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Elastic constants of nematics
Comparison between molecular theory and computer simulations

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We compare the ratios of the Frank elasticity coefficients calculated within a recently developed molecular theory, based on the approximation of perfect local orientational order, with the results of computer simulations presented by Frenkel, Allen, Tjipto-Margo and Evans for fluids of hard prolate and oblate ellipsoids. Good agreement is found for high densities, which correspond to those of thermotropic nematics, and for realistic values of the axial ratio. By constrast, at lower densities the approximation of perfect local order appears to be inadequate and the results of computer simulations follow the predictions of mean-field-like theories.

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1. Introduction

The molecular-statistical theory of the curvature elasticity of nematic liquid crystals has been developed by many authors (see, for example [1–8]). The broad interest in this problem from the theoretical point of view is partially determined by the fact that the elasticity coefficients of nematics generally are not very sensitive to the details of the molecular structure and are determined mainly by average geometrical parameters [9]. In fact, many compounds with different molecular structures but approximately the same axial ratio possess rather similar values of the elasticity coefficients K_1 and K_3 [9], as was noticed first by Schadt and Müller [10] who compared the values of K_1 and K_3 for a number of nematics composed of molecules with different rings. Thus there is a good possibility of obtaining reasonable results using very simple molecular models which can be treated effectively within the molecular-statistical approach.

The first calculations of the elasticity coefficients were performed in the molecular field approximation [1–4] and the results accounted for the full anisotropy of the Frank elastic coefficients and also described qualitatively the temperature variation of these parameters [3, 4]. At the same time, the quantitative agreement between theory and experiment remained rather poor [9]. Later, the general expressions for the elasticity coefficients were obtained using the density functional theory of liquid crystals [5–8]. In this approach the coefficients are expressed in terms of the (pair) direct correlation function of the nematic fluid. The actual calculations, however, were performed with the help of simple approximations for the correlation function.

Very recently a different approach has been proposed which is based on the approximation of perfect local orientational order in anisotropic fluids [11]. This approximation can be considered as a simple (but rather crude) alternative to the mean field theory, since it is assumed that the molecular symmetry axes are approximately parallel within the direct correlation radius which is of the order of molecular length. This model description of strong short-range orientational correlations in nematics has

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been considered previously in the analysis of the viscosity [12], of the diffusion [13] and of the static structure factor [14, 15]. The approximation of perfect local order has been used in [11] to get simple analytical expressions for the elasticity coefficients of the model nematic composed of molecules with ellipsoidal equipotential surfaces. In such model systems, it is possible to perform the local transformation to a reference hard sphere fluid which is characterized by an isotropic correlation function. As shown in [11], this approach yields expressions for the K_1/K_3 which are closer to experimental data for rigid molecules than the results of the mean field theory.

A more detailed comparison of different models for intermolecular correlations in nematics has become possible recently, since computer simulations of the elasticity coefficients have been performed for nematics composed of ellipsoidal and spherocylindrical particles [16, 17]. In this paper we compare the results of these simulations with the results of the analytical theory [11], based on the approximation of perfect local order combined with an affine transformation model, and also with the results of two mean field-like theories discussed in [16]. We also make an attempt to draw some conclusions about the role of short-range orientational correlations in nematics at various densities.

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2. Simple expressions for the elasticity coefficients

According to [11], the model of perfect local orientational order corresponds to the following approximation for the direct correlation function of two neighbouring molecules in the anisotropic fluid

$$C_2(\mathbf{u}_1,\mathbf{r}_{12},\mathbf{u}_2)=4\pi C_2^{\mathrm{ord}}(\mathbf{r}_{12},\mathbf{u}_1)\delta(\mathbf{u}_1-\mathbf{u}_2)+\mathrm{const.}, \tag{1}$$

for $r_{12}<r_c^0$ where r_c^0 is the direct correlation radius and the unit vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ determine the orientations of the symmetry axes of the molecules **1** and **2**. This approximation implies that the molecular symmetry axes are parallel when the intermolecular separation is less than the direct correlation radius r_c^0. For $r_{12}>r_c^0$ the orientational correlations are assumed to decay rapidly. The approximation of perfect local order seems to be reasonable for nematic fluids composed of strongly anisotropic particles. It should be noted that a similar assumption has been shown to be successful even for the isotropic phase of fluids composed of molecules which are much less anisotropic than those of typical mesogens [17]. It is assumed that the local order characterized by the pair correlation is also present in the isotropic phase not far from the transition point and that only the long-range orientational order, which is determined by the one-particle distribution function, disappears.

The analytical results for the elasticity coefficients have been obtained in [11] in this approximation using the simple model of nematics composed of particles with ellipsoidal equipotential surfaces. The properties of such a fluid can be linked with those of a reference fluid of spherical particles at the same density which is characterized by the direct correlation function C_{ref}.

The final expressions for the elasticity coefficients can be written as [11]

$$\left.\begin{aligned}
K_1&=\bar{K}(1+\Delta-9\Delta(\bar{P}_4/\bar{P}_2)+\left(\frac{39}{11}\Delta+6\right)(\bar{P}_4/\bar{P}_2)^2),\\
K_2&=\bar{K}(1-2\Delta-3\Delta(\bar{P}_4/\bar{P}_2)+\left(-\frac{141}{11}\Delta+6\right)(\bar{P}_4/\bar{P}_2)^2),\\
K_3&=\bar{K}(1+\Delta+12\Delta(\bar{P}_4/\bar{P}_2)+\left(\frac{102}{11}\Delta+6\right)(\bar{P}_4/\bar{P}_2)^2),
\end{aligned}\right\} \tag{2}$$

with

$$\Delta=\frac{2}{7}\frac{Q^2-1}{Q^2+2} \tag{3}$$

and

$$\left.\begin{aligned}\bar{K}&=\tfrac{1}{3}R_A Q^{-2/3}(Q^2+2)(\bar{P}_2)^2,\\ \text{with}\quad R_A&=\left(\frac{1}{3}\right)\int r^2 C_{\text{ref}}(r)\,d\mathbf{r}\end{aligned}\right\} \tag{4}$$

where $Q=L/D$ is the molecular axial ratio and $\bar{P}_2$, $\bar{P}_4$ are the orientational order parameters; the first one is the Maier–Saupe order parameter S.

It should be noted that the general structure of equations (2) is practically the same as in the molecular-field approximation [2, 3] (since in both cases the expansion in terms of the orientational order parameters had been performed). On the other hand the dependence of the coefficients on the molecular parameters is essentially different.

In equation (4), the parameter R_A, which is determined by the direct correlation function of the reference fluid of spherical particles, influences only the absolute value of the average elastic constant $\bar{K}$. At the same time the ratios of the elasticity coefficients depend only on the molecular axial ratio Q and on the order parameters $\bar{P}_2$ and $\bar{P}_4$. Thus it is possible to perform a direct comparison between the results of this theory and of computer simulations [16] by calculating the ratios of the elasticity coefficients and taking the values of the order parameters from simulations. This comparison is performed in the following section.

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3. Comparison between theory and simulations

In the table we present the values of the ratios K_3/K_2 and K_1/K_2 calculated with the help of equations (2) and the corresponding results of the computer simulations taken from [16]. For comparison, we also present the results of two other mean-field-like theories which are discussed in more detail in [16], where they are denoted as 'direct integration' and 'perturbation' (see table 1 of [16]). The ratios of elasticity coefficients have been calculated for several axial ratios Q which correspond to rod-like and disc-like particles and also for different values of the orientational order parameters. The values of $\bar{P}_4$ and $\bar{P}_2$ are taken also from simulation and correspond to different densities ρ^*. Part of these data are also presented in graphical form in figure 1 and figure 2 for prolate and oblate ellipsoids, respectively.

One can see from the table and the figures that for realistic values of the axial ratio $Q=5$ (prolate ellipsoids) and $Q=0{\cdot}2$ (oblate ellipsoids), and for high densities which correspond to those of thermotropic nematics, there is a good agreement between the results of computer simulations and the present theory, both for rod-like and disc-like particles. At the same time, the results of the two 'mean-field' theories are not very close to the simulation results. By contrast, at lower densities the results of the computer simulations follow the predictions of the 'mean-field' theories, while the approximation of perfect local orienational order appears to be inadequate.

This behaviour can be understood if we take into account that at lower densities the present system mimics, in fact, a lyotropic liquid crystal with relatively high free volume per particle. In such systems, one can hardly expect a perfect orientational order even

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Ratios of the Frank elasticity coefficients. Comparison of data inferred from simulations [16] with results obtained subject to the approximation of perfect local order (equation (2)), and with values based on perturbation and direct integration methods [16].

				Perfect local order		Computer simulation		Perturbation		Direct integration	
Q	ρ^*	P_2	P_4/P_2	K_1/K_2	K_3/K_2	K_1/K_2	K_3/K_2	K_1/K_2	K_3/K_2	K_1/K_2	K_3/K_2
5	0·370	0·28	0·214	2·38	5·04	1	2				
	0·407	0·73	0·507	2·30	6·10	1·30	3·41	1·62	4·46	1·83	5·17
	0·444	0·82	0·634	2·32	5·88	1·30	3·16	1·44	5·83	1·71	7·24
	0·481	0·87	0·713	2·33	5·71	2·54	5·97	1·24	6·44	1·52	8·55
10	0·222	0·6	0·367	2·77	7·78	1·67	2·19				
	0·259	0·8	0·613	2·78	7·65	1·41	5·38	1·63	8·06	2·77	12·70
	0·370	0·93	0·86	2·79	6·81	1·49	2·44	0·83	12·3		
0·2	0·370	0·7	0·471	0·84	0·37	0·84	0·36				
	0·407	0·78	0·551	0·84	0·37	0·94	0·23	0·51	0·24	0·50	0·21
	0·444	0·85	0·67	0·83	0·38	0·88	0·20	0·55	0·20	0·54	0·15
	0·481	0·88	0·761	0·82	0·40	0·73	0·32	0·57	0·17	0·56	0·12
0·1	0·222	0·74	0·527	0·83	0·35	0·60	0·26				
	0·259	0·83	0·663	0·83	0·36	0·70	0·15	0·52	0·20	0·54	0·15
	0·370	0·94	0·862	0·81	0·39	0·87	0·17	0·58	0·13	0·58	0·06

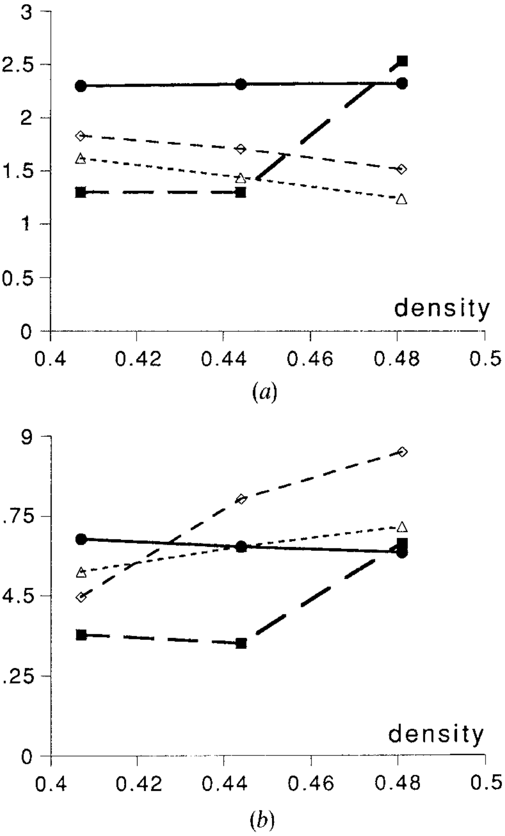

Figure 1. Comparison between the results of the theory [11] and of the computer simulations [16] for the ratios K_1/K_2 (*a*) and K_3/K_2 (*b*) of the elasticity coefficients for rod-like molecules; (●) theory, based on the approximation of perfect local orientational order [11]; (■) computer simulations [16]; (◇) and (△) 'mean field' theories discussed in [16].

within a group of neighbouring molecules. At the same time, the 'mean-field' theories, discussed in detail in [16], should work well in this limit. Indeed, the difference between the two theories, which use the perturbation method and the direct integration, respectively, is not very great [16]. In the first theory, the one-particle distribution function is expanded in terms of the orientational order parameters, while in the second theory, the correlation function is directly integrated using the general expressions for the elasticity coefficients [5]. In both cases, however, the orientational correlations are taken into account within the lowest order approximation (which corresponds to the first Mayer graph in the expansion of the direct correlation function). This approximation is similar to the Onsager model (except for the density dependence) and is known to give good results when the volume fraction of particles in not too large.

Note that at higher densities there is a 'change of tendency' in the behaviour of the results of computer simulations. Indeed, the ratios K_3/K_2 and K_1/K_2 deviate from the results of the 'mean-field' theories and grow rapidly in the direction of the values obtained in the approximation of perfect local order. We can interpret this fact as an onset of strong short-range orientational correlations which become very important at high densities (and high values of the nematic order parameter). It is also interesting to

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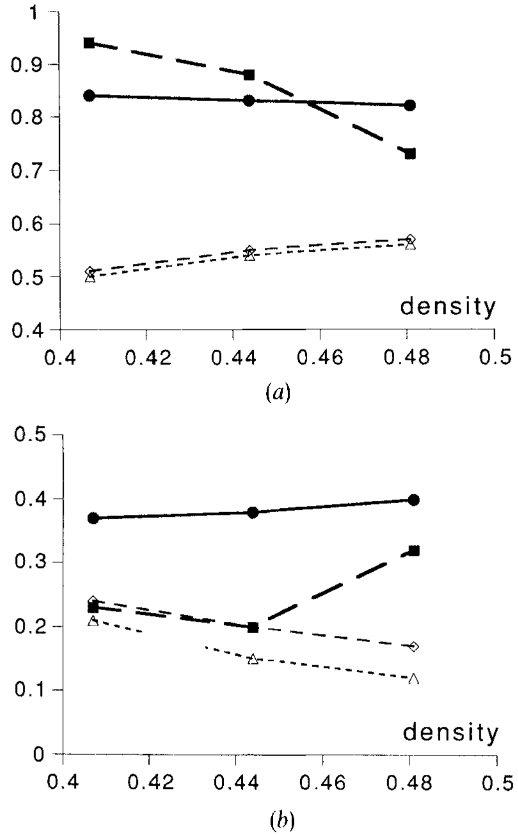

Figure 2. Comparison between the results of the theory [11] and of the computer simulations [16] for the ratios K_1/K_2 (*a*) and K_3/K_2 (*b*) of the elasticity coefficients for disc-like molecules; (●) theory, based on the approximation of perfect local orientational order [11]; (■) computer simulations [16]; (◇) and (△) 'mean field' theories discussed in [16].

note that the agreement between the theory and the computer simulations is better for disc-like particles. This fact is also not in contradiction with simple intuition, since two neighbouring 'discs' should have a stronger tendency to be parallel in comparison with two rods at the same density.

4. Conclusions

As shown in the previous section, the ratios of the elasticity coefficients calculated with the help of the very simple equations (2) appear to be in reasonable agreement with computer simulations for realistic densities and molecular axial ratios. This indicates that a strong short-range orientational order is indeed present in such systems. On the other hand, the role of short-range orientational correlations is obviously overestimated in this simple model and a more realistic theory should be based on a weaker approximation for the direct correlation function. It should be noted also that there are at least two additional factors which can be important in real liquid crystals and which have not been taken into account in the simple theory presented in [11].

Firstly, the approximation (1) for the direct correlation function can be reasonable only at short intermolecular distances. At large separations the molecules are no longer parallel and the long-range 'tail' of the correlation function must be taken into account separately. The most simple possibility is to write the direct correlation function as a sum of two terms:

$$C_2(1,2)=C_{2s}(1,2)-V_{lr}(1,2)/kT,$$

where $C_{2s}(1,2)$ is the short range part of the correlation function, which can be approximated by equation (1), and $V_{ir}(1,2)$ is the long-range part of the intermolecular interaction potential. This long-range part of $C_2(1,2)$ should make an additional contribution to the elasticity coefficients of nematics.

Secondly, one can readily find the specific intermolecular interactions in real nematics which are not described within the ellipsoidal model. For example, side by side interactions between elongated molecules can be important since they are responsible for short-range smectic correlations. These forces should be taken into account in particular when the temperature range of the nematic phase is small due to a strong tendency to form smectic phases.

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