Friction Tensor of Flexible Polymer Chains in Nematic Liquid Crystals

Shi-Qing Wang

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

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ABSTRACT: Hydrodynamic properties of a flexible polymer chain in low molecular weight liquid crystals (LC) have been studied. The starting point is the derivation of the hydrodynamic Oseen tensor for anisotropic fluids that satisfy a modified Navier–Stokes equation. The nematics of LC breaks the spatial isotropy and leads to a necessary introduction of the friction tensor Σ for polymers. The general expression for Σ is obtained as a formal perturbation expansion within the Kirkwood–Riseman theory, and the component corresponding to the polymer diffusive motion along the nematic direction is evaluated explicitly by using the renormalization group method and by considering the smallness of one of the Leslie coefficients of the nematic solvent. The result depends on the LC Miesowicz viscosities in a nontrivial way, yet the molecular weight dependence is still universal.

I. Introduction

Over the past several decades both equilibrium and transport properties of polymers in *isotropic* solvents have been extensively studied. Now many books exist[1-4] that review experimental results as well as classical and modern theories of polymer solutions. The ideas of scaling laws[2] and renormalization group theories[4] have been particularly successful in analyzing and rationalizing experimentally observed universal behaviors of uncharged linear flexible polymers in isotropic solutions. For polyelectrolytes, stiff chains, and polymers with complex architectures or chemical combinations (copolymers, random branched polymers, etc), their statistical mechanical theories are highly nontrivial even in the infinite-dilution limit. On the other hand, the *non-Newtonian* problem of a single linear flexible chain in a *strong* simple shear flow has not been settled despite enormous efforts made in the past 30 years starting with Rouse[5] and Zimm.[6] Furthermore, except for a few cases[7-10] little attention has been paid to polymer chains in solution with liquid crystals (LC) as *anisotropic* solvents. As more people are beginning to work on polymeric liquid crystals, it becomes important to obtain some basic understanding of conformational and dynamic properties of macromolecules in nematic LC.

Conformations of flexible polymer chains in LC depend on microscopic interactions between the polymeric monomers and anisotropic molecules of LC. A molecular-level statistical mechanical theory of such interactions is not available, and how they change or invalidate scaling relations between equilibrium properties and the molecular weight is unknown. Thus it remains to be shown how an increase in the nematic strength would lead to a coil-collapse phase transition in the flexible polymer immersed in the anisotropic solvent. It is interesting and useful to ask whether there exist any *good* nematic solvents for flexible polymers in the sense that polymers take an *expanded* averaged shape in those good solvents. There is also the important question of how linear flexible polymers contribute to the elasticity of liquid crystals, i.e., how the Frank elastic constants depend upon the molecular weight and polymer concentration. Answers to these questions will undoubtedly increase our understanding of polymers in their liquid crystalline phase.

Rather than looking for solutions to the above-mentioned *equilibrium* problems of polymer–nematics, here we would like to study the dynamics of polymers in LC. We begin by giving a derivation of the modified hydrodynamic Oseen tensor for an anisotropic fluid. Then the hydrodynamic interaction (HI) among polymer segments is incorporated to evaluate the tensorial friction for the polymer as a function of the polymeric molecular weight and Leslie viscosities of the nematic liquid crystal. It is found that the dynamic exponent is unaffected by the solvent anisotropy although the HI parameter becomes a highly complicated function of the Miesowicz viscosity coefficients. The existence of a HI fixed point derived from our renormalization group analysis indicates the universality of dynamic properties of polymers in a low molecular weight liquid crystal. This suggests that the modification of Miesowicz viscosity coefficients of the liquid crystal dispersion due to flexible polymers should also be universal and can be looked at in a similar way. We will perform such an evaluation of these Miesowicz viscosities in a future publication, while the present work is merely a beginning of a series of investigations into the viscoelastic properties of liquid crystal dispersions of polymers.

In section II, the Leslie viscous stress tensor is introduced into the Stokes equation and the fluid propagator of this modified Navier–Stokes equation is derived as the new Oseen type hydrodynamic tensor. The Kirkwood–Riseman theory for polymer dynamics in nematics is then described in terms of the "anisotropic" Oseen tensor in section III. The friction tensor of flexible polymers in liquid crystals is defined, and one of its components is evaluated to first order in hydrodynamic interactions within the scheme of a renormalization group theory. The paper ends with a brief discussion in section IV.

II. Hydrodynamic Interactions in Anisotropic Fluids

Simple fluids are normally composed of isotropic molecules and their properties are therefore independent of any specific direction(s). The isotropy of normal liquids allows for a convenient description of the fluid motion via the well-known Navier–Stokes equation for the velocity field. In particular, for incompressible fluids the viscous term involves the *square* of the Laplace differential operator. Such a mathematical structure leads directly to the simplistic long-range $1/R$ dependence of hydrodynamic interactions between two objects R distance apart. The purpose of this section is to study the motion of anisotropic fluids in terms of their fluid mechanical equation. Below we first write down the equation of motion, and

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then its Green function is conveniently obtained in the Fourier representation.

The first phenomenological theory of the stress tensor for nematic liquid crystals is that of Ericksen and Leslie. It requires six viscosity coefficients $\{\alpha_i\}$ to completely specify the viscous stress, which has the form[2,11]

$$\sigma' = \alpha_1(\mathbf{nn}{:}A)\mathbf{nn} + \alpha_2\mathbf{nN} + \alpha_3\mathbf{Nn} + \alpha_4 A + \alpha_5\mathbf{nn}\cdot A + \alpha_6 A\cdot\mathbf{nn} \quad (2.1)$$

where A is the symmetric part of the velocity gradient tensor

$$A = (1/2)[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\mathrm{T}}] \quad (2.1a)$$

and the vector $\mathbf{N}$ is given by

$$\mathbf{N} = \mathrm{d}\mathbf{n}/\mathrm{d}t - (1/2)[(\nabla\mathbf{v})^{\mathrm{T}} - \nabla\mathbf{v}]\cdot\mathbf{n} \quad (2.1b)$$

and $\mathbf{n}$ is the unit vector in the nematic direction. Here we consider a very strong externally applied magnetic field that keeps the solvent oriented in the *fixed* direction $\mathbf{n}$ in the presence of polymer chains. Thus from now on, we take $\mathrm{d}\mathbf{n}/\mathrm{d}t = 0$. The $(\nabla\mathbf{v})^{\mathrm{T}}$ in (2.1a,b) denotes the transpose of the dyadic $\nabla\mathbf{v}$. In terms of the stress tensor σ', the hydrodynamic equation for anisotropic fluids can be written as

$$\rho\frac{\partial\mathbf{v}}{\partial t} + \nabla\cdot\sigma' + \nabla p = \mathbf{f} \quad (2.2)$$

where ρ is the fluid density, p the hydrostatic pressure, and $\mathbf{f}$ the force density in the fluid. To see the structure of this partial differential equation more clearly, below we convert it to an algebraic equation by going to the Fourier space $\mathbf{k}$.

We are interested in the steady-state (i.e., long time) solution of (2.2). Since the solvent dynamics is much faster than the polymer relaxation times on the scale of the polymer dimension, the Markovian approximation can be applied to the solution to (2.2). So we set $\partial\mathbf{v}/\partial t = 0$ and make a Fourier transform of (2.2)

$$(\eta_{\mathrm{a}}k^2 + \epsilon_1 k_{\mathrm{n}}{}^2)\mathbf{v}(\mathbf{k}) + \epsilon_2(k^2\mathbf{n} - k_{\mathrm{n}}\mathbf{k})\upsilon_{\mathrm{n}} + \alpha_1(k_{\mathrm{n}}/k)^2(k^2\mathbf{n} - k_{\mathrm{n}}\mathbf{k})\upsilon_{\mathrm{n}} = t(\mathbf{k})\cdot f(\mathbf{k}) \quad (2.3)$$

where k_{n} is the component of $\mathbf{k}$ in the nematic direction $\mathbf{n}$, i.e., $k_{\mathrm{n}} = \mathbf{n}\cdot\mathbf{k}$, and the longitudinal velocity υ_{n} is just $\upsilon_{\mathrm{n}} = \mathbf{n}\cdot\mathbf{v}(\mathbf{k})$. In deriving (2.3), we substituted (2.1), (2.1a), and (2.1b) for σ' into (2.2) and took $\mathrm{d}\mathbf{n}/\mathrm{d}t = 0$. The viscosity parameters ϵ_1 and ϵ_2 are combinations of the Miesowicz viscosities (η_{a}, η_{b}, and η_{c}) of the nematic liquid crystal[11] i.e.

$$\epsilon_1 = (1/2)(\alpha_5 - \alpha_2) = \eta_{\mathrm{c}} - \eta_{\mathrm{a}} \quad (2.4a)$$

$$\epsilon_2 = (1/2)(\alpha_3 + \alpha_6) = \eta_{\mathrm{b}} - \eta_{\mathrm{a}} \quad (2.4b)$$

and $t(\mathbf{k})$ is the transverse projection operator given by $t(\mathbf{k}) = I - \mathbf{kk}/k^2$, with I being the unit tensor. Equation 2.3 has been obtained by eliminating the pressure p in (2.2) using the incompressibility condition $\mathbf{k}\cdot\mathbf{v}(\mathbf{k}) = 0$. It is straightforward to derive $\mathbf{v}$ from (2.3) in terms of $\mathbf{f}$

$$\mathbf{v}(\mathbf{k}) = [T(\mathbf{k}) + G(\mathbf{k})]\cdot\mathbf{f}(\mathbf{k}) \quad (2.5)$$

where T is like an Oseen tensor[1,12] proportional to $t(\mathbf{k})$ and is given by

$$T = t(\mathbf{k})/(\eta_{\mathrm{a}}k^2 + \epsilon_1 k_{\mathrm{n}}{}^2) \quad (2.6)$$

and tensor G has the following messy expression:

$$G = -(k^2\mathbf{nn} - k_{\mathrm{n}}\mathbf{kn})\cdot t(\mathbf{k})\{(\epsilon_2 + \alpha_1 k_{\mathrm{n}}{}^2/k^2)/(\eta_{\mathrm{a}}k^2 + \epsilon_1 k_{\mathrm{n}}{}^2) \times [\eta_{\mathrm{a}}k^2 + \epsilon_1 k_{\mathrm{n}}{}^2 + (\epsilon_2 + \alpha_1 k_{\mathrm{n}}{}^2/k^2)(k^2 - k_{\mathrm{n}}{}^2)]\} \quad (2.7)$$

The solution (2.5) with (2.6) and (2.7) describes how the force disturbance $\mathbf{f}$ produces a velocity field $\mathbf{v}$ in a nematic fluid and it is the central result of this section.

In the next section we examine the hydrodynamic behavior of a flexible polymer chain in such a nematic LC as discussed above. Since the continuum hydrodynamic description of the nematic liquid has been adopted, the polymer segment under consideration is assumed to be much larger than the individual anisotropic molecules of the solvent. In particular, the Rouse–Zimm frictional beads[5,6] (comprising a number of repeated chemical units) are hypothesized to be so large compared to solvent molecules that a friction constant can be meaningfully assigned to each such bead. This kind of condition is actually necessary in most microscopic molecular models for polymer dynamics.[1]

III. Kirkwood–Riseman Formulation of Polymer–Nematics

A. Kirkwood–Riseman Theory of Polymers in LC. There exist numerous models for polymer solution hydrodynamics, ranging from the rigid-body treatment of Kirkwood and Riseman[1,12] to the Langevin kinetic description.[13] For zero frequency and linear transport properties, it has been well established that the Kirkwood–Riseman (KR) formulation is completely equivalent to that of the Kirkwood diffusion equation. We will base our calculation on the Kirkwood–Riseman model as it is also simpler both conceptually and mathematically. Imagine an experiment in which a flexible polymer chain is pulled by an infinitesimal force $\mathbf{F}$ with an infinitesimally small drift velocity $\mathbf{v}_{\mathrm{d}}$ in a nematic solvent. Then each polymer segment is exerting a force on the solvent. The basic equation of the KR model of polymer–nematics is the force equation for the ith segment with friction tensor ζ

$$\mathbf{F}_i = \zeta\cdot(\mathbf{v}_{\mathrm{d}} - \mathbf{v}_i) \quad (3.1)$$

where $\mathbf{v}_i$ is the solvent velocity at the ith segment entirely due to the hydrodynamic disturbance from other segments along the chain. Before we make use of the results obtained in the previous section, it is important to realize that the polymer is moving with so small a velocity of $\mathbf{v}_{\mathrm{d}}$ as not to disturb the nematic field $\mathbf{n}$. Thus, even in the presence of polymers the pure nematic solvent is in the stationary state ($\mathrm{d}\mathbf{n}/\mathrm{d}t = 0$). Applying (2.5), we have

$$\mathbf{v}_i = \sum_{j=1}^{n}(T + G)_{ij}\cdot\mathbf{F}_j \quad (3.2)$$

where n is the number of segments in the chain and the Fourier transforms of T and G have been given in the previous section. The friction tensor Σ of a flexible polymer chain in the nematic solvent is then defined as the proportionality tensor of the configurational averaged polymer force to the drift velocity

$$\bar{\mathbf{F}} = \sum_{j=1}^{n}\langle\mathbf{F}_j\rangle = \Sigma\cdot\mathbf{v}_{\mathrm{d}} \quad (3.3)$$

and its tensorial expression is obtained via substitution of (3.2) into (3.1)

$$\Sigma = n\zeta - \zeta\cdot\sum_{i,j=1}^{n}\langle(T + G)_{ij}\rangle\cdot\zeta + O(\zeta^3) \quad (3.4)$$

The expansion (3.4) in powers of ζ has been argued to be valid, and the truncation to first order (as explicitly given here) is believed to be an excellent approximation to the asymptotic series.[14] For the nematic solvent with director $\mathbf{n}$, we can safely assume that the matrix of ζ is diagonal;

e.g., $\mathbf{n}\cdot\zeta\cdot\mathbf{n} = \zeta_{\parallel}$ is the parallel component and $\mathbf{t}\cdot\zeta\cdot\mathbf{t} = \zeta_{\mathrm{tt}}$ is one of the perpendicular components corresponding to the direction **t** for which $\mathbf{n}\cdot\mathbf{t} = 0$. That is, the polymer segment has a friction constant $\zeta_{\parallel}$ with respect to its motion in the **n** direction and a friction ζ_{tt} for the directions perpendicular to **n**. It is easy to show that Σ is also a diagonal matrix whose nonvanishing components $\Sigma_{\parallel}$ and Σ_{tt} are associated respectively with the polymer's center-of-mass diffusion along the nematic direction **n** and with directions perpendicular to **n**.

B. Evaluation of Polymer Friction Constant $\Sigma_{\parallel}$. In this paper, we are interested in polymer frictional properties in nematic liquid crystals and especially in the evaluation of the "parallel" friction coefficient $\Sigma_{\parallel}$ of a flexible polymer. In a future publication we will report on the intrinsic Miesowicz viscosities of polymer–liquid crystal solutions. From (3.3) we obtain the formal expression for $\Sigma_{\parallel}$

$$\Sigma_{\parallel} = n\zeta_{\parallel} - \zeta_{\parallel}^{2}\sum_{i,j=1}^{n}\langle (T_{ij} + G_{ij})_{\mathrm{nn}}\rangle + O(\zeta_{\parallel}^{3}) \qquad (3.5)$$

where the Fourier transform of $(T + G)_{\mathrm{nn}}$ has a simple form, according to (2.6) and (2.7)

$$(T + G)_{\mathrm{nn}} = \mathbf{n}\cdot t(\mathbf{k})\cdot\mathbf{n}/[\eta_{\mathrm{a}}k^{2} + \epsilon_{1}k_{\mathrm{n}}^{2} + (\epsilon_{2} + \alpha_{1}k_{\mathrm{n}}^{2}/k^{2})(k^{2} - k_{\mathrm{n}}^{2})] \qquad (3.6)$$

with the projection tensor $t(\mathbf{k})$ given above in (2.5). For typical liquid crystals, the value of α_1 is much smaller in comparison with η_{a} and ϵ_1 (e.g., for MBBA, $\alpha_1 = 6.5$, $\eta_{\mathrm{a}} = 41.6$, and $\epsilon_1 = 61.9$). Consequently, neglecting the term involving α_1, (3.6) can be simplified to

$$(T + G)_{\mathrm{nn}} = \mathbf{n}\cdot t(\mathbf{k})\cdot\mathbf{n}[\eta_{\mathrm{c}}k_{\mathrm{n}}^{2} + \eta_{\mathrm{b}}(k^{2} - k_{\mathrm{n}}^{2})]^{-1} \qquad (3.7)$$

where use has been made of (2.4a) and (2.4b). Notice that if the solvent was an isotropic simple liquid we would recover the familiar Oseen tensor since the denominator of $(T + G)$ becomes ηk^2 upon setting $\eta_{\mathrm{b}} = \eta_{\mathrm{c}} = \eta$. For ordinary nematic LC, the difference between η_{b} and η_{c} is indeed significant (for MBBA, $\eta_{\mathrm{b}} = 23.8$ and $\eta_{\mathrm{c}} = 103.5$), leading to a strong anisotropy in hydrodynamic interactions. In terms of (3.7) and passing to the continuous-chain limit, we explicitly rewrite (3.5) as

$$\Sigma_{\parallel} = n\zeta_{\parallel} - \zeta_{\parallel}^{2}\int_{0}^{N}\mathrm{d}\tau\int_{0}^{N}\mathrm{d}\tau'\int_{k}(1 - k_{\mathrm{n}}^{2}/k^{2})[\eta_{\mathrm{c}}k_{\mathrm{n}}^{2} + \eta_{\mathrm{b}}(k^{2} - k_{\mathrm{n}}^{2})]^{-1}\langle\exp\{\mathbf{k}\cdot[\mathbf{R}(\tau) - \mathbf{R}(\tau')]\}\rangle \qquad (3.8)$$

where $\int_k$ is the integration in the d-dimensional **k** space, $\mathbf{R}(\tau)$ denotes the position of the polymer segment τ along the chain contour of length N, and the average $\langle ... \rangle$ is over the distribution function for polymer conformations $\{\mathbf{R}(\tau)\}$. Higher order terms in (3.8) are neglected in our first-order renormalization group calculation.

In order to evaluate the average in (3.8) we need to specify the conformational distribution for polymer chains in nematic liquid crystals. Assuming that the interaction between the polymer segments and the nematics is of the Maier–Saupe type and the backbone of the chain is still Gaussian, we show in Appendix A that the configuration of the polymer chain is an anisotropic random walk. Thus the mean square of the end-to-end distance has a larger projection along the LC nematic director but is still proportional to the chain contour length (or molecular weight). The value of the average in (3.8) has been obtained in (A.3), and the integrations over τ, τ', and **k** are performed in Appendix B. The final result reads

$$\Sigma_{\parallel} = f_{\parallel}z_{\mathrm{H}}^{\circ}[1 - (2/\epsilon)z_{\mathrm{H}}^{\circ} + O(z_{\mathrm{H}}^{\circ 2})] \qquad (3.9)$$

where $\epsilon = 4 - d$ (d = spatial dimensionality). The hydrodynamic interaction parameter z_{H}°, given in (B.6), is a highly complex function of the LC Miesowicz viscosities but its scaling relationship with the chain length is as simple as $(2\pi N)^{\epsilon/2}$, just as in the isotropic case.[14] The friction constant $f_{\parallel}$ is related to z_{H}° through

$$f_{\parallel}z_{\mathrm{H}}^{\circ} = n\zeta_{\parallel} \qquad (3.10)$$

and therefore scales with the chain length N as $N^{1-\epsilon/2}$ (i.e., $N^{1/2}$ in three dimensions). The singularity $1/\epsilon$ appearing in (3.9) can be removed by means of standard renormalization group procedures. We will not reiterate our renormalization group analysis of (3.9) since it has been done many times in the literature.[13-15] Basically we define a renormalized variable u_{H} through

$$u_{\mathrm{H}}^{\circ} = u_{\mathrm{H}}(1 + 2u_{\mathrm{H}}/\epsilon + ...)$$

where the dimensionless u_{H}° is related to z_{H}° in terms of the hydrodynamic blob size L; i.e., $z_{\mathrm{H}}^{\circ} = (2\pi N/L)^{\epsilon/2}u_{\mathrm{H}}^{\circ}$. The renormalized friction coefficient of a polymer dispersed in LC is given by

$$\Sigma_{\parallel} = f_{\parallel}(2\pi N)/^{\epsilon/2-u_{\mathrm{H}}}u_{\mathrm{H}} \qquad (3.11)$$

where the dimensionless parameter u_{H} can be written[16] in terms of the hydrodynamic scaling variable ξ

$$u_{\mathrm{H}} = (\epsilon/2)[\xi/(1 + \xi)](2\pi N/L)^{-(\epsilon/2)/(1+\xi)} \qquad (3.12)$$

The variable ξ is a phenomenological parameter and increases with polymer mass. In the nondraining limit $\xi \to \infty$, u_{H} approaches the fixed point $u_{\mathrm{H}}^{*} = \epsilon/2$. For $d = 3$, i.e., $\epsilon = 1$, we find from (3.11)

$$\Sigma_{\parallel}^{*} = f_{\parallel}u_{\mathrm{H}}^{*} = 9\pi(\pi/2)^{1/2}[{}_{2}F_{1}(d/2-1/2,1;d/2;1-q\eta_{\mathrm{b}}/\eta_{\mathrm{c}}) - (1/d)G_{d}(q,\eta_{\mathrm{b}}/\eta_{\mathrm{c}})]^{-1}\eta_{\mathrm{c}}\langle R_{\mathrm{G}}^{2}\rangle^{1/2} \qquad (3.13)$$

where the second equality follows from the relation (3.10) and (B.6) and $\langle R_{\mathrm{G}}^{2}\rangle$ is the mean square of the radius of gyration. The projection $R_{\parallel}^{\mathrm{H}}$ of the hydrodynamic radius onto the nematic direction is then given by the "Stokes formula" $\Sigma_{\parallel}^{*} = 6\pi\eta_{\mathrm{c}}R_{\parallel}^{\mathrm{H}}$. We see clearly that the hydrodynamic radius $R_{\parallel}^{\mathrm{H}}$ scales in the same way as the static radius $\langle R_{\mathrm{G}}^{2}\rangle^{1/2}$ in the nondraining limit.

IV. Discussion

It should be noted that the anisotropy in hydrodynamic interactions (HI) introduced by the solvent *nematics* is *different* from that due to an externally applied *flow* field.[15] Namely, the anisotropy in HI is due to the *deformed* shape of polymers in the presence of flow, while its nature may solely rise from the *anisotropic* hydrodynamic motion of solvents in the case of nematics. In the case of either solvent nematics or flow, the fixed-point or scaling law is not changed. On one hand, the *flow* introduces additional finite terms[15] for the shear intrinsic viscosity of polymers in isotropic solvents. On the other hand, the *nematic solvent* merely leads to a complex expression for the hydrodynamic interaction (HI) parameter z_{H}° (see (B.6) in Appendix B). Now we are left with the impression that the definition of z_{H}° is *arbitrary* as far as its prefactor is concerned. This is true to some extent, as evidenced by different definitions in the literature (aside from the different notations used).[13-16] The rule is that (a) the definition of z_{H}° should make the final expression of the calculated quantity (friction coefficient $\Sigma_{\parallel}$ of (3.9) in our present case) as simple as possible and (b) z_{H}° should be independent of the external conditions such as flow. Therefore, the finite terms introduced by the flow *cannot* be absorbed into a redefinition of z_H° which would give rise to a flow-dependent HI parameter. In our case, z_H° only depends upon the *solvent* characteristics (Miesowicz viscosities) as it should.

We have studied the hydrodynamic behavior of a flexible polymer chain in a nematic liquid crystal within the Kirkwood–Riseman theory for polymer dynamics by using the phenomenological description of Ericksen and Leslie for nematodynamics. Our theoretical prediction of the universal scaling law for the friction coefficient (3.13), i.e., $\Sigma_\parallel^* \propto \eta_c \langle R_G^2 \rangle^{1/2}$, is the first of its kind and can be readily examined by experiment. Since the prefactor in (3.13) is a highly complex function of viscosity ratio η_b/η_c and anisotropy q, experimental results will not be "universal" in the sense that the hydrodynamic radius $R_\parallel^H$ defined below (3.13) will vary from one nematic solvent to another; i.e., it is not a function of the molecular weight of polymers *alone* but also explicitly depends on such solvent properties as Miesowicz viscosities and the interaction between the solvent and polymer characterized by the chain anisotropy q. This situation is different from polymers in isotropic solvents where hydrodynamic properties of the polymer are generally considered as universal and independent of the solvent viscosity.

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Appendix A

We first recall that a flexible polymer in Θ solvents has the following Edwards Hamiltonian:

$$H_0 = (1/2)\int_0^N \mathrm{d}\tau \left|\frac{\partial \mathbf{R}}{\partial \tau}\right|^2 \qquad \text{(A.1)}$$

where $\mathbf{R}(\tau)$ is the position of the segment τ along the chain length N. Assuming the interaction between chain segments and the LC nematics is that of the Maier–Saupe type, we take the following total Hamiltonian of a flexible chain in LC:

$$H\{\mathbf{R}\} = H_0 - [(q-1)/2q]\int_0^N \mathrm{d}\tau \left(\frac{\partial \mathbf{R}}{\partial \tau}\cdot\mathbf{n}\right)^2 \qquad \text{(A.2)}$$

where q (>1) is a temperature-dependent parameter and $\mathbf{n}$ denotes the direction of the LC nematic field. With this Hamiltonian, we can readily calculate the factor in (3.8) as

$$\langle \exp\{i\mathbf{k}\cdot[\mathbf{R}(\tau) - \mathbf{R}(\tau')]\}\rangle = \int D\{\mathbf{R}\} \exp(-H\{\mathbf{R}\}) \exp\{i\mathbf{k}\cdot [\mathbf{R}(\tau) - \mathbf{R}(\tau')]\} = \exp\{-(1/2)|\tau - \tau'|[k^2 + (q-1)k_n^2]\} \qquad \text{(A.3)}$$

Thus in the absence of polymer–nematic interactions, $q = 1$ and the second term in the exponential of the right-hand side of (A.3) vanishes, recovering the isotropic chain limit.

Appendix B

The integrations over τ, τ', and $\mathbf{k}$ in (3.8) are carried out below. First, the $\mathbf{k}$-space integration can be rewritten using (A.3)

$$\int_k (1 - k_n^2/k^2)[\eta_c k_n^2 + \eta_b(k^2 - k_n^2)]^{-1} \exp\{-(1/2)|\tau - \tau'|[k^2 + (q-1)k_n^2]\} = \phi_1 - \phi_2 \qquad \text{(B.1)}$$

By dimensional scaling we find that both ϕ_1 and ϕ_2 go as $|\tau - \tau'|^{\epsilon/2-1}$, where $\epsilon = 4 - d$, and d is the spatial dimensions. More explicitly, by utilizing the equality

$$A^{-1} = \int_0^\infty \mathrm{d}\lambda \exp(-\lambda A) \qquad \text{(B.2)}$$

we proceed as follows:

$$\phi_1 \int_0^\infty \mathrm{d}\lambda \int_k \exp\{-[(q/2)|\tau - \tau'| + \eta_c\lambda]k_n^2 - [(1/2)|\tau - \tau'| + \eta_b\lambda](k^2 - k_n^2)\} = (1/2\eta_c)q^{1/2}(2\pi)^{-d/2}|\tau - \tau'|^{\epsilon/2-1}\int_0^\infty \mathrm{d}\lambda\, (1 + \lambda)^{-1/2}(1 + q\eta_b\lambda/\eta_c)^{-(d-1)/2} = (2\pi)^{-d/2}|\tau - \tau'|^{\epsilon/2-1}[q^{1/2}/(d - 2)\eta_c]\ {}_2F_1(d/2-1/2,1;d/2;1-q\eta_b/\eta_c] \qquad \text{(B.3)}$$

where ${}_2F_1$ is the hypergeometric function and becomes unity when the argument is zero, i.e., when $q = 1$ and $\eta_b = \eta_c$, which is the case for an isotropic solvent. Similarly, after using (B.2) twice, we can perform the k integration and obtain ϕ_2 as

$$\phi_2 = (2\pi)^{-d/2}|\tau - \tau'|^{\epsilon/2-1}[q^{1/2}/(d - 2)\eta_c]G_d(q,\eta_b/\eta_c) \qquad \text{(B.4)}$$

where the function G_d has the following integral representation:

$$G_d(x,y) = \int_0^\infty \mathrm{d}\alpha \int_0^\infty \mathrm{d}\alpha'\, (1 + \alpha + \alpha')^{-3/2}[1 + x(\alpha + \alpha' y)]^{-(d-1)/2} \qquad \text{(B.5)}$$

which can be readily evaluated for any $x,y > 0$. After substitution of (B.1) with (B.3) and (B.4) in (3.8) we can integrate over τ and τ' to obtain (3.9), where the hydrodynamic interaction (HI) parameter z_H° is defined as a function of $\zeta_\parallel/\eta_c$, q, and η_b/η_c as well as the polymer chain length N

$$z_H^\circ = [\zeta_\parallel(2\pi N)^{\epsilon/2}/\eta_c(1 - \epsilon^2/4)(2\pi)^2] \times [{}_2F_1(d/2-1/2,1;d/2;1-q\eta_b/\eta_c) - (1/d)G_d(q, \eta_b/\eta_c)] \qquad \text{(B.6)}$$

When compared to the same HI parameter for isotropic solvents, the essential difference is that the prefactor in (B.6) is a highly nonsimplistic function of the Miesowicz viscosity ratio η_b/η_c and the chain anisotropy q.

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