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Frank Elastic Constants of the Hard-Rod Liquid Crystal

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The elastic constants of a hard-rod liquid crystal are calculated using the Onsager theory, with results similar to those given by Priest.

A suspension of long hard rods will form a liquid crystal at sufficiently high concentrations. A theory of this phase transition based on the Mayer cluster expansion has been given by Onsager.[1] In its simplest form, the theory is a version of molecular-field theory, which can be shown[2] to be quantitatively accurate for extremely long rods ($L/D > 100$) and qualitatively accurate for $L/D \gtrsim 10$. Even though the more commonly studied liquid crystals do not meet these prerequisites, it is still an important program to calculate as many of the physical properties of the long-rod liquid crystal as possible.

Priest[3] has recently calculated the curvature elastic constants for such a system. In this paper, that result will be derived in a different way which avoids spherical-harmonic expansions. The starting point are the assertions (i) that the response of the liquid crystal to a weak-ordering field which varies slowly in space is just that the preferred orientation aligns everywhere along that field; (ii) that the relative probability of a molecule at r having orientation $\hat{m}$ is $f(\hat{m}\cdot\hat{n}(\vec{r}))$, where $\hat{n}(\vec{r})$ is the local preferred orientation and f is the same distribution function which Onsager finds for the case that $\hat{n}$ is independent of position; and (iii) the extra free energy due this variation of $\hat{n}(\vec{r})$ can be calculated as

$$\Delta F=\tfrac{1}{2}kT\rho^2\iint f(\hat{l}\cdot\hat{n}(\vec{r}))\,\delta(\vec{r},\hat{l};\vec{s},\hat{m})\times[f(\hat{m}\cdot\hat{n}(\vec{s}))-f(\hat{m}\cdot\hat{n}(\vec{r}))]\,d\vec{r}\,d\vec{s}\,d\hat{m}\,d\hat{l}, \tag{1}$$

where $\delta(\vec{r},\hat{l};\vec{s},\hat{m})$ is the contact function, which is unity if a particle at $\vec{r}$ with orientation $\hat{l}$ would intersect a particle at $\vec{s}$ with orientation $\hat{m}$, and vanishes otherwise. These assertions can be established for a generalization of the Onsager expansion by recourse to the arguments that Priest gives. Equation (1) is essentially the same as Priest's equation (28).

We will now evaluate Eq. (1) to second order in the derivatives of $\hat{n}$. The slow spatial variation of $\hat{n}(\vec{r})$ allows us to write

$$f(\hat{m}\cdot\hat{n}(\vec{s}))-f(\hat{m}\cdot\hat{n}(\vec{r}))=f'(\hat{m}\cdot\hat{n}(\vec{r}))\{(\vec{\xi}\cdot\vec{\nabla}_r)[\hat{n}(\vec{r})\cdot\hat{m}]+\tfrac{1}{2}(\xi\cdot\vec{\nabla}_r)^2[\hat{n}(\vec{r})\cdot\hat{m}]\}+\tfrac{1}{2}f''(\hat{m}\cdot\hat{n}(\vec{r}))\{(\vec{\xi}\cdot\vec{\nabla}_r)[\hat{n}(\vec{r})\cdot\hat{m}]\}^2+\cdots, \tag{2}$$

where $\vec{\xi}=\vec{s}-\vec{r}$ and f' and f'' represent first and second derivatives of the distribution function with respect to its argument. Replacing the term in the square brackets in Eq. (1) by Eq. (2) results in the following:

$$\begin{aligned}\frac{\Delta F}{kT}=&\tfrac{1}{2}\rho^2\int f(\hat{l}\cdot\hat{n}(\vec{r}))\,\delta(\vec{\xi};\hat{l},\hat{m})f'(\hat{m}\cdot\hat{n}(\vec{r}))\times\{(\vec{\xi}\cdot\vec{\nabla}_r)[\hat{n}(\vec{r})\cdot\hat{m}]\}\,d\vec{\xi}\,d\vec{r}\,d\hat{l}\,d\hat{m}\\&-\tfrac{1}{2}\rho^2\int[(\vec{\xi}\cdot\vec{\nabla}_r)(\hat{n}(\vec{r})\cdot\hat{l})f'(\hat{l}\cdot\hat{n}(\vec{r}))\times\delta(\vec{\xi};\hat{l},\hat{m})f'(\hat{m}\cdot\hat{n}(\vec{r}))\times[(\xi\cdot\vec{\nabla}_r)(\hat{n}(\vec{r})\cdot\hat{m})]\,d\vec{\xi}\,d\vec{r}\,d\hat{l}\,d\hat{m},\end{aligned} \tag{3}$$

where an integration by parts has been used to combine the second-order terms.

We may now proceed to do the integrals over $\vec{\xi}$. If the first term of Eq. (3) fails to vanish, then the liquid crystal must be a "cholesteric" with a finite twist in the equilibrium state. The first term of Eq. (3) will automatically vanish if $\delta(\vec{\xi})$ is an even function of $\vec{\xi}$; this corresponds to the case of nematic liquid crystals. Further discussion will be restricted to this latter case.

We introduce the representation

$$\vec{\xi}=x\hat{l}+y\hat{m}+z(\hat{l}\times\hat{m})\,|\,\hat{l}\times\hat{m}\,|^{-1}. \tag{4}$$

Reference to Fig. 1 shows that two rods will always overlap if $-\tfrac{1}{2}L < x, y < \tfrac{1}{2}L$ and $-D < z < D$. It is also possible for two rods to overlap with x or y slightly outside the stated interval, but this possibility will be ignored as being a correction of order D/L. Then the domain of integration is a rectangular box in the x, y, z space. Since x, y, z are independent variables,

$$\int \delta(\vec\xi;\hat l,\hat m)(\vec\xi\cdot\vec u)(\vec\xi\cdot\vec v)d\vec\xi$$
$$=\tfrac{1}{8}DL^4|\hat l x \hat m|[(\hat m\cdot\vec u)(\hat m\cdot\vec v)+(\hat n\cdot\vec u)(\hat n\cdot\vec v)]$$
$$+\tfrac{2}{3}L^2D^3|\hat l\times\hat m|^{-1}(\hat l\times\hat m)\cdot\vec u(\hat l\times\hat m)\cdot\vec v \tag{5}$$

for any vectors $\vec u$ and $\vec v$. The last term will be neglected ($D/L \ll 1$). Thus, the integration of Eq. (3) gives

$$\Delta F=-\tfrac{1}{12}\rho^2kTL^4D\int f'(\hat l\cdot\hat n)f'(\hat m\cdot\hat n)|\hat l\times\hat m|$$
$$\times\{[(\hat l\cdot\vec\nabla)(\hat n\cdot\hat l)][(\hat l\cdot\vec\nabla)(\hat n\cdot\hat m)]$$
$$+[(\hat m\cdot\vec\nabla)(\hat n\cdot\hat l)][(\hat m\cdot\vec\nabla)(\hat n\cdot\hat m)]\}d\vec r\,d\hat m\,d\hat n, \tag{6}$$

where the explicit mention of the $\vec r$ dependence of $\hat n$ has been dropped. As desired, this result involves only the gradients of $\hat n$, and is second order in them.

The Frank elastic constants are defined by

$$\Delta F=\frac{1}{2}\int[K_{11}(\vec\nabla\cdot\hat n)^2+K_{22}(\hat n\cdot(\vec\nabla\times\hat n))^2$$
$$+K_{33}(\hat n\times\vec\nabla\times\hat n)^2]d\vec r\,. \tag{7}$$

By considering the three cases of purely one type of distortion, Eq. (6) can be rewritten as an evaluation for K_{11}, K_{22}, and K_{33}; in each case

$$K_{ii}=-\tfrac{1}{6}\rho^2kTL^4D\iint f'(\hat l\cdot\hat x)$$
$$\times f'(\hat m\cdot\hat x)|\hat l\times\hat m|\{i\}d\hat m\,d\hat n, \tag{8}$$

where (i) for $\hat n=\hat x+y\hat y$ (splay),

$$\{1\}=(\hat m\cdot\hat y)(\hat l\cdot\hat y)[(\hat l\cdot\hat y)^2+(\hat m\cdot\hat y)^2]; \tag{9a}$$

(ii) for $\hat n=\hat x+z\hat y$ (twist),

$$\{2\}=(\hat m\cdot\hat y)(\hat l\cdot\hat y)[(\hat l\cdot\hat z)^2+(\hat m\cdot\hat z)^2]; \tag{9b}$$

and (iii) for $\hat n=\hat x+x\hat y$ (bend),

$$\{3\}=(\hat m\cdot\hat y)(\hat l\cdot\hat y)[(\hat l\cdot\hat x)^2+(\hat m\cdot\hat x)^2]. \tag{9c}$$

There remains to evaluate these integrals for various choices of $f(\hat m\cdot\hat x)$. This has been done numerically for the case $f_A(\cos\theta)=\text{const.}$ $\times\exp(A\cos^2\theta)$ with various values of A, and for the choice

$$f_0(\alpha=\cos\theta)=1.483\exp(-6.92+4.58\alpha^2$$
$$+2.07\alpha^4-2.01\alpha^6+2.28\alpha^8), \tag{10}$$

TABLE I. Elastic constants.

Form of f	A	$S=\langle P_2(\theta)\rangle$	K_{11}[a]	K_{22}[a]	K_{33}[a]
f_A	6	0.71	0.063	0.021	0.24
f_A	7	0.76	0.066	0.022	0.30
f_A	8	0.79	0.068	0.023	0.35
f_A	9	0.82	0.066	0.022	0.39
f_A	10	0.84	0.065	0.022	0.44
f_0		0.80	0.062	0.021	0.392

[a] The values quoted are for the dimensionless quantities K_{ii}/ρ^2L^4DkT.

which is an approximate solution to the Onsager integral equation near the phase transition.[4] The results are given in Table I. It might be noted that $K_{22}=\frac{1}{3}K_{11}$, independent of the form of f.

A principal difference between the present approach and that of Priest is that it has not been necessary to introduce a Legendre-function expansion for f. This is important since such expansions are not very rapidly convergent near the phase transition.[5] Another difference is that Priest keeps some terms of higher order in D/L. These are not significant because there are corrections to the molecular-field theory of the same order[2] and because the shape of the ends of the rods can make changes[6] of the order of D/L. In order to translate the present results into a form comparable with Priest's, one factor of ρkT must be replaced by $\frac{1}{2}(4.541)kT_c$. The results are otherwise the same.

It is difficult to apply these results to the more commonly studied liquid crystals (such as MBBA[7]) not just because these are thermotropic (where the theory as presented here is not), but also because D/L is much too large to permit the third virial terms to be ignored. Such application does give order of magnitude agreement, however. The results may be directly applied to a mixture of PBLG and PBDG, which forms a nematic liquid crystal.[8] For this system, $D\sim 25$ Å, and for L/D

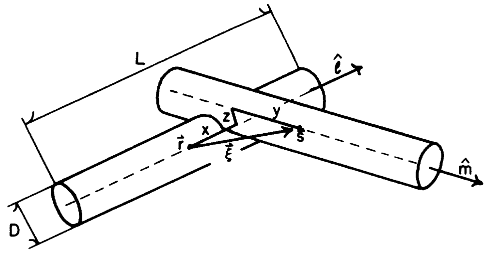

FIG. 1. Geometry of two intersecting rods. The distance $\vec\xi$ between the rods can be expressed as $\vec\xi=x\hat l+y\hat m+z(\hat l\times\hat m)|\hat l\times\hat m|^{-1}$.

~ 50, $\frac{1}{4}\pi D^2 L\rho \sim 0.1$ at the phase transition ($T = 300$ °K). Then using the values from Table I for f_0, $K_{11} = 4.2 \times 10^{-7}$, $K_{22} = 1.4 \times 10^{-7}$, and $K_{33} = 26.0 \times 10^{-7}$ dyn. These values are comparable to those that have been measured in other systems and thus presumably are measurable. Priest's equation (38) for the same system would give $K_{11} = 2.8 \times 10^{-7}$, $K_{22} = 0.9 \times 10^{-7}$, and $K_{33} = 6.7 \times 10^{-7}$ dyn, where the values[4] $\langle P_2 \rangle = 0.796$ and $\langle P_4 \rangle = 0.517$ consistent with f_0 have been used.

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