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The elastic constants of nematics

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It is pointed out that some often cited molecular statistical calculations of the elastic constants of nematics are based on a postulated instead of a derived expression for the distortion free energy density. In particular attention is paid to the contradictory results of Priest and Poniewierski and Stecki for hard rod systems. The appropriate way to calculate the elastic constants of hard rod models from first principles is discussed briefly.

The purpose of this paper is two-fold. First we discuss briefly a hardly noted fundamental problem inherent in the commonly adopted approach of formulating a molecular–statistical theory of the Frank elastic constants of nematic liquid crystals. Secondly, we give a short presentation of the elements of a theory that was recently proposed in order to solve that problem.

The first approach to derive the expressions for the Frank elastic constants in terms of the relevant molecular–statistical quantities was given by Priest [1]. He took into account the effect of the distortion on both the internal energy, as previously done by Nehring and Saupe [2], and the entropy of the system. A famous result of his theory is the derivation of the following expressions for the elastic constants of a system consisting of hard spherocylinders using the Onsager approximation:

$$\left.\begin{aligned} \frac{K_1}{K} &= 1 + \Delta - 3\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle} + \dots, \qquad \frac{K_2}{K} = 1 - 2\Delta - \Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle} + \dots, \\ \frac{K_3}{K} &= 1 + \Delta + 4\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle} + \dots, \end{aligned}\right\} \tag{1}$$

where K_1, K_2 and K_3 are, respectively, the elastic constants for splay, twist and bend, $K = \frac{1}{3}(K_1 + K_2 + K_3)$, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are the expectation values of the second and fourth Legendre polynomials, respectively, and the quantities Δ and Δ' depend on the ratio $R = D/L$ of the capped spherocylinders with width D and length $D + L$, and are given by

$$\Delta = \frac{2(1 - R^2)}{7 + 20R^2}, \qquad \Delta' = \frac{27(1 - \frac{8}{3}R^2)}{16(7 + 20R^2)}. \tag{2}$$

A second approach was formulated by Poniewierski and Stecki [3] by considering the free energy of the distorted nematic liquid crystal as a functional of the single-particle distribution function. These authors also calculated the Frank elastic constants

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of a system consisting of hard spherocylinders in the Onsager approximation and obtained different expressions for the quantities Δ and Δ′:

$$\Delta = \frac{2 - 3R^2}{7(1 + 3R^2)}, \qquad \Delta' = \frac{54(\frac{1}{16} - \frac{1}{6}R^2)}{7(1 + 3R^2)}. \tag{3}$$

Both approaches have in common that their starting point is a *postulated* distortion free energy density. This means that these approaches are far from a true molecular–statistical theory, as the purpose of a molecular–statistical theory must be, by definition, the derivation of the distortion free energy density. Therefore, the fundamental problem arises concerning the truth of the postulated distortion free energy densities. The need for a derivation of the distortion free energy density from first principles can be felt even more strongly when one considers the difference between the results of Priest and those of Poniewierski and Stecki, assuming that both calculations have been carried out correctly. In that case an alarming situation arises, as the difference points out that the proposed free energy densities for the distorted state are unequal, violating the physical requirement that this quantity must be unique. Although Poniewierski and Stecki themselves did note the difference between their result and that of Priest, they did not pay any serious attention to this discrepancy because of found numerical insignificance. Thus, they completely overlooked the fundamental problem raised by their result. In order to stress the difference between both results, we consider a system of infinitely long spherocylinders, i.e. $R = 0$, in the limit of perfect nematic order, i.e. $\langle P_2 \rangle \approx 1$ and $\langle P_4 \rangle \approx 1$. Undoubtedly the validity of this extrapolation may be questioned because of the violation of the assumption underlying the derivation of equations (2) and (3) that the order parameters $\langle P_n \rangle$ decrease with increasing n. However, the validity itself is not the point. The meaning of the extrapolation is to show clearly the difference between both results, while they must be equal as they deal with the same physical system. According to Priest the splay constant is given by $K_1 = \frac{9}{16}K$, whereas the approach of Poniewierski and Stecki gives $K = -\frac{9}{56}K$. Thus, the result of Priest is still acceptable, although probably not correct, whereas the result of Poniewierski and Stecki is physically absurd, as it states that the state is unstable.

Apart from the fundamental problem concerning the justification of the proposed distortion free energy density, the commonly adopted approaches [1–4] give rise to a problem concerning the understanding of the calculation of the elastic constants of hard core systems as pointed out by the following consideration. The elastic constants are related to the derivatives of the intermolecular interaction. It is clear that these derivatives show a singular behaviour in the case of hard core potentials. The problem is now that the approaches mentioned do not give any information on the appearance of these singularities or on the way in which they are removed.

In order to solve these problems a true molecular–statistical theory [5] has been proposed. The starting point of this theory is the unperturbed nematic equilibrium state of the system. Without loss of generality, the uniaxial axis of this state may be taken along the space-fixed z axis. This symmetry breaking can be brought about by applying a magnetic field along that direction and then letting the field strength go to zero. The next step is to apply a small distortion. This can be done by applying an additional but small space-dependent magnetic field. The result is equivalent to the application of a position-dependent rotation of the molecules in the original non-distorted state. It suffices to apply a small rotation by $\theta(\mathbf{r})$ about the space-fixed

y axis because of the uniaxiality of the nematic state. The elements of the second-rank orientational tensor $\mathbf{Q}^{\mathrm{P}}$, describing the orientation of a molecule in the distorted state, are now related to those of the original orientational tensor $\mathbf{Q}$ in the following way

$$Q^{\mathrm{P}}_{\alpha\beta} = R_{\alpha\gamma}(\theta)\, R_{\beta\delta}(\theta)\, Q_{\gamma\delta}, \tag{4}$$

where the Greek indices denote x, y and z, summation over repeated Greek indices is implied and the transformation matrix $R(\theta)$ is given by

$$R(\theta) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix}. \tag{5}$$

Denoting the interaction energy between two molecules 1 and 2 in an unperturbed state by $V_{12} = V(\mathbf{r}_{12}, \mathbf{Q}_1, \mathbf{Q}_2)$, with $\mathbf{r}_{12}$ the intermolecular distance vector, the energy change of this state due to the distortion is

$$\Delta_{12} = V(\mathbf{r}_{12}, \mathbf{Q}^{\mathrm{P}}_1, \mathbf{Q}^{\mathrm{P}}_2) - V(\mathbf{r}_{12}, \mathbf{Q}_1, \mathbf{Q}_2). \tag{6}$$

In order to find the expressions for the elastic constants this expression must be expanded as a Taylor series and only terms of the order $\partial_\nu\theta$, $\partial_\nu\partial_\mu\theta$ and $\partial_\nu\theta\,\partial_\mu\theta$ are kept. The microscopic analogue of the Frank distortion free energy density is then obtained by applying thermodynamic perturbation theory using the distortion $\theta(\mathbf{r})$ as a measure for the magnitude of the perturbation.

The Frank elastic constants are determined by the difference between the free energies of the distorted and unperturbed state. It suffices to approximate that energy difference Δf by

$$\Delta f = \frac{1}{2}\sum_{k,l}\langle\Delta_{kl}\rangle - \frac{1}{8}\beta\left[\left\langle\left(\sum_{k,l}\Delta_{kl}\right)^2\right\rangle - \left\langle\sum_{k,l}\Delta_{kl}\right\rangle^2\right], \tag{7}$$

where $\langle A\rangle$ denotes the average of the quantity A with respect to the unperturbed ensemble. Clearly Frank's elasticity theory goes beyond linear response theory, i.e. the term linear in Δ. The non-linear contribution is sometimes neglected (see, for example [6]). However, this is certainly not justified for a number of models.

In order to calculate the elastic constants of hard core systems, the hard core interaction must be conceived as the limit of a smoothly behaving interaction in view of the discontinuous character of the hard core potential. An example of such a smooth potential is

$$V(\mathbf{r}_{12}, \mathbf{Q}_1, \mathbf{Q}_2) = A\left[\frac{1}{2} - \frac{1}{\pi}\arctan\left(\frac{|\mathbf{r}_{12}| - D_{12}}{\varepsilon}\right)\right], \tag{8}$$

where $\mathbf{r}_{12} = |\mathbf{r}_{12}|\mathbf{u}_{12}$ and the function $D_{12} = D(\mathbf{u}_{12}, \mathbf{Q}_1, \mathbf{Q}_2)$ is the closest distance of approach of molecules 1 and 2. This potential leads to a discontinuity in the limit $\varepsilon \to 0$, where the interaction behaves as a step function with height A. The hard core model is obtained by taking first the limit $\varepsilon \to 0$ and then the limit $A \to \infty$. Only in this way can the appearing singularities and their consequences be analysed properly. It appears that the contribution to the elastic constants due to linear response theory diverges in the hard core limit. Finite values for the elastic constants are obtained as this divergence is cancelled by a similar term of the non-linear contribution to the distortion free energy. Thus, the non-linear contribution plays a crucial part in the calculation of the elastic constants of hard core systems. The results for the Onsager hard rod model can be obtained by finding the appropriate form of D_{12}. This seems, however, of little physical interest in view of the fact that (*a*) the elastic constants of that model increase with temperature, whereas they decrease experimentally, and (*b*) the validity of the Onsager approach gets lost in the ordered state [7].

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