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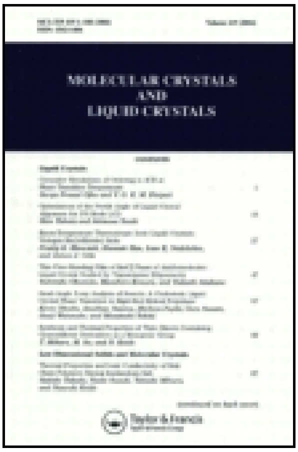

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Elastic Constants of Nematic Liquid Crystals From Molecular Dynamics Simulations

Joachim Stelzer [a] , Lech Longa [b] & Hans-Rainer Trebin [a]

[a] Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57/VI, Stuttgart, Germany

[b] Jagiellonian University, Department of Statistical Physics, Reymonta 4, Kraków, Poland

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ELASTIC CONSTANTS OF NEMATIC LIQUID CRYSTALS FROM MOLECULAR DYNAMICS SIMULATIONS

JOACHIM STELZER*, LECH LONGA†,
and HANS-RAINER TREBIN*
* Institut für Theoretische und Angewandte Physik,
Universität Stuttgart, Pfaffenwaldring 57/VI, Stuttgart, Germany
† Jagiellonian University, Department of Statistical Physics,
Reymonta 4, Kraków, Poland

Abstract The Frank-Oseen elastic constants K_{11}, K_{22} and K_{33} as well as the surface constants K_{13} and K_{24} have been calculated for Gay-Berne nematic liquid crystal with anisotropy parameters $\kappa = 3$ and $\kappa' = 5$. In deriving the elastic constants a direct correlation function approach of Poniewierski and Stecki[1] in a version proposed by Lipkin *et al.*[5] was choosen. The final formulas have been expressed in terms of the orientational order parameters and of the angular coefficients of the direct correlation function of an unoriented nematic. The latter have been determined exactly from the molecular dynamics simulations in the NVT ensemble. Results for the surface elastic constants, qualitatively different than those obtained from all previous treatments, clearly show that the surface deformations are strongly sensitive to details of the direct correlation function. Obtained values of surface elastic constants are partly negative and an order of magnitude smaller than bulk elastic constants.

The static, long-wavelength deformations of nematic liquid crystals are usually described by the Frank-Oseen bulk free energy[2], which is expressed by three independent elastic distortion modes of the director field $\boldsymbol{n}$:

$$F_{bulk} = \int \mathrm{d}^3\boldsymbol{r} \left[\frac{1}{2} K_{11}(\mathrm{div}\boldsymbol{n})^2 + \frac{1}{2} K_{22}(\boldsymbol{n} \cdot \mathrm{curl}\boldsymbol{n})^2 + \frac{1}{2} K_{33}(\boldsymbol{n} \times \mathrm{curl}\boldsymbol{n})^2 \right], \quad (1)$$

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[3]:

$$F = F_{bulk} + \int \mathrm{d}^3\boldsymbol{r} \left[K_{13}\,\mathrm{div}(\boldsymbol{n}\,\mathrm{div}\boldsymbol{n}) - (K_{22} + K_{24})\,\mathrm{div}(\boldsymbol{n}\,\mathrm{div}\boldsymbol{n} + \boldsymbol{n} \times \mathrm{curl}\boldsymbol{n}) \right], \quad (2)$$

called *splay-bend* and *saddle-splay*, respectively.

The elastic free energy depends on five material parameters. Three of them are volume constants (K_{11}, K_{22}, K_{33}) and two surface constants (K_{13}, K_{24}), measuring the strength of the different elastic distortion modes. In continuum mechanics the elastic constants are treated as phenomenological, adjustable parameters.[4]

The microscopic expressions for the elastic constants most often used have been proposed by Poniewierski and Stecki[1]. We use simpler expressions as proposed by Lipkin *et al.*[5]. These are derived from a functional expansion of the microscopic free energy up to pair correlations and read:

$$\beta K_{11} = \frac{1}{2} \int r_x^2\, c(\vec{r}, \Omega_1, \Omega_2)\, \rho'(\cos\theta_1)\, \rho'(\cos\theta_2) e_{1x}\, e_{2x}\, r^2\, \mathrm{d}r\, \mathrm{d}\Omega\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2 \tag{3}$$

$$\beta K_{22} = \frac{1}{2} \int r_x^2\, c(\vec{r}, \Omega_1, \Omega_2)\, \rho'(\cos\theta_1)\, \rho'(\cos\theta_2) e_{1y}\, e_{2y}\, r^2\, \mathrm{d}r\, \mathrm{d}\Omega\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2 \tag{4}$$

$$\beta K_{33} = \frac{1}{2} \int r_z^2\, c(\vec{r}, \Omega_1, \Omega_2)\, \rho'(\cos\theta_1)\, \rho'(\cos\theta_2) e_{1x}\, e_{2x}\, r^2\, \mathrm{d}r\, \mathrm{d}\Omega\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2 \tag{5}$$

$$\beta K_{13} = -\frac{1}{2} \int r_x r_z\, c(\vec{r}, \Omega_1, \Omega_2)\, \rho(\cos\theta_1)\, \rho'(\cos\theta_2) e_{2x}\, r^2\, \mathrm{d}r\, \mathrm{d}\Omega\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2 \tag{6}$$

$$K_{24} = \frac{1}{2}\,(K_{11} - K_{22}), \tag{7}$$

are the starting point of our calculations. The relation (7) has been derived in a general way by Nehring *et al.*[3]

In the expressions (3-7) β represents the inverse temperature, $\boldsymbol{r}$ is the separation of a pair of molecules, $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are the orientation unit vectors of the two molecules and $c(\boldsymbol{r}, \Omega_1, \Omega_2)$ is the direct pair correlation function of a reference isotropic state. Finally, $\rho'(\cos\theta)$ is the derivation of the orientational distribution function $\rho(\cos\theta)$ with respect to its argument.

For linear molecules we can still simplify the expressions (3-7) by making use of the spherical harmonics expansion of the direct correlation function[6]:

$$c(\boldsymbol{r}, \Omega_1, \Omega_2) = \\ 4\pi \sum_{l_1 l_2 l}^{even} \sum_{m_1 m_2 m} c_{l_1,l_2,l}(r)\, C_{l_1,l_2,l;m_1,m_2,m}\, Y_{l_1,m_1}(\Omega_1)\, Y_{l_2,m_2}(\Omega_2)\, Y^*_{l,m}(\Omega). \tag{8}$$

Here $c_{l_1,l_2,l}(r)$ are the radial expansion coefficients and $C_{l_1,l_2,l;m_1,m_2,m}$ are Clebsch-Gordan coefficients. Due to the $\mathcal{D}_\infty$-symmetry of the nematic phase only even numbers for l_1, l_2, l have to be taken into account.

A similar expansion for the orientational distribution function with the director parallel to the z-direction of the coordinate system reads[6]:

$$\rho(\cos\theta_i) = \frac{\rho_0}{4\pi} \sum_n^{even} (2n+1)\, \overline{P_n}\, P_n(\cos\theta_i), \tag{9}$$

where ρ_0 is the particle density, P_n are the Legendre polynomials and $\overline{P_n}$ are the orientational order parameters defined as

$$\overline{P_n} = \frac{1}{\rho_0} \int \mathrm{d}\Omega_i P_n(\cos\theta_i)\, \rho(\cos\theta_i). \tag{10}$$

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After inserting (8) and (9) into (3-7) and making use of the properties of spherical harmonics[6] we finally can express the elastic constants as simple functions of $\overline{P_n}$ and $c_{l_1,l_2,l}(r)$.

For calculation of the elastic constants the orientational order parameters $\overline{P_n}$ and the functions $c_{l_1,l_2,l}(r)$, have been determined from the molecular dynamics simulations. Thereby the central difficulty was the evaluation of the coefficients $c_{l_1,l_2,l}(r)$ for all relevant radial separations. We applied the following procedure: for molecular separations less than half of the boxlength $r_{box}/2$ we determined from simulations the radial expansion coefficients $g_{l_1,l_2,l}(r)$ of the pair distribution function $g(\boldsymbol{r}, \Omega_1, \Omega_2)$. For distances larger than $r_{box}/2$ the mean-spherical approximation has been assumed for the direct correlation function

$$c_{l_1,l_2,l}(r) = -\beta V_{l_1,l_2,l}(r), \qquad r > r_{box}/2. \tag{11}$$

The procedure is justified as $c_{l_1,l_2,l}(r)$ has the range of the intermolecular potential V.

Now both informations were used to determine the $c_{l_1,l_2,l}(r)$. This was done by relating $g_{l_1,l_2,l}(r)$ to $c_{l_1,l_2,l}(r)$ through Ornstein-Zernicke equation[7] and by applying a Wiener-Hopf factorization[8]. In this way we generalized the Baxter equations for evaluating the direct correlation function.[6,9-13] They were next solved by an iterative procedure similar to that discussed by Jolly *et al.*[14]. To improve convergence a successive overrelaxation technique was used[15]. Details will be presented elsewhere.

The molecular dynamics simulations have been performed for uniaxial molecules interacting through a Gay-Berne pair potential[16]. The anisotropy parameters κ and κ' of the potential have been chosen equal 3 and 5, respectively, in agreement with those studied earlier by Miguel and Rull[17]. Simulations have been performed for temperatures and densities corresponding to a stable nematic phase. These were found from the phase diagram of Miguel and Rull[17].

A reduced system of units has been used, i.e. all quantities have been related to potential parameters σ_0 and ϵ_0 which, in turn, have been set equal to unity, as well as molecular mass and momentum of inertia[15]. Temperature has been kept constant by use of a Nosé-Hoover technique[18,19] The integration of the equations of motion has been performed with a leap-frog algorithm as recently proposed by Toxvaerd[20] for translational motion. We have worked out an extension of this algorithm to rotational motion.

All simulations have been performed with periodic boundary conditions for a rectangular box containing 405 particles. As initial configuration a tetragonal lattice with an ideal orientation of the molecules has been set up. Equations of motion were solved with the time step equal 0.001 (in reduced units). Starting from the lattice, the first 5000 equilibrating steps have been followed by 40000 steps for averaging over the quantities of interest. To save computer time, a potential cutoff of 4.0 (in reduced units) has been taken regard of.

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As an example of numerical calculations the lowest-order coefficients $g_{l_1,l_2,l}$ are plotted in Figure 1.

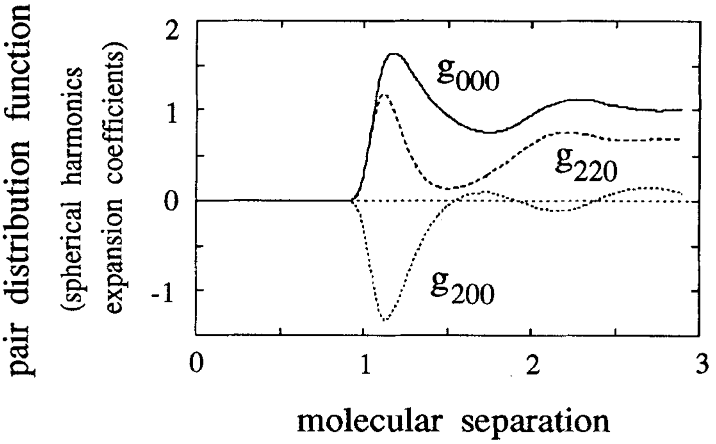

FIGURE 1 Spherical harmonics expansion coefficients of pair distribution function in molecular-fixed frame.

In Figure 2 we present some of the space-fixed expansion coefficients of the direct correlation function (times r^4) that enter the calculations of the elastic constants. From the plots we recognize that for each order of the expansion the $l = 0$-modes c_{220} and c_{440} give the most important contribution to elasticity.

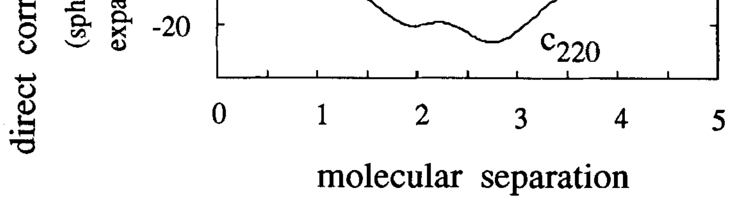

FIGURE 2 Spherical harmonics expansion coefficients of direct correlation function (times r^4) in space-fixed frame.

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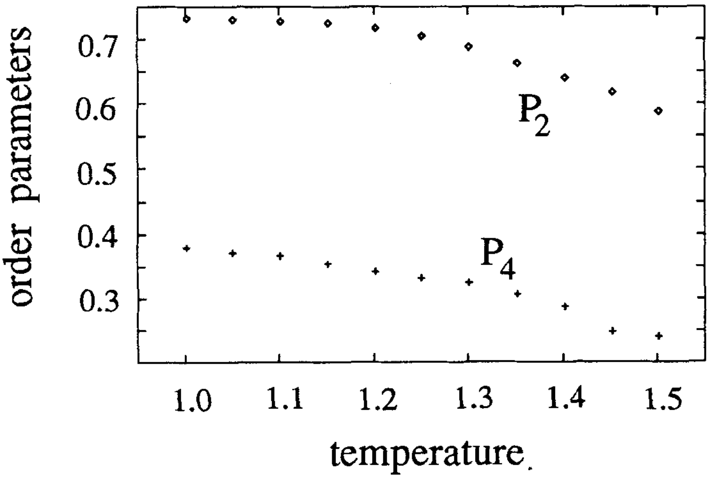

FIGURE 3 Temperature dependence of orientational order parameters.

Figure 3 shows temperature variation of the orientational order parameters $\overline{P_2}$ and $\overline{P_4}$. They were calculated for fixed density equal 0.33 (in reduced units). The temperature covered the interval where the nematic phase of the Gay-Berne fluid was stable. The curves reveal behaviour of the nematic order as predicted *e.g.* by the Maier-Saupe theory[21,22]. On approaching the nematic-isotropic phase transition the orientational order is strongly decreasing, showing approximately a square-root dependency on the reduced temperature $\sqrt{(T_c - T)/T_c}$, where T_c is the transition temperature.

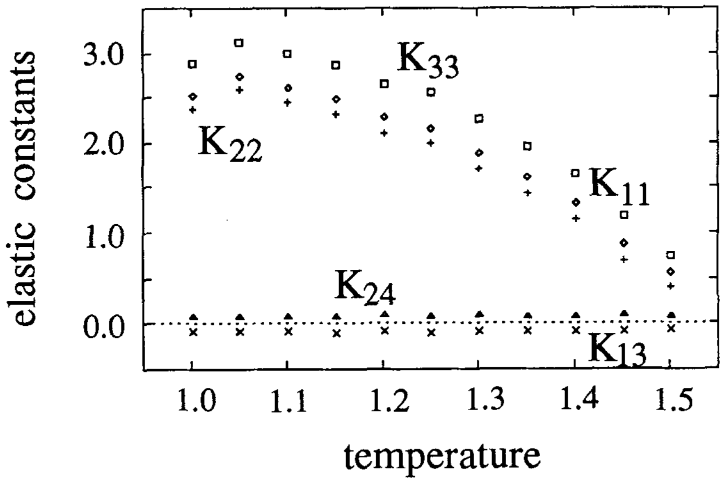

FIGURE 4 Temperature dependence of elastic constants.

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Combining the results of Figures 1-3 the temperature dependence of the elastic constants is finally shown in Figure 4. For the temperature interval (1.0-1.2) we find a slight linear increase of the elastic constants. In the Poniewierski-Stecki approach this behaviour is due to the explicit dependence on β in (3)-(7). For higher temperatures (1.2-1.5) the strong decrease of the nematic order parameters yields decrease of the anisotropy of the bulk elastic constants: the curves are decaying and approaching a common limiting value.

Within our model we find that the bulk elastic constants are about an order of magnitude larger than the surface constants. This is due to the fact that for each order of the expansion (8) the $l = 0$-modes of the direct correlation function give the dominant contribution to elasticity. They are absent for the surface constant K_{13}. Furthermore, our calculations yield negative values for the K_{13}, which is in agreement with former estimates of Nehring *et al.*[23] The surface constant K_{24} is found to be half of the difference between K_{11} and K_{22}, again being in agreement with suggestions of Nehring *et al.*[23].

Interestingly, our results are qualitatively different from those obtained by Teixeira *et al.*[24]. Since in our approach we evaluated exactly the spherical harmonics expansion coefficients of the direct correlation function and avoided approximations done in Teixeira *et al.*[24] we conclude that the surface constants are much sensitive to details of the direct correlation function than the bulk ones.

Finally, our analysis gives absolute values of the elastic constants, not just their ratios. As the expressions (3)-(7) indicate, the elastic constants are obtained in the unit of reduced temperature.

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