ that satisfies the reptation equation:[11]

$$\frac{\partial}{\partial t}S_{\alpha\beta}(s,t) = D_{\mathrm{c}}\frac{\partial^2}{\partial s^2}S_{\alpha\beta}(s,t) \tag{18}$$

where $D_{\mathrm{c}}$ is the diffusion constant of the primitive chain along the tube. At the chain end, $S_{\alpha\beta}$ would vanish since there are no topological constraints.[12] Thus,

$$S_{\alpha\beta}(s,t) = 0 \qquad \text{at} \quad s = 0, L \tag{19}$$

Equations 18 and 19 determine $S_{\alpha\beta}(s,t)$. To obtain $\bar{Q}_{\alpha\beta}(t)$, we integrate eq 17 for $s$ from 0 to $L$ to obtain

$$\bar{Q}_{\alpha\beta}(t) = \bar{S}_{\alpha\beta}(t) + \epsilon\bar{Q}_{\alpha\beta}(t) \tag{20}$$

or

$$\bar{Q}_{\alpha\beta}(t) = \frac{1}{1-\epsilon}\bar{S}_{\alpha\beta}(t) \tag{21}$$

Thus, once $S_{\alpha\beta}(s,t)$ is obtained, $Q_{\alpha\beta}(s,t)$ is determined by eq 17 and 21.

So far we have been considering monodisperse systems. It is easy to generalize the theory for polydisperse systems. Let us consider, as an example, a bidisperse system, i.e., a blend of long and short polymers of the same species. Quantities referring to each polymers are specified by the subscripts L and S, respectively. Let $\phi_{\mathrm{L}}$ and $\phi_{\mathrm{S}}$ be the volume fractions of long and short polymers. For such blend, eq 20 is written as

$$\bar{Q}_{\mathrm{L}}(t) = \bar{S}_{\mathrm{L}}(t) + \epsilon(\phi_{\mathrm{L}}\bar{Q}_{\mathrm{L}}(t) + \phi_{\mathrm{S}}\bar{Q}_{\mathrm{S}}(t)) \tag{22}$$

$$\bar{Q}_{\mathrm{S}}(t) = \bar{S}_{\mathrm{S}}(t) + \epsilon(\phi_{\mathrm{L}}\bar{Q}_{\mathrm{L}}(t) + \phi_{\mathrm{S}}\bar{Q}_{\mathrm{S}}(t)) \tag{23}$$

Here for the sake of simplicity, $Q_{\alpha\beta}$ is abbreviated as $Q$. Equations 22 and 23 are solved as

$$\bar{Q}_{\mathrm{L}}(t) = \frac{1-\epsilon\phi_{\mathrm{S}}}{1-\epsilon}\bar{S}_{\mathrm{L}}(t) + \frac{\epsilon\phi_{\mathrm{S}}}{1-\epsilon}\bar{S}_{\mathrm{S}}(t) \tag{24}$$

$$\bar{Q}_{\mathrm{S}}(t) = \frac{\epsilon\phi_{\mathrm{L}}}{1-\epsilon}\bar{S}_{\mathrm{L}}(t) + \frac{1-\epsilon\phi_{\mathrm{L}}}{1-\epsilon}\bar{S}_{\mathrm{S}}(t) \tag{25}$$

Let $\tau_{\mathrm{L}}$ and $\tau_{\mathrm{S}}$ be the characteristic relaxation times of $\bar{S}_{\mathrm{L}}(t)$ and $\bar{S}_{\mathrm{S}}(t)$, respectively. The explicit forms of $\tau_{\mathrm{L}}$ and $\tau_{\mathrm{S}}$ are discussed in ref 13. An important point is that $\tau_{\mathrm{L}}$ varies with $\phi_{\mathrm{L}}$ due to the effect of constraint release, while $\tau_{\mathrm{S}}$ is independent of $\phi_{\mathrm{L}}$. Thus, the relaxation behavior of $\bar{S}_{\mathrm{S}}(t)$ is essentially independent of $\phi_{\mathrm{L}}$.[14] On the other hand, as it is indicated by eq 25, the relaxation of $\bar{Q}_{\mathrm{S}}(t)$ does depend on $\phi_{\mathrm{L}}$ due to the nematic interaction. This behavior is indeed observed by Kornfield et al.[3] Conversely, $\bar{S}_{\mathrm{L}}(t)$ and $\bar{S}_{\mathrm{S}}(t)$ are known if $\bar{Q}_{\mathrm{L}}(t)$ and $\bar{Q}_{\mathrm{S}}(t)$ are measured.

Finally, a comment is made for the stress optical law. In the present theory, we introduced two order parameters, $S$ and $Q$, each being related to stress and birefringence respectively. For a polydisperse system, the time dependences of $Q$ and $S$ are different from each other, as is indicated by eq 24 and 25. Thus, at first sight it might appear that the present theory is contradictory to the stress optical law which states that the total stress is proportional to the total birefringence. This is not the case. From eq 24 and 25, it follows that

$$\phi_{\mathrm{L}}\bar{Q}_{\mathrm{L}}(t) + \phi_{\mathrm{S}}\bar{Q}_{\mathrm{S}}(t) = \frac{1}{1-\epsilon}(\phi_{\mathrm{L}}\bar{S}_{\mathrm{L}}(t) + \phi_{\mathrm{S}}\bar{S}_{\mathrm{S}}(t)) \tag{26}$$

The right-hand side is proportional to the total birefringence $\Delta n_{\alpha\beta}$ and the left-hand side to the total stress $\sigma_{\alpha\beta}$. Thus, eq 26 guarantees that the linear relation between the stress and birefringence holds even if $\bar{S}(t)$ and $\bar{Q}(t)$ have different time dependences.

We have shown a new modification of the reptation theory. The modification does not affect the previous reptation theory in any fundamental way. Also it is consistent with the stress optical law. The present theory enables us to study the reptation dynamics, especially the effect of constraint release by spectroscopic techniques.

## References and Notes

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(11) A modified equation for $S$ would be required if constraint release is important, but here for simplicity we disregarded it.
(12) One can assume that the tube segments at the chain ends are oriented due to the nematic interaction. In this case, one has to solve the boundary value problem similar to that of Merrill et al. In this paper, we do not pursue this model since the essential aspects of the nematic interaction is accounted for by eq 17.
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(14) Precisely speaking, due to the effect of constraint release, $\tilde{S}_S(t)$ depends on $\phi_L$, but this dependence would be much less than that for $\tilde{Q}_S(t)$.

# Increase of the Mobility of Knotted Macromolecules

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A basic feature of polymer dynamics is the entanglements. Entanglements are of importance in concentrated polymer solutions and gels and are examined in connection with, e.g., diffusive motion of polymers.[1,2] However, a simple example is already provided by self-entangled macromolecules, which give rise to knots. In this note we focus on knotted macromolecules. Experimentally, the production of knotted polymers has very recently become possible by treating relaxed circular DNA molecules with topoisomerases.[3] With this method one obtains (at least for small numbers of crossings) all topologically possible forms.[4] This fortunate fact opens now the possibility of relating theoretical predictions to experiments. We note that for each knot its minimal number of crossings (usually designated as "nodes") is an important topological characteristic quantity; evidently any knot may take forms with more crossings—but these may be disentangled without cutting the knot. Now, diffusion experiments show that the knots are separable according to their number of nodes. Firstly, one observes that knots with a larger number of nodes diffuse faster, which is intuitively understandable because of the compactness of a knot with many nodes.[5] Furthermore, in addition to this, knots with the same number of nodes have closely similar friction coefficients: especially for electrophoresis in agarose gel, where the mobility of the knots increases linearly with the number of nodes.[3]

To examine the diffusional behavior of knotted molecules theoretically, we first remark that the wealth of topologically possible patterns is hardly amenable to an exact treatment. Thus, here we consider only knots with all nodes pulled together. Such a pattern can be simply modeled by a flexible polymer chain with Gaussian statistics under the restrictions of being closed and forming as many loops emerging from a center as there are nodes in the knot. This model can be viewed as being made from a star-branched molecule by replacing the linear star arms by closed loops (compare Figure 1). Hence, our pattern displays both star and ring aspects.

For dilute solutions, it is now straightforward to obtain the friction coefficient (which is proportional to the inverse of the diffusion coefficient) for such patterns. Following Kirkwood,[6] the friction coefficient $f$ (which is the proportionality factor between the total mean force $\mathbf{F}$ on the molecule and its mean velocity $\mathbf{u}$, i.e., $\mathbf{F} = f\mathbf{u}$) is approximately given by

$$f = N\zeta\left[1 + \frac{\zeta}{6\pi\eta N}\sum_{\mu,\nu=1}^{n}\int_0^{N_\mu}\mathrm{d}t\int_0^{N_\nu}\mathrm{d}s\ \langle R^{-1}(\mu t,\nu s)\rangle\right]^{-1} \tag{1}$$

In eq 1, $\zeta$ denotes the friction constant for one monomer, $N_\mu$ is the number of monomers on the $\mu$th loop, $N$ is the total number of monomers, and $n$ denotes the number of loops. The viscosity of the solvent, is $\eta$, and $R^{-1}(\mu t,\nu s)$ is the inverse distance between the $s$th monomer on the $\nu$th loop and the $t$th monomer on the $\mu$th loop. To calculate the configurational average of the inverse distance, one has to consider the distribution function for the distance vector $\mathbf{R}(\mu t,\nu s)$ between the monomers:[7,8]

$$P(\mathbf{R}(\mu t,\nu s)) = \left[\frac{3\det D}{2\pi a^2 \det C}\right]^{3/2}\exp\left[-\frac{3\det D}{2a^2\det C}(\mathbf{R}(\mu t,\nu s))^2\right] \tag{2}$$

Here, $a$ denotes the bond length, and the symmetric $(n + 1) \times (n + 1)$ matrix $\mathbf{C}$ is given by the elements $C_{\alpha\beta}$, which equal (for $\nu \geq \mu$)

$$(1 - \delta_{\mu\nu})\Big[\sum_{m=\mu}^{\nu-1} N_m + s - t\Big] + \delta_{\mu\nu}|t - s|$$

if $\alpha = \beta = n + 1$

$$N_\alpha\delta_{\alpha\beta} \tag{3}$$

if $1 \leq \alpha,\beta \leq n$, and

$$\sum_{m=1}^{n}\sum_{p=1}^{N_m}[\varphi_{\nu,s}(m,p) - \varphi_{\mu,t}(m,p)][\varphi_{\alpha,N_\alpha}(m,p) - \varphi_{\alpha-1,N_{\alpha-1}}(m,p)]$$

if $1 \leq \alpha \leq n$ and $\beta = n + 1$, where

$$\begin{aligned}\varphi_{\lambda,x}(m,p) &\equiv 1 \qquad \text{if } m < \lambda,\ 1 \leq p \leq N_m \\ &\qquad\qquad \text{or if } m = \lambda,\ 1 \leq p \leq x \\ &\equiv 0 \qquad \text{otherwise}\end{aligned} \tag{4}$$

The $n \times n$ matrix $\mathbf{D}$ is given by $D_{\alpha\beta} = N_\alpha\delta_{\alpha\beta}$ for all $1 \leq \alpha,\beta \leq n$. From eq 3 and 4 one calculates the ratio of the determinants

$$\begin{aligned}\det C/\det D &= |t - s| - (t - s)^2/N_\mu \qquad \text{if } \mu = \nu \\ \det C/\det D &= t + s - s^2/N_\nu - t^2/N_\mu \qquad \text{if } \mu \neq \nu\end{aligned} \tag{5}$$

Because the mean inverse distance results in

$$\langle R^{-1}(\mu t,\nu s)\rangle = (6/\pi a^2)^{1/2}(\det D/\det C)^{1/2} \tag{6}$$

the double sum reads in the continuum limit

$$\sum_{\mu,\nu}\int_0^{N_\mu}\mathrm{d}t\int_0^{N_\nu}\mathrm{d}s\ \langle R^{-1}(\mu t,\nu s)\rangle = (6\pi/a^2)^{1/2}\Big[\sum_\mu {N_\mu}^{3/2} + \sum_\mu\sum_{\nu\neq\mu}(N_\nu N_\mu)^{1/2}({N_\nu}^{1/2} + {N_\mu}^{1/2} - (N_\nu + N_\mu)^{1/2})\Big] \tag{7}$$

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