

Statistical theory of the Frank elastic constants

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We show that with some weak assumptions molecular expressions for Frank elastic constants of nematics, containing the direct correlation function, are equivalent to such expressions obtained from the theory of hydrodynamic fluctuations.

In one of our previous papers¹ we derived microscopic expressions for the Frank elastic constants of nematic liquid crystals, containing the Ornstein-Zernike direct correlation function $c(1,2)$. The expressions were derived by expanding the functional of the total free energy of the system in gradients of the one-particle distribution function $\rho_1(1)$. There also exist other microscopic expressions,^{2,3} directly related to autocorrelation functions and are obtained by considering the hydrodynamic fluctuations of the local symmetry axis of the nematic phase. These expressions naturally contain the function $U_2(1,2) \equiv \rho_2(1,2) - \rho_1(1)\rho_1(2)$, where $\rho_2(1,2)$ is the two-particle distribution function.

In this paper we prove that, with some assumptions, these two approaches, and the final expressions for the Frank constants, are equivalent. The problem in its formal aspects is similar to that appearing in the statistical theory of the surface tension.⁴

Let us follow first the theory of the hydrodynamic fluctuations. The fluctuations of the local symmetry axis are described by the following elements of the susceptibility matrix (see, e.g., Ref. 3),

$$\chi_{n_i n_j}(\vec{r} - \vec{r}') \equiv \beta \langle n_i(\vec{r}') n_j(\vec{r}') \rangle \quad (i, j = 1, 2) \quad (1)$$

where

$$n_i(\vec{r}) \equiv (\delta_{ik} - n_i^0 n_k^0) R_{kl}(\vec{r}) n_l^0 / \rho S, \\ R_{ij}(\vec{r}) \equiv \sum_{\alpha} (\Omega_i^{\alpha} \Omega_j^{\alpha} - \frac{1}{3} \delta_{ij}) \delta(\vec{r} - \vec{r}^{\alpha}),$$

$\beta \equiv 1/k_B T$, S stands for the order parameter, ρ the number density, and $\vec{\Omega}^{\alpha}$ for the unit vector along the long axis of the α th molecule whose center of mass position is \vec{r}^{α} . $\langle \rangle$ indicates an equilibrium average and we use the grand canonical ensemble.

The average of $R_{ij}(\vec{r})$ in an undistorted but oriented nematic, is given by

$$\langle R_{ij}(\vec{r}) \rangle = \rho S (n_i^0 n_j^0 - \frac{1}{3} \delta_{ij}), \quad (2)$$

where \vec{n}^0 is the unit vector in the preferred direction. It follows from (2) and the definition of $n_i(\vec{r})$ that $\langle n_i(\vec{r}) \rangle = 0$. If \vec{n}^0 is parallel to the three-axis one can write

$$n_i(\vec{r}) = R_{i3}(\vec{r}) / \rho S \quad (i = 1, 2). \quad (3)$$

In the absence of a magnetic field one finds the following expressions for the Fourier transforms of $\chi_{n_1 n_1}$ and $\chi_{n_2 n_2}$ (Refs. 3 and 5):

$$\chi_{n_1 n_1}(\vec{k}) = \int e^{-i\vec{k}(\vec{r} - \vec{r}')} \chi_{n_1 n_1}(\vec{r} - \vec{r}') d(\vec{r} - \vec{r}') \\ = (K_1 k_1^2 + K_3 k_3^2)^{-1}, \quad (4a)$$

$$\chi_{n_2 n_2}(\vec{k}) = (K_2 k_1^2 + K_3 k_3^2)^{-1}, \quad (4b)$$

with K_1 , K_2 , and K_3 denoting the Frank constants. The vector \vec{k} is assumed to lie in the 1-3 plane. The Frank constants are given by the sum rules. For example,

$$1/K_1 = \lim_{k_1 \rightarrow 0} \lim_{k_3 \rightarrow 0} k_1^2 \chi_{n_1 n_1}(\vec{k}). \quad (5)$$

A calculation of the average in (1) leads immediately to the microscopic expressions for the susceptibilities and, hence the Frank constants, containing the function $U_2(1,2)$. Before we write them down let us notice first that all pair correlation functions in the uniform nematic of linear rigid molecules have the form

$$X(1,2) = X(\vec{r}^2 - \vec{r}^1, \vec{\Omega}^1, \vec{\Omega}^2). \quad (6)$$

In the following we shall write $X(1,2) = X(\vec{r}^2 - \vec{r}^1)$, where $X(\vec{r})$ is understood to be an operator acting on functions of $\vec{\Omega}$, and defined by

$$X(\vec{r})|\psi\rangle\langle\vec{\Omega})\equiv\int X(\vec{r},\vec{\Omega},\vec{\Omega}')\psi(\vec{\Omega}')d\vec{\Omega}' . \quad (7)$$

Now, we find from (1), (4a), and (4b) that

$$\chi_{n_i n_i}(\vec{r}-\vec{r}')=\frac{\beta}{(\rho S)^2}\langle\Omega_i\Omega_3|\mathcal{G}(\vec{r}-\vec{r}')|\Omega_i\Omega_3\rangle . \quad (8a)$$

$$1/K_i=\frac{\beta}{(\rho S)^2}\lim_{k_1\rightarrow 0}\lim_{k_3\rightarrow 0}k_1^2\langle\Omega_i\Omega_3|U_2(\vec{k})|\Omega_i\Omega_3\rangle , \quad (8b)$$

[$i=1,2$ and the summation convention is not used in (8a) and (8b)],

$$1/K_3=\frac{\beta}{(\rho S)^2}\lim_{k_3\rightarrow 0}\lim_{k_1\rightarrow 0}k_3^2\langle\Omega_1\Omega_3|U_2(\vec{k})|\Omega_1\Omega_3\rangle , \quad (8c)$$

where $\mathcal{G}(\vec{r}^2-\vec{r}^1)=\mathcal{G}(1,2)\equiv U_2(1,2)+\rho_1(1)\delta(1,2)$, and $U_2(\vec{k})$ is the Fourier transform of $U_2(\vec{r}^2-\vec{r}^1)=U_2(1,2)$.

The expressions for the Frank constants¹ in terms of the direct correlation function $c(1,2)=c(\vec{r}^2-\vec{r}^1)$ are as follows:

$$K_1'=\frac{1}{2\beta}\int\langle L_2\rho_1|c(\vec{r})|L_2\rho_1\rangle x^2 d\vec{r} , \quad (9a)$$

$$K_2'=\frac{1}{2\beta}\int\langle L_1\rho_1|c(\vec{r})|L_1\rho_1\rangle x^2 d\vec{r} , \quad (9b)$$

$$K_3'=\frac{1}{2\beta}\int\langle L_2\rho_1|c(\vec{r})|L_2\rho_1\rangle z^2 d\vec{r} , \quad (9c)$$

where

$$L_1=i(\sin\varphi\partial/\partial\theta+\cot\theta\cos\varphi\partial/\partial\varphi) ,$$

$$L_2=i\left[-\cos\varphi\frac{\partial}{\partial\theta}+\cot\theta\sin\varphi\partial/\partial\varphi\right] ,$$

and $L_3=-i\partial/\partial\varphi$ are components of the angular momentum operator \vec{L} . It turns out that with some weak assumptions $K_i=K_i'$ ($i=1,2,3$). Nematics are usually diamagnetic. Since the influence of the magnetic field on intermolecular interaction is very small it is reasonable to neglect it. If we do so we can write the following relation

$$\vec{L}|\rho_1\rangle=-\beta\int\mathcal{G}(\vec{r})|\vec{L}V_{\text{ext}}\rangle d\vec{r} , \quad (10)$$

where V_{ext} is the external potential due to the uniform magnetic field \vec{H} . The relation¹⁰ is analogous to that derived by Lovett⁶ and connecting $\vec{V}_{\vec{r}}\rho_1$ with $\vec{V}_{\vec{r}}V_{\text{ext}}$. In our case of diamagnetic molecules we have

$$V_{\text{ext}}=-\frac{1}{2}(A_{\parallel}-A_{\perp})(\vec{H}\cdot\vec{\Omega})^2-\frac{1}{2}A_{\perp}\vec{H}^2 , \quad (11)$$

with A_{\parallel} and A_{\perp} referring to the longitudinal and transversal magnetic polarizability of one molecule.

Now we proceed to show that $K_1=K_1'$. Let us notice first that we can write another expression for K_1 . Namely, in the presence of the uniform magnetic field \vec{H} , parallel to \vec{n}^0 , we have^{3,5}

$$\chi_{n_1 n_1}(\vec{k})=(K_1 k_1^2+K_3 k_3^2+\chi_a H^2)^{-1} , \quad (12)$$

with $\chi_a\equiv\chi_{\parallel}-\chi_{\perp}$ standing for the anisotropic part of the magnetic susceptibility. Hence, from (8a), (11), and (12)

$$\begin{aligned} K_1 &= -\frac{1}{2}\chi_a^2\lim_{H\rightarrow 0}H^4\frac{\partial^2}{\partial k_1^2}\chi_{n_1 n_1}(\vec{k})\Bigg|_{\vec{k}=0} \\ &= \frac{1}{2}\beta\left[\frac{\chi_a}{\rho S A_a}\right]^2\lim_{H\rightarrow 0} \\ &\quad \times\int\langle L_2 V_{\text{ext}}|\mathcal{G}(\vec{r})|L_2 V_{\text{ext}}\rangle x^2 d\vec{r} , \quad (13) \end{aligned}$$

where $A_a\equiv A_{\parallel}-A_{\perp}$. As far as the magnetic couplings between molecules are assumed to be small it can be written⁵

$$\chi_a=\rho S A_a . \quad (14)$$

To transform the integral appearing in (13) we use the identity

$$\begin{aligned} \mathcal{G}(\vec{r}) &= \int\mathcal{G}(\vec{r}'')\mathcal{G}^{-1}(\vec{r}'-\vec{r}'') \\ &\quad \times\mathcal{G}(\vec{r}-\vec{r}')d\vec{r}'d\vec{r}'' , \quad (15) \end{aligned}$$

where the inverse of $\mathcal{G}(\vec{r})$ is related to the direct correlation function as follows⁷:

$$\mathcal{G}^{-1}(\vec{r})=\delta(\vec{r})/\rho_1-c(\vec{r}) . \quad (16)$$

From (15) and from the fact that $\int x^2\delta(\vec{r})d\vec{r}=0$ we obtain

$$\int \langle L_2 V_{\text{ext}} | \mathcal{G}(\vec{r}) | L_2 V_{\text{ext}} \rangle x^2 d\vec{r} = - \int \langle V_{\text{ext}} | \mathcal{G}(\vec{r}') \mathcal{G}^{-1}(\vec{r}) \mathcal{G}(\vec{r}'') | L_2 V_{\text{ext}} \rangle \times x^2 d\vec{r} d\vec{r}' d\vec{r}'' . \quad (17)$$

Finally, from (10), (13), (14), (16), and (17) we find that

$$K_1 = \frac{-1}{2\beta} \int \langle L_2 \rho_1 | \mathcal{G}^{-1}(\vec{r}) | L_2 \rho_1 \rangle x^2 d\vec{r} = K'_1 .$$

Of course, we prove in the same manner that $K_2 = K'_2$ and $K_3 = K'_3$.

The expressions (9a)–(9c) seem more useful for

a calculation of elastic constants than expressions (8b)–(8c). It follows from the fact that the function $c(\vec{r})$ is believed to be a short-range function. Thus, it is easier to find some approximation for $c(\vec{r})$ than for $U_2(\vec{r})$, the Fourier transform of which must have the $1/k^2$ singularity to give elastic constants of finite values.

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