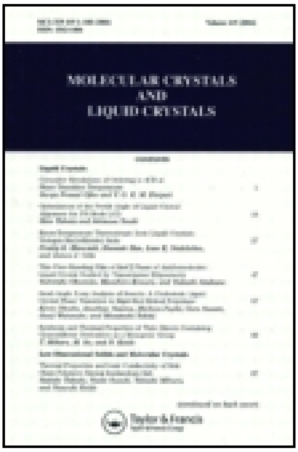

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Calculation of Bulk Elastic Constants of Gay-Berne Nematic Liquid Crystals from New Direct Correlation and Pair Distribution Functions

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In our earlier work [Phys. Rev. E, 82, 041701 (2010)], the bulk elastic constants were calculated using Poniewierski-Stecki expressions and the new direct correlation function. We calculated the bulk elastic constants, K_{11}, K_{22} *and* K_{33} *of Gay-Berne nematic liquid crystals at constant temperature and density using the expressions proposed by Stelzer and co-workers [J. Chem. Phys. 103, 3098 (1995)]. The angular coefficients of the direct correlation function, which enter the final equations, have been determined using the new direct correlation and pair distribution functions. By study of the model at a fixed temperature over a wide range of densities for molecular elongation,* $k = 3$, *the detailed information is provided on the elastic behavior of the Gay-Berne nematic. The results of our calculations are qualitatively in agreement with the molecular dynamic simulation results.*

Keywords Direct correlation function; elastic constants; Gay-Berne; nematic liquid crystals; prolate molecule

I. Introduction

The elastic, long-wavelength deformations of nematic liquid crystals are usually described by the Frank-Oseen bulk energy [1], which is expressed by three independent elastic distortion modes of a positionally dependent *director* unit vector field, $\hat{n}$:

$$F_{bulk} = \frac{1}{2}\left\{\int d\vec{r}[K_{11}(\vec{\nabla}\cdot\hat{n})^2 + K_{22}(\hat{n}\cdot\vec{\nabla}\times\hat{n})^2 + K_{33}(\hat{n}\times\vec{\nabla}\times\hat{n})^2]\right\} \tag{1-1}$$

called splay, twist and bend, respectively. Nehring and Saupe have supplemented the bulk free energy of Frank and Oseen by two additional terms that describe director deformations near surfaces:

$$F = F_{bulk} + \left\{\int d^2\vec{r}[K_{13}\vec{\nabla}.(\hat{n}(\vec{\nabla}\cdot\hat{n})) - (K_{22}+K_{24})\vec{\nabla}.(\hat{n}+\hat{n}\times\vec{\nabla}\times\hat{n})]\right\} \tag{1-2}$$

which called splay-bend and saddle-splay terms, respectively.

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The elastic free energy of nematics depends on five material parameters, three of which are volume constants (K_{11}, K_{22}, K_{33}) and the remaining two are surface constants, K_{13} and K_{24}, measuring the strength of the different elastic distortion modes.

The microscopic expressions for the bulk elastic constants most often used have been proposed by Poniewierski and Stecki [2]. These are derived from a fundamental expression of the microscopic free energy up to pair correlations and read:

$$K_{11} = \frac{K_B T}{2} \int r_x^2 C(\vec{r}_{12}, \widehat{u}_1, \widehat{u}_2) \rho^{(1)'} (Cos\theta_1) \times \rho^{(1)'} (Cos\theta_2)\, u_{1x} u_{2x} d\vec{r}_{12} d\widehat{u}_1 d\widehat{u}_2 \quad (1\text{-}3)$$

$$K_{22} = \frac{K_B T}{2} \int r_x^2 C(\vec{r}_{12}, \widehat{u}_1, \widehat{u}_2) \rho^{(1)'} (Cos\theta_1) \times \rho^{(1)'} (Cos\theta_2)\, u_{1y} u_{2y} d\vec{r}_{12} d\widehat{u}_1 d\widehat{u}_2 \quad (1\text{-}4)$$

$$K_{33} = \frac{K_B T}{2} \int r_z^2 C(\vec{r}_{12}, \widehat{u}_1, \widehat{u}_2) \rho^{(1)'} (Cos\theta_1) \times \rho^{(1)'} (Cos\theta_2)\, u_{1x} u_{2x} d\vec{r}_{12} d\widehat{u}_1 d\widehat{u}_2 \quad (1\text{-}5)$$

In the expressions (1-3) to (1-5), K_B and T are Boltzman constant and the temperature, $\vec{r}$ is the separation vector of a pair of molecules, $\hat{u}_1$ and $\hat{u}_2$ are the orientation unit vectors of the two molecules and $C(\vec{r}, \hat{u}_1, \hat{u}_2)$ is the direct pair correlation function of a reference isotropic system. Finally, $\rho^{(1)'}(u_{iz})$ is the derivative of the one-particle orientational distribution function $\rho^{(1)}(u_{iz})$ of nematics with respect to its argument.

In earlier work [3], the bulk elastic constants of hard ellipsoid nematic molecules have been studied. We neglect the effect of surface-like terms and calculate the bulk elastic constants of Gay-Berne nematic liquid crystals. In the next section, we introduce one particle distribution and the new direct correlation function (DCF). In section 3 the Stelzer expressions for bulk elastic constants of uniaxial nematic are introduced. Lastly, we summarized the results and discussion.

II. One-Particle Distribution Function and Direct Correlation Function of Ellipsoidal Molecules

A one-particle distribution function of homogeneous nematic liquid, $\rho^{(1)}(\vec{r}, \widehat{u})$, is independent of $\vec{r}$ and can be written as

$$\rho^{(1)}(\vec{r}, \widehat{u}) = \rho_\circ f(\widehat{u}) \quad (2\text{-}1)$$

where $\rho_\circ$ is number density of liquid and $f(\widehat{u})$ is normalized one-particle angular distribution function for which

$$\int f(\widehat{u}) d\widehat{u} = 1. \quad (2\text{-}2)$$

If $\widehat{n} = \widehat{z}$, we have

$$f(\widehat{u}) = f(\widehat{u} \cdot \widehat{n}) = f(\cos\theta) \quad (2\text{-}3)$$

and

$$f(\cos\theta) = \sum_{l,even} a_l P_l(\cos\theta) = \sum_{l,even} \frac{2l+1}{4\pi} \times \langle P_l \rangle\, P_l(\cos\theta). \quad (2\text{-}4)$$

Where $P_l\,(\cos\theta)$ is the even Legendre polynomial. If we consider $x = (\cos\theta)$, then the orientational order parameter of nematic phase is:

$$\langle P_l \rangle = \int_0^1 P_l\,(x) f\,(x)\,dx. \tag{2-5}$$

From Ref. [4] we chose $\langle P_2 \rangle = 0.68$ and $\langle P_4 \rangle = 0.34$ for elongation ($k = b/a$ is the length to breath ratio of uniaxial ellipsoid) $k = 3.0$ at $T = 1.0$ (the temperature that exist theoretical and experimental data).

The DCF of the hard ellipsoid (HE) fluid was calculated by Allen et al. [5] using computer simulation method. They found their results closest to the DCF given by Marko [6]. Hence, Avazpour and Moradi [7] used the improved Pynn- Wulf [8] expression for the DCF and pair correlation of hard ellipsoids proposed by Marko:

$$C_{Modif}(\vec{r}, \hat{u}_1, \hat{u}_2, \eta) = C_{PY-Roth}\left(\frac{r}{\sigma(\hat{u}_1, \hat{u}_2, \hat{r})}, \eta\right) \times (1 + \alpha P_2\,(\hat{u}_1 \cdot \hat{u}_2)) \tag{2-6}$$

$$g(\vec{r}, \hat{u}_1, \hat{u}_2, \eta) = g_{HS}\left(\frac{r}{\sigma(\hat{u}_1, \hat{u}_2, \hat{r})}, \eta\right) \times (1 + \alpha P_2\,(\hat{u}_1 \cdot \hat{u}_2)) \tag{2-7}$$

where $C_{PY-Roth}$, g_{HS} are the new DCf and pair correlation of hard spheres [7], respectively. $\sigma(\vec{r}, \widehat{u}_1, \widehat{u}_2)$ is Berne-Pechukas closest distance of two ellipsoid molecules and α is a parameter. The closet approach distance of HE proposed by Rickayzen [7] is given as:

$$\sigma(\vec{r}, \widehat{u}_1, \widehat{u}_2) = \sigma_\circ \left\{ 1 - \frac{\chi}{2}\left[\frac{(\widehat{u}_1 \cdot \widehat{r}_{12} + \widehat{u}_2 \cdot \widehat{r}_{12})^2}{1 + \chi \widehat{u}_1 \cdot \widehat{u}_2} + \frac{(\widehat{u}_1 \cdot \widehat{r}_{12} - \widehat{u}_2 \cdot \widehat{r}_{12})^2}{1 - \chi \widehat{u}_1 \cdot \widehat{u}_2}\right] \right.$$
$$\left. - \lambda \frac{[(\widehat{u}_1 \cdot \widehat{r}_{12})^2 - (\widehat{u}_2 \cdot \widehat{r}_{12})^2]^2}{1 - \chi^2 (\widehat{u}_1 \cdot \widehat{u}_2)^2} \right\}^{\frac{-1}{2}} \tag{2-8}$$

where $\lambda = 1 - \chi - \frac{4b^2}{(a+b)^2}$ and $\chi = \frac{k^2-1}{k^2+1}$.

$C_{PY\_Roth}\,(r/\sigma)$ were obtained [7, 9] as:

$$C_{PY-Roth}\,(r/\sigma) = \frac{1}{3} C_{PY}\,(r/\sigma) + \frac{2}{3} C_{Roth}\,(r/\sigma) \tag{2-9}$$

Using $C_{PY\_Roth}\,(r/\sigma)$ instead of $C_{PY}\,(r/\sigma)$ and replace the closest approaches distance of Berne-Pechukas by Rickayzen closest approach in Eq. (2-6), the new DCF, $(C_{Modif}(r/\sigma))$, were calculated for HE fluid [7]. For ellipsoids of elongation $k \leq 5$ and packing fraction $\eta = 0.45$, the parameter $\alpha = -0.29 + 0.315\,k + 0.025\,k^2$ is deduced [3].

We study the influences of Gay-Berne molecular interactions on the K_{ii} of the uniaxial nematic phase using Stelzer expressions and $C_{Modif}\,(r/\sigma)$ by assuming a pair potential function to have the form [10]

$$u\,(\hat{u}_1, \hat{u}_2, r) = 4\varepsilon\,(\hat{u}_1, \hat{u}_2, r) \left\{ \left[\frac{1}{r - \sigma\,(\hat{u}_1, \hat{u}_2, r) + 1}\right]^{12} - \left\{ \left[\frac{1}{r - \sigma\,(\hat{u}_1, \hat{u}_2, r) + 1}\right]^{6} \right\} \right. \tag{2-10}$$

where ε is the energy parameter. The energy parameter ε is:

$$\varepsilon(\widehat{u}_1, \widehat{u}_2, \vec{r}) = \varepsilon(\widehat{u}_1, \widehat{u}_2) \varepsilon'^2(\widehat{u}_1, \widehat{u}_2, \vec{r}) \tag{2-11}$$

and

$$\varepsilon(\hat{u}_1, \hat{u}_2) = \varepsilon_0\left[1 - \chi^2(\hat{u}_1, \hat{u}_2)^2\right]^{-\frac{1}{2}}, \tag{2-12}$$

$$\varepsilon'(\vec{r}, \hat{u}_1, \hat{u}_2) = 1 - \frac{\chi}{2}\left[\frac{(\hat{u}_1 \cdot \hat{r} + \hat{u}_2 \cdot \hat{r})^2}{r^2[1 + \chi'(\hat{u}_1 \cdot \hat{u}_2)]} + \frac{(\hat{u}_1 \cdot \hat{r} - \hat{u}_2 \cdot \hat{r})^2}{r^2[1 - \chi'(\hat{u}_1 \cdot \hat{u}_2)]}\right], \tag{2-13}$$

where χ and χ' denote the anisotropic of molecular shape and the potential energy, respectively,

$$\chi = \frac{k^2 - 1}{k^2 + 1}, \qquad \chi' = \frac{k'^{1/2} - 1}{k'^{1/2} + 1}. \tag{2-14}$$

The most important parameters of the potential are the anisotropy parameters k and k', where k' is the well-depth ratio for the side-by-side and end-to-end configurations.

This potential describes quite well thermotropic liquid crystals composed of moderately nonspherical molecules as demonstrated most clearly by computer simulations [4]. In our calculations, the anisotropy parameters, k and k' of the potential have been chosen 3 and 5 respectively.

The DCF of a system with interaction, $u(\vec{X}_1, \vec{X}_2)$, with the low density approximation [11] is

$$C(\vec{X}_1, \vec{X}_2) = C_\circ(\vec{X}_1, \vec{X}_2) - \beta u(\vec{X}_1, \vec{X}_2) g_\circ(\vec{X}_1, \vec{X}_2) \tag{2-15}$$

where $C_\circ(\vec{X}_1, \vec{X}_2)$ and $g_\circ(\vec{X}_1, \vec{X}_2)$ are DCF and pair correlation function of HE molecules, respectively.

III. Calculation of the Bulk Elastic Constants of Uniaxial Nematics: The Stelzer Expressions

For linear molecules and within the unoriented nematic approximation, the expansion of the DCF (in a space-fixed frame) is:

$$\begin{aligned} C(\mathrm{X}, \mathrm{X}') = C\,(r, \hat{u}_1, \hat{u}_2) = \textstyle\sum_{l1l2l\, m_1m_2m} C_{l1l2l}\,(r) \\ \times\ C_{l_1,l_2,l;m_1,m_2,m} \times Y_{l_1m_1}\,(\hat{u}_1)\, Y_{l_2m_2}\,(\hat{u}_2)\, Y_{lm}\,(\hat{u}) \end{aligned} \tag{3-1}$$

Here$C_{l_1,l_2,l}\,(r)$ are the spherical harmonic expansion coefficients of the DCF, $C_{l_1,l_2,l;m_1,m_2,m}$ are Clebsch–Gordon coefficients, $Y_{l,m}$ are the spherical harmonics. The local D_∞-symmetry guarantees that only even numbers for l_1, l_2 and l enter the expansion.

In body fixed frame

$$C_{l_1,l_2,m}\,(r) = \int C\,(r, \hat{u}_1, \hat{u}_2) Y_{l_1m}\,(\hat{u}_1)\, Y_{l_2m_-}\,(\hat{u}_2)\, d\hat{u}_1 d\hat{u}_2 \tag{3-2}$$

and

$$C_{l_1,l_2,l}\,(r) = \textstyle\sum_m \sqrt{\dfrac{4\pi}{2l+1}}\, C_{l_1,l_2,l;m_1,m_2,m} C_{l_1,l_2,m}\,(r) \tag{3-3}$$

After inserting Eqs. (2-4) and (3-1) into Eqs. (1-3)–(1-5) and making use of the properties of spherical harmonics, the angular integrations can be performed explicitly and the elastic constants are expressed as a series of $\langle P_l \rangle$ and $C_{l_1,l_2,l}(r)$. The final Estelzer equations for the bulk elastic constants read [4]:

$$\beta K_{11} = K(1, 1, 1, 1, 1, 1) \tag{3-4}$$

$$\beta K_{22} = K(1, -1, 1, -1, 1, -1) \tag{3-5}$$

$$\beta K_{33} = K(-2, 0, -2, 0, -2, 0) \tag{3-6}$$

where $\beta = 1/K_B T$ and the six numbers are to be inserted for the a_i in the following Estelzer expression,

$$\begin{aligned} K(a_1, a_2, a_3, a_4, a_5, a_6) = \frac{1}{12}\rho^2 \sum_n^{even} \Bigg[& (2n+1)\frac{(n+1)!}{(n-1)!}\langle P_n\rangle^2 \left(\sqrt{\frac{4\pi}{2n+1}} I_{n,n,0} \right. \\ & \left. + a_1\sqrt{\frac{4\pi}{5}} I_{n,n,2} C_{n,n,2;1,-1,0} + a_2\sqrt{\frac{6\pi}{5}} I_{n,n,2} C_{n,n,2;1,1,2}\right) \\ & + \sqrt{(2n+1)(2n-3)}\sqrt{\frac{(n+1)!}{(n-3)!}}\langle P_n\rangle \langle p_{n-2}\rangle \\ & \left(a_3\sqrt{\tfrac{4\pi}{5}} I_{n,n-2,2} C_{n,n-2,2;1,-1,0+} a_4\sqrt{\frac{6\pi}{5}} I_{n,n-2,2} C_{n,n-2,2;1,1,2}\right) \\ & + \sqrt{(2n+1)(2n+5)}\sqrt{\frac{(n+3)!}{(n-1)!}}\langle P_n\rangle \langle p_{n+2}\rangle \\ & \left(a_5\sqrt{\frac{4\pi}{5}} I_{n,n+2,2} C_{n,n+2,2;1,-1,0+}\ a_6\sqrt{\frac{6\pi}{5}} I_{n,n+2,2} C_{n,n+2,2;1,1,2}\right)\Bigg] \end{aligned} \tag{3-7}$$

In the expressions above $I_{l_1,l_2,l}$ are abbreviations for the radial integrals over the expansion coefficients $C_{l_1,l_2,l}(r)$ of the DCF,

$$I_{l_1,l_2,l} = \int dr r^4 C_{l_1,l_2,l}(r). \tag{3-8}$$

Using (3-2), (2-10), (2-15) and $C_{Modif}(r/\sigma)$, the function $C_{l_1,l_2,l}(r)$ has been determined. For calculation of the integrals, we use the Monte Carlo integration method [12] with Fortran codes [13].

From Ref. [4] we chose $\langle P_2\rangle = 0.68$ and $\langle P_4\rangle = 0.34$ for elongations $k = 3.0$ at $T = 1.0$ (the temperature that correlates to theoretical and experimental data) and nematic bulk density$\rho_0 = 0.32$. A reduced system of units has been used, i.e., all quantities have been related to potential parameters σ_0 and ε_0 which have been set equal to unity.

V. Results and Discussions

Our calculated results have been compared with molecular dynamics simulation results of Ref. [4,14]. As seen from Fig. 1 and Table 1, quantities obtained based on the results of the new DCF are in qualitative agreement with those given in Refs. [4,14]. The simulation values of elastic constants provided by the Gay-Berne potential show that the inequality $K_{33} > K_{11} > K_{22}$ applies in nematic liquid crystal with $k = 3.0$ which is confirmed in the present work (see Table 1 and Fig. 1). The disagreement of the absolute value of our K_{ii}'s with $K_{ii}^{Simulation}$ at high densities for $k = 3.0$, is due to low-density approximation of

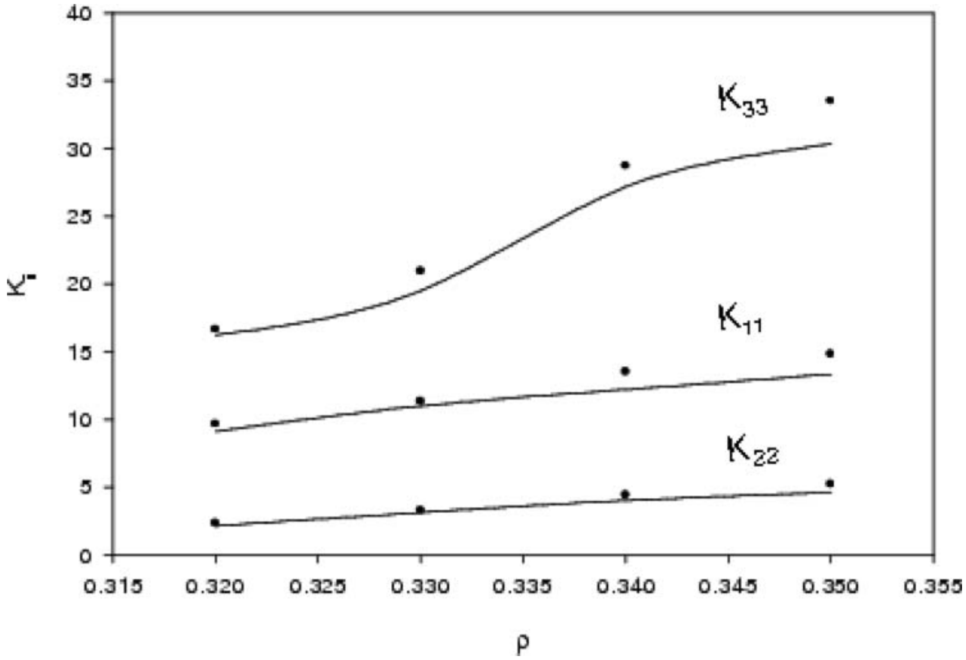

Figure 1. The bulk elastic constant for Gay-Berne nematic liquid crystal as a function of ρ. Continuum lines are due to present work. Circles are due to Ref. [4,14].

the DCF in our calculations. According to Fig. 1, it is found that K_{33} is very sensitive to variations of ρ, but the K_{22} is not.

The experimental measurement of the ratios of K_{33}/K_{11} and K_{22}/K_{11} in uniaxial nematic liquid crystals have been determined [15,16]. We require a decrement of K_{33}/K_{11} quantity to improve liquid crystal displays [16], therefore K_{22}/K_{11} and K_{33}/K_{11} were studied. The values of Fig. 2 show that the value ofK_{22}/K_{11} has little increase with an increase of ρ while K_{33}/K_{11} increases from 1.7804 to 2.2727 and osillate.

The qualitative agreement of our results with the Stelzer results, prove that this new correlation function and Stelzer expresions is suitable to study the effects of temperature, different intermolecular interactions, molecular size and the number density in calculation of the elastic constants of Gay-Berne nematic liquid crystals. We have applied our model

Table 1. Values of elastic constants by new direct correlation function and given values of Refs. [4,14] for Gay-Berne prolate nematic. These results have been determined for ellipsoid of revolution systems with $k = 3.0$, $\rho = 0.32$, $T = 1.0$, $\langle P_2 \rangle = 0.68$ and $\langle P_4 \rangle = 0.34$. The values of K_{ii} are given in the unit of 10^{-7}

	K_{11}		K_{22}		K_{33}	
$k = 3$	Our work	Refs. 4, 14	Our work	Refs. 4, 14	Our work	Refs. 4, 14
	9.1200	9.6505	2.1500	2.3145	16.2372	16.637

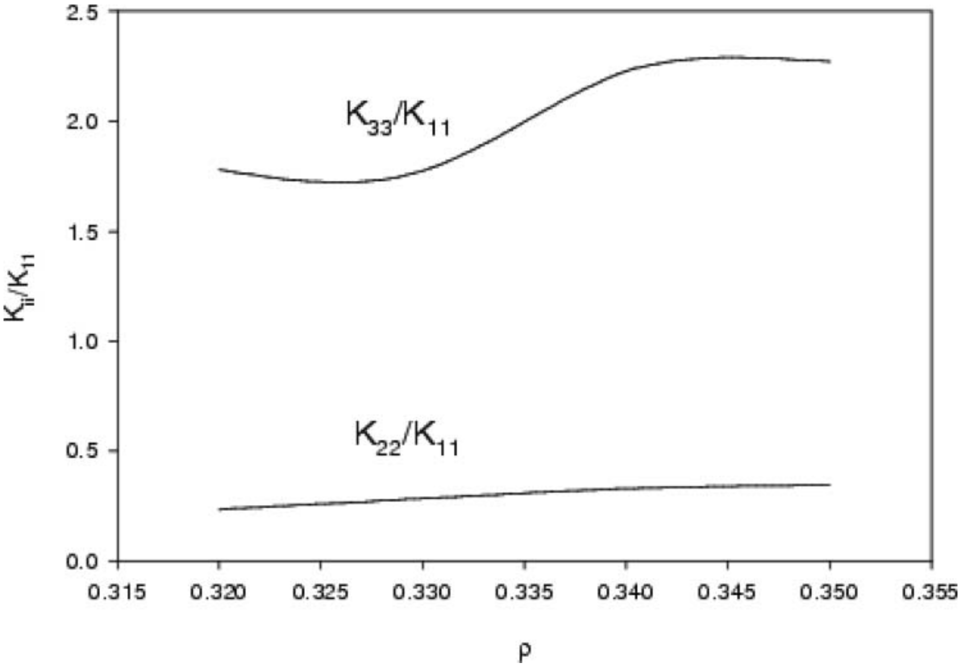

Figure 2. The ratio of bulk elastic constants for Gay-Berne nematic liquid crystal as a function of ρ in our calculations.

for the study of uniaxial nematic liquid crystals. It can also be applied to study the elastic properties of biaxial nematic liquid crystals.

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