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On the Frank Elastic Constants of Lyotropic Polymer Liquid Crystals

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ABSTRACT: The Frank elastic constants of lyotropic polymer liquid crystals are formulated using an equivalent freely-jointed chain model, which can be uniquely defined by the parameters of the corresponding wormlike chain and the polymer concentration. The contribution of the higher virial terms to the elastic constants was taken into account on the basis of the scaled particle theory used previously for undistorted nematic polymer solutions. The fomulated elastic constants are applicable to systems with any polymer conformation from the rod limit to the coil limit and at arbitrary concentration and degree of orientation. The theoretical elastic constants for twist and bend distortions agree semiquantitatively with most experimental results for the elastic constants of lyotropic liquid crystals of poly(γ-benzyl glutamate) with no adjustable parameters.

1. Introduction

In a liquid crystal state, mesogenic molecules orient themselves in some preferred direction. Owing to this preference, the molecules produce a stress in the system against orientational distortion.[1,2] The elasticity in nematics and cholesterics is characterized by the three Frank elastic constants for splay, twist, and bend distortions. These elastic constants for polymer liquid crystals have been theoretically discussed by many investigators.[3−16] However, previous formulations were made under restricted conditions and/or by using some approximations: (1) the polymer conformation was assumed to be of the rigid rod or of the coil limit; (2) in the free energy expression of the system, the third and the higher virial terms were often neglected; (3) the orientational distribution function was sometimes expressed in terms of spherical harmonic expansions truncated at low order or via a Gaussian trial function; (4) the orientational state is often assumed to be very high or very low. These restrictions and approximations make it difficult to *quantitatively* compare the theoretical results with experimental data.

As will be described in the following sections, the present formulation of the elastic constants is free from the above restrictions and approximations. The contribution of the higher virial terms in the free energy to the elastic constants is taken into account on the basis of the scaled particle theory previously used successfully for undistorted nematic polymer solutions[17] (cf. Section 2). The orientational distribution function is expressed by the Onsager trial function,[18] which is known to be a good approximation at arbitrary degrees of orientation (cf. Section 4).

As pointed out by Khokhlov and Semenov,[19] the free energy of the undistorted nematic phase is strongly affected by chain flexibility even for very stiff polymers. Thus chain flexibility may play an important role also in the elastic constants of stiff polymer solutions in a distorted nematic state. The incorporation of the chain flexibility effect in the theory of the elastic constants requires knowledge of the chain statistics in the nematic state. The chain statistics are determined not only by the intrinsic stiffness of the individual chains but also by the nematic field produced by the surrounding polymer chains, so that theoretical treatments of the chain flexibility effect on the elastic constants are rather involved.

In the present formulation, we have considered the chain flexibility effect in terms of a simplified polymer chain model, the equivalent freely-jointed chain model. As explained in Section 3, the nematic solution of this model chain is assumed to have the same order parameter as the corresponding wormlike chain system, and the former chain is uniquely defined by the wormlike chain parameters and the polymer concentration. The suitability of this model is examined by comparing the elastic constants of the present theory with those derived on the basis of the wormlike chain model in the coil limit (Section 5).

Finally, in Section 6, the elastic constants of the present theory are compared with experimental elastic constants for liquid crystalline poly(γ-benzyl glutamate) (PBG) solutions.[20−25,58] Since all the molecular parameters of PBG appearing in the theory have already been determined independently from previous solution studies,[17] the comparison between theory and experiment for the elastic constants has no adjustable parameters.

2. Free Energy Expression

The density functional formalism[26,27] writes the Helmholtz free energy F of an *inhomogeneous system* as a functional of the nonuniform generalized density distribution $\rho(\mathbf{x})$:

$$F[\rho(\mathbf{x})] = F^{\mathrm{id}}[\rho(\mathbf{x})] + F^{\mathrm{ex}}[\rho(\mathbf{x})] \tag{2.1}$$

where $\mathbf{x}$ represents the coordinates of all degrees of freedom of a constituent molecule. The first term is F of the ideal noninteracting system, which may be written

$$F^{\mathrm{id}}[\rho(\mathbf{x})] = \int \rho(\mathbf{x})\{E_{\mathrm{in}}(\mathbf{x}) + k_{\mathrm{B}}T[\ln(\Lambda^3\rho(\mathbf{x})) - 1]\}\,\mathrm{d}\mathbf{x} \tag{2.2}$$

with the internal energy $E_{\mathrm{in}}(\mathbf{x})$ of the molecule and an arbitrary length Λ whose precise value is usually unimportant for observable properties; the term $E_{\mathrm{in}}(\mathbf{x})$ is not necessary for rigid body particles. On the other hand, the second term in eq 2.1 represents an excess free energy due to interactions among molecules. This free energy is related to the two-particle direct correlation function $C(\mathbf{x}_1,\mathbf{x}_2;[\rho(\mathbf{x})])$ of the system which has the singlet distribution $\rho(\mathbf{x})$ by

$$F^{\mathrm{ex}}[\rho(\mathbf{x})] = -k_{\mathrm{B}}T\int \mathrm{d}\mathbf{x}_1\int \mathrm{d}\mathbf{x}_2\ \bar{C}(\mathbf{x}_1,\mathbf{x}_2;[\rho(\mathbf{x})])\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) + \ldots \tag{2.3}$$

where

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$$\bar{C}(\mathbf{x}_1,\mathbf{x}_2;[\rho(\mathbf{x})]) \equiv \int_0^1 (1-\lambda) C(\mathbf{x}_1,\mathbf{x}_2;[\lambda\rho(\mathbf{x})])\,\mathrm{d}\lambda \qquad (2.4)$$

Singh and Singh[14] employed the Percus–Yevick approximation of the direct correlation function extended to hard ellipsoid systems, using the decoupling approximation[27] to calculate the elastic constants for distorted nematics. While their expressions for $C(\mathbf{x}_1,\mathbf{x}_2)$ may be accurate for ellipsoids with small axial ratios, applicability of them to long polymer chains with flexibility is questionable. The third virial coefficient of long hard rods calculated from their $C(\mathbf{x}_1,\mathbf{x}_2)$ does not agree with that estimated from direct numerical calculations of the ternary cluster integral.[28] Furthermore, the convergence of spherical harmonic expansions used by them becomes poor with increasing axial ratio.[14]

Recently,[17,29] we applied the scaled particle theory (SPT) to obtain F of an undistorted nematic solution containing wormlike spherocylinders with cylinder length L_c and hard-core diameter d. By using the generalized density distribution $\rho(\mathbf{x})$, we can write the SPT result for the excess free energy F^{ex} in the undistorted nematic state as

$$F^{\mathrm{ex}} = -\frac{1}{2}k_{\mathrm{B}}T\int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\,[H_{\mathrm{A}}(\phi)\Phi_0(\mathbf{x}_1,\mathbf{x}_2) + H_{\mathrm{I}}(\phi)\Phi_0'(\mathbf{x}_1,\mathbf{x}_2) + \Phi_{\mathrm{w}}(\mathbf{x}_1,\mathbf{x}_2)]\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) \qquad (2.5)$$

with $\rho(\mathbf{x}_i) = \rho_{\mathrm{N}}(\mathbf{x}_i)$ (the generalized density distribution of the undistorted nematic state). Here $\mathbf{x}$ represents the coordinates of all degrees of freedom of the wormlike chain, and $k_{\mathrm{B}}T$ has the usual meaning. The coefficients $H_{\mathrm{A}}(\phi)$ and $H_{\mathrm{I}}(\phi)$ are defined respectively by

$$H_{\mathrm{A}}(\phi) \equiv \frac{1}{1-\phi}\left[1 + \frac{2(X'+1)\phi}{(3X'+2)(1-\phi)}\right] \qquad (2.6)$$

$$H_{\mathrm{I}}(\phi) \equiv \frac{3}{4(1-\phi)^2}\left[1 - \frac{5X'^{\,2}+6X'+2}{(3X'+1)^2}\phi\right] - \frac{1}{4\phi}\ln(1-\phi) \qquad (2.7)$$

with $X' \equiv L_c/d$, the polymer volume fraction ϕ, and the Mayer functions Φ_0, Φ_0', and Φ_{w} with respect to the hard-core potential in the “crossed” and “noncrossed” configurations and a (weak) soft attractive potential w, respectively.

The Mayer functions for a wormlike spherocylinder can be regarded as functions of the distance p between the closest points s and s' on the cylinder contours of two interacting spherocylinders as well as the two unit tangent vectors $\mathbf{a}_s$ and $\mathbf{a}'_{s'}$ to the contour points.[29] Here s and s' denote the contour distances from the midpoint of the cylinder contour to the closest contour point. With these quantities, Φ_0, Φ_0', and Φ_{w} can be expressed by

$$\Phi_0 = \begin{cases} -1, & |s| \text{ and } |s'| < L_c/2,\ |p| \le d \\ 0, & \text{otherwise} \end{cases}$$

$$\Phi_0' = \begin{cases} -1, & s \text{ (or } s') = \pm L_c/2,\ |s'| \text{ (or } |s|) \\ & \qquad \le L_c/2,\ |p| \le d \\ 0, & \text{otherwise} \end{cases} \qquad (2.8)$$

$$\Phi_{\mathrm{w}} \cong \begin{cases} \dfrac{-w(p;\mathbf{a}_s,\mathbf{a}'_{s'})}{k_{\mathrm{B}}T}, & |s| \text{ and } |s'| < L_c/2,\ |p| > d \\ 0, & \text{otherwise} \end{cases}$$

where $w(p;\mathbf{a}_s,\mathbf{a}'_{s'})$ is a function of p, $\mathbf{a}_s$, and $\mathbf{a}'_{s'}$. We have used the high-temperature approximation for Φ_{w} and neglected a small contribution in the noncrossed configuration to Φ_{w}. In eq 2.5, we have neglected the higher order perturbation terms with respect to w.

In what follows, we use eq 2.5 as F^{ex} of inhomogeneous systems. At a sufficiently low concentration, $C(\mathbf{x}_1,\mathbf{x}_2)$ is known to equal to the Mayer function $\Phi(\mathbf{x}_1,\mathbf{x}_2)$,[26] so that we can show that eq 2.5 becomes identical with eq 2.3. Straley,[4,5] Poniewierski and Stecki,[6] and Doi and Kuzuu[30] used eq 2.5 with $H_{\mathrm{A}}(\phi) = 1$ and $H_{\mathrm{I}}(\phi) = \Phi_{\mathrm{w}} = 0$ for an inhomogeneous hard rod system.

With increasing polymer concentration, $C(\mathbf{x}_1,\mathbf{x}_2)$ deviates from $\Phi(\mathbf{x}_1,\mathbf{x}_2)$ and eq 2.5 is not necessarily identical with eq 2.3. However, it is noted that, for a system of *uniform* hard spheres, eq 2.5 derived from the SPT gives the same result as the Percus–Yevick F^{ex}.[26] Furthermore, in previous studies,[17,29] experimental results for the osmotic pressure, osmotic compressibility, and light-scattering correlation length of several liquid-crystalline stiff-polymer solution systems were favorably compared with theoretical results calculated using eq 2.5. It was shown that the third virial coefficient calculated from eq 2.5 is very close to the numerical results.[31] Thus, we can say that eq 2.5 gives sufficiently accurate predictions for thermodynamic and long-distance spatial properties of liquid-crystalline polymer solutions.[32] It is worthwhile noting that Gelbart and Ben-Shaul[9] and Lee[16] also approximated the $\bar{C}(\mathbf{x}_1,\mathbf{x}_2)$ function in eq 2.3 by the Mayer function with a concentration-dependent scaling factor for their calculation of the elastic constants of nematics.

3. Equivalent Freely-Jointed Chain Model

It is known that the wormlike chain (WC) is a suitable model to describe solution properties of most actual stiff-chain polymers. Its model chain parameters, the persistence length q and the contour length L (or the number N of Kuhn statistical segments), can be determined from dilute solution properties (e.g., the radius of gyration and intrinsic viscosity) by established methods.[33–35] However, since this model represents a continuous chain, the chain conformation must be specified by use of an *infinite* number of vectors, say, the unit tangent vectors $\mathbf{a}_l$ along the contour points l ($0 \le l \le L$). The full expression for the orientational distribution function of the vectors is not available, and thus the calculations of F^{id} and F^{ex} given by eqs 2.2 and 2.3 are not easy. Grosberg and Zhestkov[11] treated the elasticity in nematic solutions of the WC by using a theoretical approach similar to the theory of Khokhlov and Semenov[19,36] for undistorted nematic solutions of the WC, but they obtained explicit expressions of the Frank elastic constants only in some special cases (cf. Section 5).

In the present study, we consider an equivalent freely-jointed chain (EFJC) and replace the WC in a nematic solution by the EFJC. The EFJC consists of N_κ rod segments of length κ which are connected linearly by flexible joints and have the same contour length L, hard-core diameter d, and soft attractive potential w as those of the corresponding WC. The number N_κ of equivalent segments is determined so that the solution of the EFJC has the same degree of orientation as that of the WC solution in the undistorted nematic state. From eqs A.6 and A.7 in the Appendix, we have

$$N_\kappa = 1 + \frac{N}{3}\left\{1 + \frac{1}{2}\tanh\left[\frac{2}{5}N(\alpha - 1)\right]\right\}\Big/\left(\frac{1}{\alpha} - \pi e^{-\alpha}\right) \qquad (3.1)$$

where N is the number of Kuhn statistical segments of the WC, and α is the variational parameter which is included in the Onsager trial function[18] for the (averaged) orientational distribution function $f(\mathbf{a})$ of the tangent vector $\mathbf{a}$:

$$f(\mathbf{a}) = \frac{\alpha \cosh(\alpha \mathbf{a}\cdot\mathbf{n})}{4\pi \sinh \alpha} \tag{3.2}$$

The parameter α is determined by solving eq A.7 with $\sigma = \sigma_{\mathrm{WC}}$.

If eq 3.1 does not yield an integer solution to N_κ, the EFJC may not seem to *physically* make sense. However, in the following discussion, N_κ is not required mathematically to be an integer. Thus we do not impose the integer condition on N_κ in the following and take the EFJC with noninteger N_κ as a *mathematical model*.

The equivalent segment length κ of the EFJC can be calculated from the relation

$$\kappa = 2qN/N_\kappa \tag{3.3}$$

where q is the persistence length of the WC. Using eq 3.1, we can show that κ is equal to L in the rod limit and to $(4q/\alpha)(1 - \pi\alpha e^{-\alpha})$ in the coil limit. This length κ plays a similar role to Odijk's deflection length[37,38] λ in the theory of polymer liquid crystals. Odijk defined λ by a simple scaling argument for the WC in a nematic solution to be

$$\lambda = q/\alpha \tag{3.4}$$

While λ depends only on the polymer concentration through α for a given polymer, κ varies with both the polymer molecular weight and the concentration according to eq 3.1. The equivalent segment length κ is 4 times larger than λ in the coil limit. (α is usually so large in nematic solutions that the term $\pi\alpha e^{-\alpha}$ in κ in the coil limit is negligible.)

4. Frank Elastic Constants

The distortion in a nematic liquid crystal can be classified into three kinds: splay, twist, and bend, which are specified by numbering 1, 2, and 3, respectively. The response to each pure distortion is described in terms of the elastic constant K_i (i = 1, 2, and 3). If we use Cartesian coordinates (x, y, z) where the z-axis is chosen to be the orientation direction at the origin, the director $\mathbf{n}(\mathbf{r})$ can be expressed by

$$\mathbf{n}(\mathbf{r}) = \mathbf{e}_z + (q_1 x + q_2 y + q_3 z)\mathbf{e}_x \tag{4.1}$$

in the vicinity of the origin. Here $\mathbf{e}_z$ and $\mathbf{e}_x$ are the unit vectors in the direction of the axes indicated by the subscripts, and q_i represents the wavenumber of each distortion. Under this distortion, the free energy density $\mathcal{F}$ in a nematic solution of nonchiral molecules is given by

$$\mathcal{F} = \frac{1}{2}(K_1 q_1^{\,2} + K_2 q_2^{\,2} + K_3 q_3^{\,2}) \tag{4.2}$$

Now we consider a nematic solution of the EFJC under the distortion expressed by eq 4.1. If the polymer concentration in the solution is uniform, the generalized distribution function $\rho(\mathbf{x})$ can be written as

$$\rho(\mathbf{x}) = c' \prod_{l=1}^{N_\kappa} f(\mathbf{a}_l\cdot\mathbf{n}(\mathbf{r}_l)) \tag{4.3}$$

where $\mathbf{a}_l$ is the unit vector parallel to the segment l, $\mathbf{n}(\mathbf{r}_l)$ the director at the center-of-mass position $\mathbf{r}_l$ of the segment l, and $f(\mathbf{a}_l\cdot\mathbf{n}(\mathbf{r}_l))$ the orientational distribution function of $\mathbf{a}_l$.

In the derivation of eq 2.5 by the SPT, we did not use any chain statistics (but only assumed the "single-contact approximation"),[39,40] so that we may apply eq 2.5 to a solution of the spherocylinder whose contour obeys the statistics of the EFJC. From eqs 2.5 and 2.8, we can write the excess free energy density due to polymer interactions

$$\mathcal{F}^{\,\mathrm{ex}} = -\frac{1}{2}c_\kappa'^{\,2} k_{\mathrm{B}}T\Big\{\int_{-\kappa/2}^{\kappa/2}\mathrm{d}s\int_{-\kappa/2}^{\kappa/2}\mathrm{d}s'\int \mathrm{d}p\int \mathrm{d}\mathbf{a}\int \mathrm{d}\mathbf{a}'\,[H_{\mathrm{A}}(\phi)\Phi_0 + \Phi_{\mathrm{w}}]|\mathbf{a}\times\mathbf{a}'|f(\mathbf{a}\cdot\mathbf{n}(\mathbf{r}))f(\mathbf{a}'\cdot\mathbf{n}(\mathbf{r}')) - 8H_{\mathrm{I}}(\phi)v/N_\kappa^{\,2}\Big\} \tag{4.4}$$

where c_κ' is the number concentration of the total equivalent segments in the solution, and v is the volume of the spherocylinder.

According to Straley,[4,5] we may expand $f(\mathbf{a}'\cdot\mathbf{n}(\mathbf{r}'))$ around $\mathbf{r}$ and obtain from eq 4.4

$$\mathcal{F}^{\,\mathrm{ex}} = \mathcal{F}_{\mathrm{N}}^{\,\mathrm{ex}} - \frac{1}{2}c_\kappa'^{\,2} k_{\mathrm{B}}T\left[\sum_{i=1}^{3} q_i\int \mathrm{d}\mathbf{a}\int \mathrm{d}\mathbf{a}'\,C_i\left|\mathbf{a}\times\mathbf{a}'\right| f(a_z)a_x' f'(a_z') + \frac{1}{2}\sum_{i=1}^{3}\sum_{j=1}^{3} q_i q_j\int \mathrm{d}\mathbf{a}\int \mathrm{d}\mathbf{a}'\,D_{ij}\left|\mathbf{a}\times\mathbf{a}'\right| a_x f'(a_z)a_x' f'(a_z')\right] \tag{4.5}$$

where $\mathcal{F}_{\mathrm{N}}^{\,\mathrm{ex}}$ is the $\mathcal{F}^{\,\mathrm{ex}}$ in the undistorted nematic state given by eq A.1, $f'(a_z)$ the derivative of the function $f(a_z)$, and

$$C_i \equiv -\int_{-\kappa/2}^{\kappa/2}\mathrm{d}s\int_{-\kappa/2}^{\kappa/2}\mathrm{d}s'\int \mathrm{d}p\left[H_{\mathrm{A}}(\phi)\Phi_0 + \Phi_{\mathrm{w}} + \frac{1}{2}(\partial\Phi_{\mathrm{w}}/\partial p)\right](\mathbf{p}\cdot\mathbf{e}_i) \tag{4.6}$$

$$D_{ij} \equiv -\int_{-\kappa/2}^{\kappa/2}\mathrm{d}s\int_{-\kappa/2}^{\kappa/2}\mathrm{d}s'\int \mathrm{d}p\,[H_{\mathrm{A}}(\phi)\Phi_0 + \Phi_{\mathrm{w}}][\mathbf{e}_i\cdot(s^2\mathbf{a}\mathbf{a} + s'^{\,2}\mathbf{a}'\mathbf{a}' + \mathbf{p}\mathbf{p})\cdot\mathbf{e}_j] \tag{4.7}$$

with the vector $\mathbf{p}$ from the contour point s to s' and ($\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$) ≡ ($\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$). For nonchiral molecules, the terms in q_i as well as $q_i q_j$ ($i \neq j$) vanish by symmetry. Comparing eq 4.5 with eq 4.2, we have

$$K_i = -\frac{1}{2}c_\kappa'^{\,2} k_{\mathrm{B}}T\int \mathrm{d}\mathbf{a}\int \mathrm{d}\mathbf{a}'\,D_{ii}|\mathbf{a}\times\mathbf{a}'|a_x f'(a_z)a_x' f'(a_z') \tag{4.8}$$

Here we have neglected the change produced by distortion in the conformational entropy in $\mathcal{F}^{\,\mathrm{id}}$, because the wavelength of the distortion is usually considerably larger than the molecular size. This equation for K_i along with eq 4.7 is just the same as that of a solution of a rodlike spherocylinder with the cylinder length κ.

Distortion of the liquid crystal alters the distribution function $f(a_z)$ from that at the undistorted nematic state through the later terms of eq 4.5. Straley[5] took into account the effect of the alteration of $f(a_z)$ in a perturbative way. His analysis showed that a perturbation term proportional to C_i comes out in eq 4.8 for K_i. This perturbation term vanishes for nematic liquid crystals with $C_i = 0$. Even for cholesteric liquid crystals with a nonzero C_2, the perturbation term is much smaller than

Table 1. Frank Elastic Constants Obtained by Different Authors

	rod limit		coil limit	
author(s)	K_2d/k_BT	K_3d/k_BT	K_2d/k_BT	K_3d/k_BT
present theory	$\frac{1}{12}(L^2dc')^2H_A(\phi)\lvert I_2(S)\rvert$	$\frac{1}{12}(L^2dc')^2H_A(\phi)\lvert I_3(S)\rvert$	$\frac{4}{3}(Ld\lambda c')^2H_A(\phi)\lvert I_2(S)\rvert$	$\frac{4}{3}(Ld\lambda c')^2H_A(\phi)\lvert I_3(S)\rvert$
	$\frac{7}{96}L^2dc'\ ^a$	$\frac{1}{48}\pi(L^2dc')^3H_A{}^2(\phi)\ ^a$	$\frac{7}{24}Ld\lambda c'\ ^a$	$\frac{1}{3}Ldqc'\ ^a$
Straley[4]	$\frac{1}{12}(L^2dc')^2\lvert I_2(S)\rvert$	$\frac{1}{12}(L^2dc')^2\lvert I_3(S)\rvert$		
Kimura, Hosino, and Nokano[8]	$\frac{1}{12}L^2dc'\ ^a$	$\frac{5}{64}\pi(L^2dc')^2H_A(\phi)\ ^a$		
Grosberg and Zhestkov[11]	$\frac{1}{12}L^2dc'\ ^a$	$\approx(L^2dc')^{3\ a}$	$\frac{1}{2}Ld\lambda c'\ ^a$	$Ld(q-3\lambda)c'\ ^a$
Odijk[13]	$\frac{7}{96}L^2dc'\ ^a$	$\frac{1}{48}\pi(L^2dc')^{3\ a}$	$\approx Ld\lambda c'\ ^a$	$\approx Ldqc'\ ^a$
Shimada, Doi, and Okano[15]	$\frac{5}{28}L^2dc'S^{2\ b}$	$\frac{15}{28}L^2dc'S^{2\ b}$	$\frac{5}{28}Ldqc'S^{2\ b}$	$\frac{25}{14}Ldqc'S^{2\ b}$

[a] High orientation. [b] Low orientation. The symbol ($\approx$) indicates that the expression does not consider a numerical coefficient and λ is the deflection length defined by eq 3.4.

the unperturbed term proportional to D_{ii} in eq 4.8 for stiff polymers with $\kappa \gg d$, because the ratio D_{ii}/C_i is proportional to $(\kappa/d)^2$. Therefore, in what follows, we neglect the perturbation of $f(a_z)$ by distortion.

For usual liquid-crystalline polymer–good solvent systems, the soft attractive interaction w is so weak that we may neglect the contribution of Φ_w to K_i. For such systems, eq 4.8 can be written

$$K_i = \frac{1}{12}k_BT\kappa^4dc_\kappa'^{\ 2}H_A(\phi)I_i(S) \tag{4.9}$$

for stiff polymers with $\kappa \gg d$. Here $I_i(S)$ is the integral given by

$$I_i(S) \equiv \int d\mathbf{a}\int d\mathbf{a}'\ (a_i^{\ 2} + a_i'^{\ 2})|\mathbf{a}\times\mathbf{a}'|a_xf'(a_z)a_x'f'(a_z') \tag{4.10}$$

with $(a_1, a_2, a_3) = (a_x, a_y, a_z)$, and it can be regarded as a function of the order parameter S. We can show the relation $I_1 = 3I_2$ from eq 4.10.[13] To make the integration of eq 4.10, we use the Onsager trial function (cf. eq 3.2) for $f(a_x)$ to be consistent with the treatment of the previous section. Although Odijk[13] integrated analytically $I_i(S)$ of eq 4.10 using a Gaussian trial function (a simplified version of the Onsager trial function), the analytical integration seems not to be possible with the more accurate Onsager trial function. We made the numerical integration of $I_2(S)$ and $I_3(S)$. The results can be expressed by the empirical equations of S in the range $0.48 \le S < 1$:

$$\begin{cases} I_2(S)\left(=\frac{1}{3}I_1(S)\right) = -\frac{7}{16}\left[\frac{\pi}{3}(1-S)\right]^{1/2} \times \\ \qquad (0.1138 - 0.5579S + 1.9484S^2 - 0.5043S^3) \\ I_3(S) = -\frac{1}{2}[3\pi/(1-S)]^{1/2} \times \\ \qquad (0.0173 + 0.0851S + 0.2529S^2 + 0.6447S^3) \end{cases} \tag{4.11}$$

Here S is calculated by eq A.8. In the high-orientation limit ($S \to 1$), the above equations approach Odijk's analytical results. Lee and Meyer[12] made similar numerical calculations of $I_i(S)$ for straight hard spherocylinder solutions without using any trial function, but using $f(a_z)$ obtained by a numerical iterative method for the free energy minimization problem. At $S = 0.598$ (the lowest value of S in their calculation), our $I_2(S)$ and $I_3(S)$ are 20% larger and smaller than theirs, respectively, and become closer to theirs with increasing degree of orientation. This demonstrates that the Onsager trial function is reasonably accurate in describing the orientational distribution.

5. Comparison with Other Theories

So far, many workers formulated the Frank elastic constants K_i of polymer liquid crystals in the rod and/or coil limits. Table 1 compares K_2 and K_3 obtained by different authors. Let us first consider the rod limit. Straley[4] derived K_i for rodlike polymer solutions using the second virial approximation. His results are identical with ours in the rod limit except for the factor $H_A(\phi)$ of the higher virial correction. (We have corrected a missing factor of $^1/_2$ in his equations of K_i.) He calculated $I_i(S)$ using a simple trial function for $f(\mathbf{a})$ and obtained results similar to ours. Kimura et al.[7,8] obtained K_i for rodlike polymer solutions in a highly oriented state by using spherical harmonic expansions for the intermolecular interaction and the orientational distribution function. Their result for K_2 considering up to the fourth order of the expansions is in good agreement with ours in the same conditions, while their K_3 has polymer concentration and molecular weight dependences different from ours. This may come from their neglect of the higher terms of the spherical harmonic expansions; in the highly oriented state they were concerned with, low-order terms of the expansion are not enough to express the orientational state. Odijk[13] calculated analytically K_2 and K_3 for rodlike polymer solutions with a high degree of orientation on the basis of Straley's theory of the second virial approximation. The comparison between his and our results in the rod limit shows that the correction of higher virial terms is important for K_3 but not for K_2 in a highly oriented state.

Grosberg and Zhestkov[11] derived the expressions of K_i in a highly oriented state using a procedure similar to the theory of Khokhlov and Semenov[19,36] for undistorted nematic solutions of the WC. Their results for K_2 and K_3 in the coil limit have the same polymer concentration and molecular weight dependences as ours in the same conditions. (In a highly oriented state, 3λ in K_3 is negligible in comparison with q.) The same concentration and molecular weight dependences of K_2 and K_3 in the coil limit were also obtained by Odijk,[13]

Table 2. Comparison of the Present Theory with Experimental Data of the Ratio K_3/K_2 of PBG Solutions Determined by Light Scattering

solvent	$M/10^4$	c/g cm^{-3}	K_3/K_2		κ/nm
			expt^{a,b}	theory	
dichloromethane (80%)	7.0	0.197	9.9	6.54	34.8
+dioxane (20%)^a	7.0	0.217	11.0	8.91	31.3
	7.0	0.266	13.6	13.6	25.6
	7.0	0.311	15.8	17.5	22.1
	7.0	0.364	17.8	22.3	18.9
	7.0	0.398	20.4	25.6	17.2
dichloromethane (82%)	7.0	0.202	10.7	7.20	33.8
+dioxane (18%)^{b,c}	8.5	0.201	16.5	9.23	34.3
	9.2	0.199	19.9	9.76	34.6
	11.0	0.197	23.1	10.8	35.4
	12.7	0.198	24.0	11.6	35.4
	15.8	0.195	25.3	12.3	36.1
	16.5	0.193	25.4	12.3	36.7
	19.0	0.201	26.7	13.5	35.5
	21.0	0.195	27.3	13.4	36.5
	7.0	0.258	17.8	12.8	26.4
	8.5	0.249	24.7	13.6	27.7
	12.7	0.256	29.3	16.6	27.6

[a] Reference 23. [b] Reference 24. [c] Added a few percent of dimethylformamide.

who calculated K_i in the coil limit by simply regarding the WC in a nematic solution as a collection of rods of the length λ (the deflection length defined by eq 3.4).

However, Grosberg and Zhestkov's numerical coefficients of K_2 and K_3 are larger than ours. The difference in the coefficient of K_3 is more appreciable than that of K_2. Those differences may arise from the difference in the polymer chain statistics of the WC and EFJC. Thus the present theory may yield some errors in the elastic constants in the coil limit.

Shimada et al.[15] applied Landau and de Gennes' free energy expansion with the respect to the order parameter to derive K_i for solutions of the WC. The ratio K_3/K_2 they obtained by considering up to the second-order terms of S is 3 in the rod limit and 10 in the coil limit. It can be shown that the present theory gives the relation K_3/K_2 ($=I_3/I_2$) $= 3$ at vanishing S irrespective of the polymer conformation. Therefore the present theory agrees with Shimada et al.'s in the rod limit, but not in the coil limit, at the low orientation. The disagreement in the coil limit may also reflect the difference in the polymer chain statistics.

6. Comparison with Experimental Results of Poly(γ-benzyl glutamate) Solutions

The Frank elastic constants of liquid-crystalline solutions of poly(γ-benzyl glutamate) (PBG) (the racemic mixture or the L-enantiomer) were measured by different methods. Usually, the elastic constants of polymer liquid crystals are more difficult to measure than those of low molecular weight liquid crystals mainly due to the high viscosity of polymer samples. The Brandeis group[41] established the preparation method of a well-aligned *monodomian* specimen of PBG liquid crystals and measured the ratios K_3/K_2 and K_3/K_1 of the specimen by light scattering experiment[23,24,42] and K_3 by the Fredericks transition experiment.[23,58] The experimental results for K_3/K_2 and K_3 are listed in Tables 2 and 3, respectively.

Previously, the scaled particle theory for homogeneous wormlike hard spherocylinder systems was favorably compared with experimental data of the osmotic pressure, orientational order parameter, and isotropic–cholesteric phase boundary concentrations of poly(γ-benzyl L-glutamate) (PBLG) solutions.[17] The values of L and N appearing in the theory were calculated from the molecular weight M of each PBLG sample along with M_L (the molar mass per unit contour length) = 1450 nm^{-1} and q (the persistence length) = 150 nm, which were determined from dilute solution studies. The hard-core diameter d was chosen to be 1.4 nm, which was close to the diameter estimated from the partial specific volume of PBLG.

Table 3. Comparison of the Present Theory with Experimental Data of the Bend Elastic Constant K_3 of PBG Solutions Determined by the Fredericks Transition Method

solvent	$M/10^4$	c/g cm^{-3}	K_3/pN^c	
			expt	theory
dichloromethane (80%)	7.0	0.197	6.8	3.15
+dioxane (20%)^a	7.0	0.217	7.6	5.19
	7.0	0.266	9.5	9.22
	7.0	0.311	11.0	12.7
	7.0	0.364	18.3	17.0
	7.0	0.398	19.5	19.8
1,1,2-trichloroethane^b	6.5	0.244	13.0	6.73

[a] Reference 23. [b] Reference 58. [c] pN = 10^{-7} dyn.

Here we compare the Frank elastic constant data with the present theory, eq 4.9, by using the molecular parameters (L, N, and d) estimated in the same way as the previous studies. The two parameters κ and S appearing in eq 4.9 are calculated from the degree of orientation parameter α which is determined by the free energy minimization condition, eq A.7. Thus the comparison requires no adjustable parameters. The fifth column of Table 2 lists the theoretical results of K_3/K_2 calculated from eqs 4.9 and 4.11,[43] which agree with the experimental data in the fourth column semiquantitatively. We see that the theory predicts a slightly stronger concentration dependence (from the upper part of the table) and a weaker molecular weight dependence (from the lower part of the table) of K_3/K_2 than the experimental results.

Table 3 compares the data of K_3 for nematic PBG solutions determined by the Fredericks transition with the theoretical results calculated by eqs 4.9 and 4.11. The theoretical K_3 agrees almost quantitatively with Taratuta et al.'s experimental results but slightly underestimates Itou et al.'s. It is noted that the absolute values of those experimental K_3 contains some uncertainty, because both groups did not use the directly measured diamagnetic anisotropy $\Delta\chi$ of PBG solutions to calculate K_3. They estimated $\Delta\chi$ from the susceptibility components parallel and perpendicular to the PBG helix axis determined by Murthy et al.[44] in a different solution condition.

The twist elastic constant K_2 for cholesteric liquid crystals can be determined by the magnetically induced cholesteric-to-nematic transition experiment.[1,45] Several investigators[20–22,46–48] made this experiment for PBLG solutions with various solvents. The results of K_2 summarized in Table 4 strongly depend on the solvent. The present theory cannot explain this strong solvent dependence of K_2 measured by the magnetically induced cholesteric-to-nematic transition. Equations 4.9 and 4.11 with the molecular parameters mentioned above give K_2 in good agreement with the experimental results of dioxane solutions[21] but not with the results in other solvents. Especially, for dichloromethane solutions,[20,21] the theoretical K_2 are much smaller than the experimental K_2.

Table 4. Comparison between the Present Theory and Experiment for the Twist Elastic Constant K_2 of PBLG Solutions Determined from the Magnetically Induced Cholesteric-to-Nematic Transition

solvent	$M/10^4$	c/g cm^{-3}	P_0/μm	K_2/pN expt	K_2/pN theory
dichloromethane[a]	55	0.255	72	78.6	0.716
dichloromethane[b]	31	0.20	80	5.4	0.715
chloroform[b]	31	0.20	42	2.1	0.715
dioxane[b]	31	0.20	30	0.61	0.715
	31	0.21		0.61	0.729
	31	0.23		0.63	0.753
	31	0.255		0.66	0.770
	31	0.28		0.69	0.784
	31	0.29		0.68	0.792
	31	0.30		0.71	0.796
m-cresol[c]	24.6	0.191	53.8	2.3	0.706
	24.6	0.222	37.6	1.3	0.745
	24.6	0.254	27.8	0.91	0.774
	9.5	0.191	35.5	2.0	0.613
	14.4	0.191	43.2	2.1	0.669
	24.6	0.191	53.8	2.3	0.706

[a] Reference 20 (at ambient temperature). [b] Reference 21 (at 25 °C). [c] Reference 22 (at 30 °C).

Table 5. Comparison between the Present Theory and Experiment for the Twist Elastic Constant K_2 of PBG Solutions Calculated from the Results of Tables 1 and 2

solvent	$M/10^4$	c/g cm^{-3}	K_2/pN exp[a]	K_2/pN theory
dichloromethane (80%)	7.0	0.197	0.69	0.482
+dioxane (20%)	7.0	0.217	0.675	0.582
	7.0	0.266	0.70	0.679
	7.0	0.311	0.695	0.726
	7.0	0.364	1.03	0.761
	7.0	0.398	0.96	0.775

[a] Reference 23.

One may ascirbe the strong solvent dependence of K_2 to the variance of orientation-dependent attractive interactions among PBLG chains with solvents. Attractive interactions can affect K_i through Φ_w (see eqs 4.7 and 4.8). However, the isotropic−cholesteric phase boundary concentrations for PBLG solutions do not essentially depend on solvent,[49−51] in sharp contrast with the strong solvent dependence of K_2. Furthermore, experimental results for the phase boundaries of PBLG dissolved in various solvents were favorably compared with the scaled particle theory for hard wormlike spherocylinders with the same molecular parameters mentioned above.[17] These facts imply that attractive interactions are not so strong in PBLG solutions as to explain the strong solvent dependence of K_2.

Another diagreement between theory and experiment is observed in Table 4 for the concentration c dependence of K_2 of *m*-cresol solutions.[22] While the theory predicts a weak positive c dependence, experiment reveals a strong negative c dependence. This negative dependence is opposite to the weak positive dependence of dioxane solutions. The molecular weight dependence of K_2 for *m*-cresol solutions is weak, being consisent with the theory, although the absolute values of K_2 do not agree between theory and experiment.

The twist elastic constant K_2 can also be calculated from the Brandeis group data[23] of light scattering and the Fredericks transition (cf. Tables 2 and 3). The results are presented in Table 5. The solvent used by the Brandeis group is a mixture of dichloromethane (80%) and dioxane (20%), and their K_2 are rather closer to those in the minor solvent component, dioxane, than those in the major component, dichloromethane, listed in Table 4. Their results of K_2 are favorably compared with the theoretical values calculated by eqs 4.9 and 4.11.

The experimental K_2 listed in Table 4 seem to correlate to the cholesteric pitch P_0 at no external field which is given in the fourth column of Table 4, and K_2 of cholesteric solutions with smaller P_0 appear to be closer to theoretical K_2. It is argued that P_0 of helical polymer solutions is determined by a subtle balance of two intermolecular interactions, the repulsion of the helical hard core and the chiral dispersion force.[8,52] Thus, the solvent dependence of P_0 may be explained by a delicate change in chiral dispersion force and/or local helical structure of the polymer molecule in different solvents, but such a change would hardly affect K_2. At present, we do not know what is the origin of the strong solvent dependence of K_2. However, it may be worthwhile checking whether some small changes in helical structure of polymer molecules take place under a strong magnetic field. In such a case, the experiment of the magnetically induced cholesteric-to-nematic transition could not provide the correct K_2.

The Brandeis group[23,24] also obtained the ratio K_1/K_2 for the PBG solutions by light scattering. The values of this ratio range from 12.5 to 32 and do not fulfill the relation $K_1 = 3K_2$ obtained in the present theory (cf. Section 4). It is suggested that the failure comes from the assumption of the uniform concentration used in eq 4.3. As pointed out by de Gennes,[53] a splay distortion in nematics of long polymer chains imposes a nonuniform distribution of the polymer center of mass, so that eq 4.3 is not relevant for this distortion. This nonuniformity effect on K_1 was considered by several investigators,[11,25,53−55] but it is not discussed in this paper.

7. Concluding Remarks

The present theory has used the following important approximations to formulate the Frank elastic constants of lyotropic polymer liquid crystals:

(1) The excess free energy F^{ex} of distorted nematic systems has been approximated by eq 2.5.

(2) The polymer chain statistics in the nematic phase has been approximated by that of the equivalent freely jointed chain (EFJC) which has the degree of orientation same as the wormlike chain (WC) in the nematic phase.

Since eq 2.5 was derived on the basis of a mean-field type of theory (the scaled particle theory), approximation 1 does not accurately take into account a microscopically inhomogeneous distribution of polymer molecules or a coupling effect of the translational and orientational degrees of freedom in nematic solutions. This approximation may affect the concentration dependence of the elastic constants K_i predicted by the present theory. However, since the present theory successfully described the concentration dependence of K_3 and K_2 for PBG solutions listed in Tables 3 and 5, approximation 1 is concluded to be good within the concentration range examined.

In the coil limit, K_2 and K_3 of the present theory do not agree with the results of Grosberg and Zhestkov[11] and Shimada et al.,[15] who used the WC model, as mentioned in Section 4. Those disagreements may arise from approximation 2. The ratio K_3/K_2 of the present theory is smaller than those predicted by the theories of the WC model in the coil limit (cf. Table 1 and Section 4). Therefore approximation 2 may be responsible for the disagreement between the present theory and experiment for K_3/K_2 at high molecular weights shown in Table 2. This implies that the inaccuracy of approximation 2 is appreciable even for rigid polymers like PBG.

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Appendix. Free Energy of Undistorted Nematic Solutions

Solutions of both the wormlike chain (WC) and equivalent freely-jointed chain (EFJC) possess the same form of the excess free energy density $\mathcal{F}_{\mathrm{N}}^{\mathrm{ex}}$ in an undistorted nematic state, which is derived by the scaled particle theory (SPT) to be

$$\mathcal{F}_{\mathrm{N}}^{\mathrm{ex}} = c'^{2}k_{\mathrm{B}}T\left\{\frac{\pi}{4}L_{\mathrm{c}}^{2}dH_{\mathrm{A}}(\phi)\rho + \frac{\pi}{4}L_{\mathrm{c}}^{2}d\delta + 4vH_{\mathrm{I}}(\phi)\right\} \tag{A.1}$$

(cf. eq 2.5), where ρ is defined by

$$\rho \equiv \frac{4}{\pi}\int \mathrm{d}\mathbf{a}\int \mathrm{d}\mathbf{a}'\,|\mathbf{a}\times\mathbf{a}'|f(\mathbf{a})f(\mathbf{a}') \tag{A.2}$$

with the orientational distribution function $f(\mathbf{a})$ of the tangent vector $\mathbf{a}$ averaged along the chain contour, and δ represents the strength of the (orientation-dependent) soft attractive interaction defined by (cf. eq 2.8)

$$\delta \equiv \frac{4}{\pi d}\int \mathrm{d}\mathbf{a}\int \mathrm{d}\mathbf{a}'\int_{d}^{\infty}\mathrm{d}p\,\frac{w(p;\mathbf{a},\mathbf{a}')}{k_{\mathrm{B}}T}f(\mathbf{a})f(\mathbf{a}') \tag{A.3}$$

It is noted that ρ given by eq A.2 should not be confused with the generalized density distribution in the text.

The ideal term $\mathcal{F}^{\mathrm{id}}$ of the free energy density is different between the two model chains. For uniform nematic solutions of the EFJC, eq 2.2 can be rewritten as

$$\mathcal{F}^{\mathrm{id}} = c'k_{\mathrm{B}}T(\ln c' + \ln \Lambda^{3} - 1 + \sigma_{\mathrm{EFJC}}) \tag{A.4}$$

with

$$\sigma_{\mathrm{EFJC}} = N_{\kappa}\int f(\mathbf{a})\ln[4\pi f(\mathbf{a})]\,\mathrm{d}\mathbf{a} \tag{A.5}$$

We have added ln 4π to the integrand so as for σ_{EFJC} to be zero in the isotropic state. On the other hand, the expression of the corresponding quantity σ_{WC} for the WC as a functional of $f(\mathbf{a})$ is much more complex than eq A.5. Khokhlov and Semenov,[19] Odijk,[38] and Chen[56] proposed different expressions of σ_{WC} by using various methods.

The orientational distribution function $f(\mathbf{a})$ is determined by the minimization condition of the total free energy density $\mathcal{F} = \mathcal{F}^{\mathrm{id}} + \mathcal{F}^{\mathrm{ex}}$ with respect to the degree of orientation. Here, we use the trial function method for this minimization problem. The trial function we use is that used by Onsager[18] for rodlike polymer solutions and by Khokhlov and Semenov[19,36] for wormlike polymer solutions (see eq 3.2). With this function, the orientation-dependent parameters σ_{EFJC} and σ_{WC} are expressed as

$$\begin{cases} \sigma_{\mathrm{EFJC}} = N_{\kappa}(\ln\alpha - 1 + \pi e^{-\alpha}) \\ \sigma_{\mathrm{WC}} = \ln\alpha - 1 + \pi e^{-\alpha} + \dfrac{1}{3}N(\alpha - 1) + \\ \qquad \dfrac{5}{12}\ln\left\{\cosh\left[\dfrac{2}{5}N(\alpha - 1)\right]\right\} \end{cases} \tag{A.6}$$

and ρ can be given in a form of the asymptotic expansion of α in good accuracy.[18] (The above expression of σ_{WC} was presented by DuPré and Yang,[57] who modified Odijk's equation[38] of σ_{WC} so as to yield the limiting expressions of σ_{WC} obtained by Khokhlov and Semenov.[19]) For usual liquid-crystalline polymer−good solvent systems, the soft attractive interaction w is so weak that we can neglect the term of δ in eq A.1. Thus the free energy minimization condition gives the equation

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\alpha} + \frac{\pi}{4}L_{\mathrm{c}}^{2}dc'H_{\mathrm{A}}(\phi)\frac{\mathrm{d}\rho}{\mathrm{d}\alpha} = 0 \tag{A.7}$$

From the value of α determined by the above equation, the order parameter S is calculated by

$$S = 1 - \frac{3}{\alpha}\coth\alpha + \frac{3}{\alpha^{2}} \tag{A.8}$$

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