(c) Finally consider averages of the form

$$\left\langle \sum_{j,l=2,j\neq l} f(L_1,\ L_i,\ L_l)\right\rangle .$$

Exactly the same method that worked in (b) works again here:

$$\left\langle \sum_{j,l=2,j\neq l}^{\nu} f(L_1,\ L_i,\ L_l)\right\rangle = \nu\,!\,\rho^{\nu}\int_0^{\infty} dL_1 \int_0^{L_1} dL_2 \cdots \int_0^{L_{\nu-1}} dL_\nu \times \exp[-(L_1+L_2+\cdots+L_\nu)]\sum f(L_1,\ L_i,\ L_l) \qquad \text{(A8)}$$

Since $\sum f(L_1,\ L_i,\ L_l)$ is a symmetric function of $L_2 \cdots L_\nu$, we have

$$\begin{aligned}\langle \sum f(L_1,\ L_j,\ L_l)\rangle &= \nu\rho^{\nu}\int_0^{\infty} dL_1 \int_0^{L_1} dL_2 \int_0^{L_1} dL_3 \cdots \int_0^{L_1} dL_\nu \exp[-\rho(L_1+L_2+\cdots+L_\nu)]\sum f(L_1,\ L_i,\ L_l)\\ &= \nu(\nu-1)(\nu-2)\rho^3\int_0^{\infty} dL_1\int_0^{L_1} dL_2\int_0^{L_1} dL_3\, f(L_1,\ L_2,\ L_3)\int_0^{L_1} dL_4\cdots dL_\nu \rho^{\nu-3}\\ &\qquad \times\exp[-\rho(L_1+L_2+\cdots+L_\nu)]\\ &= \nu(\nu-1)(\nu-2)\rho^3\int_0^{\infty} dL_1\int_0^{L_1} dL_2\int_0^{L_1} dL_3\, e^{-\rho(L_1+L_2+L_3)}\,(1-e^{-\rho L_1})^{\nu-3} f(L_1,\ L_2,\ L_3)\\ &= \int_0^{\infty} dL_2\int_0^{\infty} dL_3\,\nu(\nu-1)\rho^2 e^{-\rho(L_2+L_3)}\int_{\max(L_2,L_3)}^{\infty} dL_1\, P_{\nu-2}(L_1) f(L_1,\ L_2,\ L_3)\,. \qquad \text{(A9)}\end{aligned}$$

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[1] J. M. Luttinger and H. K. Sy, preceding paper, Phys. Rev. A 7, 701 (1973). Henceforth referred to as I.

[2] The details may be found in the dissertation of one of us (H. K. S.) (Columbia University, New York, 1972) (unpublished).

[3] N. Bogoliubov, Phys. Abh. Sowjetunion 6, 1 (1962); 6, 113 (1962); 6, 229 (1960); H. Wagner, Z. Physik 195, 273 (1966).

[4] P. C. Hohenberg, Phys. Rev. 158, 383 (1967).

[5] N. Bogoliubov, Physica Suppl. 26, 1 (1960).

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Theory of the Frank Elastic Constants of Nematic Liquid Crystals*

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It is shown that the Frank elastic constants may be expressed in terms of even-order Legendre polynomials averaged over the one-molecule orientational distribution function. In particular, it is found that $(K_{11}-\overline{K})/\overline{K}=C-3C'\overline{P}_4/\overline{P}_2+\cdots$, $(K_{22}-\overline{K})/\overline{K}=-2C-C'\overline{P}_4/\overline{P}_2+\cdots$, $(K_{33}-\overline{K})/\overline{K}=C+4C'\overline{P}_4/\overline{P}_2+\cdots$, where $\overline{K}=(1/3)(K_{11}+K_{22}+K_{33})$, C and C' are constants, which depend on the details of the system, and $\overline{P}_m$ is the weighted average of the mth Legendre polynomial. Higher-order terms in these series involve $\overline{P}_6$, etc. The constants C and C' are calculated for the case of rodlike molecules interacting via a hard-core repulsion. The results are in good agreement with experiments on the substance p-azoxyanisole.

I. INTRODUCTION

The Frank elastic constants are a measure of the free energy associated with long-wavelength distortions of the nematic state in which the local preferred direction of molecular orientation varies in space. If the local preferred direction at the point $\vec{r}$ is parallel to the unit vector $\hat{n}(\vec{r})$, the free energy associated with the distortion may be written[1]

$$\Delta F=\tfrac{1}{2}\int d^3r\,[K_{11}(\nabla\cdot\hat{n})^2+K_{22}(\hat{n}\cdot\nabla\times\hat{n})^2+K_{33}(\hat{n}\times\nabla\times\hat{n})^2]\,. \qquad (1)$$

The vector $\hat{n}$ is usually called the director. The distortions corresponding to K_{11}, K_{22}, and K_{33} are called splay, torsion, and bending, respectively. These three types of distortion are illustrated in Fig. 1.

In the mean-field approximation the free energy of the nematic state can be written as a sum of three terms[2]:

$$F=E-TS_t-TS_r\,. \qquad (2)$$

Here E is the internal energy, T is the temperature, S_r is the rotational entropy, and S_t is the translational entropy. The translational entropy includes all the entropy of the system not contained in S_r. For a uniaxial system S_r is given by[2]

$$S_r=-k_BN\int h(\Omega)\ln h(\Omega)\,d\Omega\,. \qquad (3)$$

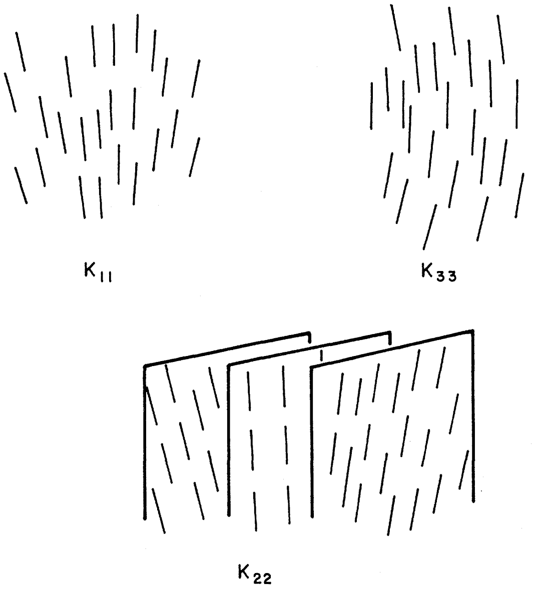

FIG. 1. Splay (K_{11}), torsion (K_{22}), and bending (K_{33}) distortions.

Here k_B is Boltzmann's constant, N is the number of molecules in the system, and $h(\Omega)$ is the one-molecule orientational distribution function. The function $h(\Omega)$ gives the probability that the unique (long) molecular axis has the orientation Ω. It has the form $h(\Omega)=h(\theta)$, where θ is the angle between the unique axis of the molecule and the local preferred direction. The entropy S_r is just an entropy of mixing.

With any distortion we may associate a wave number q. The increase in the free energy due to a long-wavelength distortion will be proportional to q^2, because the symmetry of the system ensures that distortions corresponding to q and $-q$ are equivalent. It is clear that any change in $h(\Omega)$, apart from a rotation of the preferred direction, due to a distortion, will also be of order q^2. Since the thermodynamically stable state $[\hat{n}(\vec{r})=\hat{z}]$ is stationary with respect to variation of the form of $h(\theta)$, there will be no contribution of order q^2 to the increase in the free energy from changes in the form of $h(\theta)$ caused by the distortion. Thus, to order q^2, the increase in the free energy due to a distortion may be calculated by keeping $h(\Omega)$ constant apart from rotations of the local preferred direction. In such a calculation, it is clear that the rotational entropy S_r, may be neglected.

The form of E and of $-TS_t$ may be deduced by considerations of symmetry; for example, the intermolecular interaction may be written

$$V_{12}(\Omega_1,\Omega_2,\vec{r}_{12})=\sum_{j'j''j} f_{j'j''j}(|r_{12}|)$$

$$\times\sum_{mM}(-1)^M C(j'j''j;m,M-m)$$

$$\times Y_{j',m}(\Omega_1)Y_{j'',M-m}(\Omega_2)Y_{j,-M}(\hat{r}_{12})\;. \tag{4}$$

Here $\vec{r}_{12}$ is the vector joining the centers of mass of molecules 1 and 2. The molecules are assumed to have uniaxial symmetry. The quantity $\hat{r}_{12}$ is the unit vector corresponding to $\vec{r}_{12}$. The symmetry of the system is such that $f_{j'j''j}$ is zero if j', j'', or j is odd. Also $f_{j'j''j}=f_{j''j'j}$. The anisotropic dispersion force used by Maier and Saupe[3] has only f_{220}, f_{222}, and f_{224} nonzero with

$$f_{220}:f_{222}:f_{224}::1:\sqrt{\tfrac{2}{7}}:6\sqrt{\tfrac{2}{7}}\;. \tag{5}$$

The anisotropic two-body center-of-mass (c.m.) distribution function may be similarly constructed:

$$\rho^2=\sum_{k'k''k}\rho_{k'k''k}(|r_{12}|)\sum_{Mm}(-1)^M C(k'k''k;m,M-m)$$

$$\times Y_{k',m}(\Omega_1)Y_{k'',M-m}(\Omega_2)Y_{k,-M}(\hat{r}_{12})\;. \tag{6}$$

The function ρ^2 gives the conditional probability that there will be a molecule at $\vec{r}_{12}$ with orientation Ω_2 if there is one at the origin with orientation Ω_1. The function $\rho_{k'k''k}$ has the same symmetries as does $f_{j'j''j}$. A similar expression can be written for S_t.

In Sec. II the increase in the free energy of the nematic state will be calculated for three specific distortions and the result compared with that of Eq. (1) to obtain the three elastic constants. To keep the notation simple, only the internal energy will be considered. The formal features of the result are not affected by inclusion of the translational entropy.

In Sec. III a calculation based on a specific form of the translational entropy, called the steric model, is presented. The only parameter in the results for the elastic constants is the length-to-breadth ratio of the molecule.

II. GENERAL FORM OF THE ELASTIC CONSTANTS

The internal energy of the nematic state in the mean-field approximation is

$$E=\frac{1}{2}\frac{1}{v_0}\int\!\!\int d^3R\,d^3u\,\langle V_{12}(\Omega_1,\Omega_2,\vec{u})\rho^2(\Omega_1,\Omega_2,\vec{u})\rangle_{\rm av}\;. \tag{7}$$

Here v_0 is the volume per molecule in the liquid. The angular brackets indicate a thermodynamic average with weight h. This expression assumes that the c.m. distribution of the liquid responds instaneously to changes in the orientation of the molecules. This is a reasonable assumption because the c.m. distribution is determined by the collision rate, which is fast compared with any orientation time. On substitution of Eqs. (4) and (6) we have

$$E=\frac{1}{2}\int d^3R(1/v_0)\int d^3u \sum_{j'j''j} f_{j'j''j}(|u|)$$
$$\times \sum_{k'k''k} \rho_{k'k''k}(|u|) \sum_{mMpQ} (-1)^{M+Q} C(j'j''j; m, M-m)$$
$$\times C(k'k''k; p, Q-p) \langle Y_{j',m}(\Omega_R) Y_{k',p}(\Omega_R)\rangle_{\text{av}}$$
$$\times \langle Y_{j'',M-m}(\Omega_{R+u}) Y_{k'',Q-p}(\Omega_{R+u})\rangle_{\text{av}}$$
$$\times Y_{j,-M}(\hat{u}) Y_{k,-Q}(\hat{u}) \ . \quad (8)$$

The subscripts on the molecular orientation variables Ω, have been changed from the 1 and 2 of Eq. (7) to the position vectors of molecules 1 and 2, $\vec{R}$ and $\vec{R}+\vec{u}$. This change has been made to reflect the fact that the averages over h depend on position if there is a distortion present, because in this case h depends on position. Of course, in the mean-field approximation the averages over h of the two molecular orientations are decoupled.

The most convenient procedure is now to construct, if possible, distortions corresponding to each individual K_{ii} and compute the resulting internal energy. Fortunately, this construction is possible in the long-wavelength limit. In order to do this, consider the distortion corresponding to the position-dependent director given by

$$\hat{n}(r)=\hat{z}\cos\theta_n+\hat{x}\sin\theta_n \ ,$$

with

$$\theta_n(\vec{r})=\Delta n\sin(\vec{q}\cdot\vec{r}) \ . \quad (9)$$

The Frank free energy for this form of the director is

$$F=\tfrac{1}{2}\int d^3r\,(\Delta n)^2\cos^2(\vec{q}\cdot\vec{r})$$
$$\times[K_{11}(q_x\cos\theta_n-q_z\sin\theta_n)^2+K_{22}(q_y)^2$$
$$+K_{33}(q_z\cos\theta_n+q_x\sin\theta_n)^2] \ . \quad (10)$$

For $\Delta n \ll 1$, this expression may be expanded as a power series in Δn. The leading term is proportional to $(\Delta n)^2$. The expansion has a particularly simple form for three cases:

$$\vec{q}\parallel\hat{x} \quad F=\tfrac{1}{4}V(\Delta n)^2q^2K_{11} \ ,$$
$$\vec{q}\parallel\hat{y} \quad F=\tfrac{1}{4}V(\Delta n)^2q^2K_{22} \ , \quad (11)$$
$$\vec{q}\parallel\hat{z} \quad F=\tfrac{1}{4}V(\Delta n)^2q^2K_{33} \ ,$$

where V is the volume of the system. To evaluate the K_{ii}, it is only necessary to determine the change in Eq. (8), to order $(\Delta n)^2q^2$, caused by these three distortions.

Since $f_{j'j''j}(|u|)$ is of short range, θ_n may be expanded in a power series in q. To order q^2,

$$\theta_n(\vec{R}+\vec{u})=\Delta n\{\vec{q}\cdot\vec{u}\cos(\vec{q}\cdot\vec{R})$$
$$+[1-\tfrac{1}{2}(\vec{q}\cdot\vec{u})^2]\sin(\vec{q}\cdot\vec{R})\} \ . \quad (12)$$

In order to be able to perform the integration over $\vec{u}$ for a given value of $\vec{R}$, it is useful to introduce a primed coordinate system. This is accomplished by rotating coordinates through an angle $\Delta n\sin(\vec{q}\cdot\vec{R})$ about $\hat{y}$. In the primed coordinate system the angle $\Delta\theta_n$, between the director at $\vec{R}+\vec{u}$ and the z' axis is given by

$$\vec{q}\parallel\hat{x} \quad \Delta\theta_n=\Delta n\{\cos(\vec{q}\cdot\vec{R})[qx'+\Delta n\sin(\vec{q}\cdot\vec{R})qz']$$
$$-\tfrac{1}{2}\sin(\vec{q}\cdot\vec{R})[q^2x'^2+2q^2x'z'\Delta n\sin(\vec{q}\cdot\vec{R})]\} \ ,$$
$$\vec{q}\parallel\hat{y} \quad \Delta\theta_n=\Delta n[\cos(\vec{q}\cdot\vec{R})qy'$$
$$-\tfrac{1}{2}\sin(\vec{q}\cdot\vec{R})q^2y'^2] \ , \quad (13)$$
$$\vec{q}\parallel\hat{z} \quad \Delta\theta_n=\Delta n\{\cos(\vec{q}\cdot\vec{R})[qz'-\Delta n\sin(\vec{q}\cdot\vec{R})qx']$$
$$-\tfrac{1}{2}\sin(\vec{q}\cdot\vec{R})[q^2z'^2-2q^2x'z'\Delta n\sin(\vec{q}\cdot\vec{R})]\} \ .$$

Here x', y', and z' are the coordinates of $\vec{u}$ in the primed system. In Eq. (13) terms proportional to powers of Δn higher than the second have been neglected. Note that the components of the vector $\vec{q}$ are given in the unrotated coordinate system.

It is clear that it is necessary to know $\langle Y_{k,m}(\Omega_r)\rangle_{\text{av}}$. This is most easily calculated by transforming to the coordinate system with z axis parallel to the director at r, that is, parallel to the symmetry axis of $h(\Omega)$. If the orientation of the director with respect to the space fixed axes is denoted by $\Omega_n=\{\theta_n, \varphi_n\}$,

$$[\langle Y_{k,m}(\Omega_r)\rangle_{\text{av}}]_{\text{space fixed}}=\sum_n D^{k*}_{mn}(\varphi_n,\theta_n,\gamma)$$
$$\times[\langle Y_{k,n}(\Omega_r)\rangle_{\text{av}}]_{\text{rotated-coordinate system}} \ . \quad (14)$$

Here D^k_{mn} is the rotation matrix of order k. In the rotated-coordinate system:

$$\langle Y_{k,n}(\Omega_r)\rangle_{\text{av}}=\delta_{n0}\left(\frac{2k+1}{4\pi}\right)^{1/2}\bar{P}_k \ . \quad (15)$$

Here

$$\bar{P}_k=\int_0^1 P_k(\cos\theta)h(\theta)d(\cos\theta) \ ,$$

so

$$[\langle Y_{k,m}(\Omega_r)\rangle_{\text{av}}]_{\text{space fixed}}=\left(\frac{2k+1}{4\pi}\right)^{1/2}D^{k*}_{m0}(\varphi_n,\theta_n,\gamma)\bar{P}_k$$
$$=\bar{P}_kY_{k,m}(\Omega_n) \ . \quad (16)$$

It is clear that the angle γ plays no essential role in this discussion. Using the result of Eq. (16), we have in the primed coordinate system:

$$\langle Y_{k,m}(\Omega'_{R+u})\rangle_{\text{av}}=\bar{P}_kY_{km}(\Delta\theta_n,0) \ . \quad (17)$$

In the limit that Δn becomes very small $\Delta\theta_n$ becomes very small, so $Y_{k,m}(\Delta\theta_n,0)$ may be expanded in a power series in Δn and q. Each of the terms in this series contains factors of $\cos(\vec{q}\cdot\vec{R})$ and $\sin(\vec{q}\cdot\vec{R})$. The integration over $\vec{R}$ will be zero for some of these terms. It can be readily proved that terms which give nonzero contributions to the free energy of order $(\Delta n)^2q^2$ can be obtained by consideration of the following simplified form of

TABLE I. The values of the low-order K, S, T, and B coefficients. $K(0)=0$, $K(2)=-\frac{1}{2}$, $K(4)=-\frac{5}{3}$, $S_0(m)=T_0(m)=B_0(m)=0$.

m	2	1	0	-1	-2
S_2	$\frac{1}{4}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{4}$
T_2	$-\frac{1}{4}$	0	$\frac{1}{2}$	0	$-\frac{1}{4}$
B_2	0	$\frac{1}{2}$	-1	$\frac{1}{2}$	0
S_4	$3\sqrt{3}/4$	$-\frac{3}{2}$	$\sqrt{5}$	$-\frac{3}{2}$	$3\sqrt{3}/4$
T_4	$-3\sqrt{3}/4$	0	$\sqrt{5}$	0	$-3\sqrt{3}/4$
B_4	0	$\sqrt{\frac{3}{2}}$	$-2\sqrt{5}$	$\sqrt{\frac{3}{2}}$	0

$\Delta\theta_n$ for the three cases of interest:

$$\begin{aligned}
&\vec{q}\parallel\hat{x}\quad \Delta\theta_n=\Delta n[\cos(\vec{q}\cdot\vec{R})qx'-\Delta n q^2x'z'\sin^2(\vec{q}\cdot\vec{R})]\,,\\
&\vec{q}\parallel\hat{y}\quad \Delta\theta_n=\Delta n[\cos(\vec{q}\cdot\vec{R})qy']\,, \qquad (18)\\
&\vec{q}\parallel\hat{z}\quad \Delta\theta_n=\Delta n[\cos(\vec{q}\cdot\vec{R})qz'+\Delta n q^2x'z'\sin^2(\vec{q}\cdot\vec{R})]\,.
\end{aligned}$$

It can also be shown that the integration over $\vec{R}$ gives zero for the terms of order $q\Delta n$ and $\frac{1}{2}V$ for the terms of order $(\Delta n)^2q^2$. The free energy can be calculated to order $(\Delta n)^2q^2$ by setting

$$\begin{aligned}
&\vec{q}\parallel\hat{x}\quad \Delta\theta_n=\Delta n(qx'-q^2x'z')\,,\\
&\vec{q}\parallel\hat{y}\quad \Delta\theta_n=\Delta n(qy')\,, \qquad (19)\\
&\vec{q}\parallel\hat{z}\quad \Delta\theta_n=\Delta n(qz'+q^2x'z')\,,
\end{aligned}$$

replacing the integral over R by $\frac{1}{2}V$, and setting Δn equal to one. To this order we have for $\vec{q}\parallel\hat{x}$

$$\langle Y_{j',m}(\Omega_{R+u})\rangle_{\text{av}}=q^2u^2\left[\bar{P}_{j''}\left(\frac{2j''+1}{4\pi}\right)^{1/2}K(j'')\delta_{m0}+\bar{P}_{j''}S_{j''}(m)Y_{2m}(\hat{u})\right]+\bar{P}_{j''}\left(\frac{2j''+1}{4\pi}\right)^{1/2}\delta_{m0}\,, \qquad (20\text{a})$$

$$Y_{j',m}(\Omega_R)=\left(\frac{2j'+1}{4\pi}\right)^{1/2}\delta_{m0}\bar{P}_{j'}\,. \qquad (20\text{b})$$

For the case of $\vec{q}\parallel\hat{y}$ and $\vec{q}\parallel\hat{z}$, $S_{j''}(m)$ is replaced by $T_{j''}(m)$ and $B_{j''}(m)$, respectively. This notation indicates that the distortions are splay, torsion, and bending. In Eq. (20a) some terms have been omitted. There are terms proportional to $Y_{2,m'\neq m}(\hat{u})$ in the expression for $\langle Y_{j'',m}(\Omega_{R+u})\rangle_{\text{av}}$ but, as we shall see, they do not contribute to the free energy so they have been omitted. The term in Eq. (20a) of order q^0 gives the free energy of the undistorted state. The difference between this free energy and the free energy of the distorted state must be compared with the Frank free energy of Eq. (11). This can be conveniently done by dropping the term of order q^0 at this point.

The values of the $K(j'')$ and the S, T, and B coefficients can be obtained from the explicit form of the spherical harmonic functions or from the differential equations. The values of the lower-order coefficients are given in Table I.

Equation (8) must be brought into a form such that Eq. (20) may be used. To do this it is necessary to express the product of spherical harmonic functions in such a way that Ω_{R+u} and Ω_R appear as the arguments of a product of two spherical harmonics. The result of this combination is

$$\begin{aligned}
E=\frac{V}{v_0}\frac{1}{4}\int d^3u &\sum_{j'j''j}\sum_{k'k''k} f_{j'j''j}(|u|)\rho_{k'k''k}(|u|)\frac{1}{4\pi}\sum_{ab}C(j'k'a;00)C(j''k''b;00)\\
&\times\left(\frac{(2j'+1)(2k'+1)(2j''+1)(2k''+1)}{(2a+1)(2k+1)}\right)^{1/2}\sum_{MmpQ}(-1)^{M+Q}\,C(j'k'a;m,p)\,C(j''k''b;M-m,Q-p)\\
&\times C(j'j''j;m,M-m)C(k'k''k;p,Q-p)\,Y_{j,-M}(\hat{u})Y_{k,-Q}(\hat{u})\langle Y_{a,m+p}(\Omega_R)\rangle_{\text{av}}\,\langle Y_{b,M+Q-m-p}(\Omega_{R+u})\rangle_{\text{av}}\,. \qquad (21)
\end{aligned}$$

With the aid of Eq. (20) the integration over u may be done. There remains a sum over m, p, M, Q. This sum may be evaluated. The result is

$$\begin{aligned}
\Delta E=\frac{V}{4v_0}\int_0^\infty u^4\,du\,q^2 &\sum_{j'j''j}\sum_{k'k''k}\frac{1}{(4\pi)^2}f_{j'j''j}\,\rho_{k'k''k}\,(2j+1)(2k+1)\,C(jk2;00)\\
&\times[(2j'+1)(2j''+1)(2k'+1)(2k''+1)]^{1/2}\sum_{ab}\bar{P}_a\bar{P}_bC(j'k'a;00)\,C(j''k''b;00)\\
&\times\left(\langle S,a\rangle_b\,X(j'k'a;j''k''b;jk2)+\delta_{jk}\delta_{ab}\frac{1}{2j+1}\,\frac{1}{C(jj2;00)}K(a)\,W(j'j''k'k'';ja)\right). \qquad (22)
\end{aligned}$$

Here $X(j'k'a;j''k''b;jk2)$ are the X coefficients and $W(j'j''k'k'';ja)$ are the Racah coefficients defined in Ref. 4. Equation (22) is appropriate for the case of $q\parallel\hat{x}$. For the cases of $q\parallel\hat{y}$ and $q\parallel\hat{z}$, the coefficients $\langle S,a\rangle_b$ must be replaced by $\langle T,a\rangle_b$ and $\langle B,a\rangle_b$, respectively. These coefficients are related to the $S_b(m)$ by

$$\langle S, a\rangle_b = \sum_x (-1)^x\, C(b2a; x, -x) S_b(x)\ . \tag{23}$$

They have the following properties. They are zero if either a or b is zero. Also

$$\begin{aligned} &\langle S, a\rangle_b + \langle T, a\rangle_b + \langle B, a\rangle_b = 0\ , \\ &\langle S, 2\rangle_4 = \langle S, 4\rangle_2,\ \text{etc.} \end{aligned} \tag{24}$$

The coefficients of low order are

$$\begin{aligned} &\langle S, 2\rangle_2 = \sqrt{\tfrac{1}{14}}\quad \langle T, 2\rangle_2 = -\sqrt{\tfrac{2}{7}}\quad \langle B, 2\rangle_2 = \sqrt{\tfrac{1}{14}}\ , \\ &\langle S, 4\rangle_2 = \tfrac{15}{2}\sqrt{\tfrac{1}{70}}\quad \langle T, 4\rangle_2 = \tfrac{5}{2}\sqrt{\tfrac{1}{70}}\quad \langle B, 4\rangle_2 = -10\sqrt{\tfrac{1}{70}}\ . \end{aligned} \tag{25}$$

The elastic constants are obtained by comparing Eq. (22) with Eq. (11). From these equations it is seen that one has $K_{ii} = \Delta E/(q^2V/4)$, where ΔE is as given by Eq. (22) and $\langle S, a\rangle_b$ is used for $i = 1$, $\langle T, a\rangle_b$ for $i = 2$, and $\langle B, a\rangle_b$ for $i = 3$.

We now focus on results which are the consequence of the formal features of Eq. (22) rather than on those which depend on the details of factors involving the intermolecular interactions. This is possible because Eq. (22) is of the form of an expansion of the internal energy in terms of moments of the distribution function h. It is expected that $\overline{P}_a$ will decrease rapidly as a increases. Also, each of the $\overline{P}_a$ will have a different temperature dependence. It should be possible to extract the coefficients of each of the terms $\overline{P}_a\overline{P}_b$ from the experimental data. Comparison with the theory is made easier by noting that owing to the relation of Eq. (23) the quantities $\Delta K_{ii} = K_{ii} - \overline{K}$, with $\overline{K} = \frac{1}{3}(K_{11} + K_{22} + K_{33})$, do not depend on the $K(a)$ coefficients. It may be verified that Eq. (22) gives the correct magnitude of $\overline{K}$ (to within 20%), for a simple choice of the intermolecular interaction.[5] It is therefore of interest to investigate the quantities $\Delta K_{ii}/K$. If the explicit values of the $\langle S, a\rangle_b$ are used, we have to relative order $\overline{P}_4/\overline{P}_2$:

$$\begin{aligned} \Delta K_{11}/\overline{K} &= \Delta - 3\Delta'(\overline{P}_4/\overline{P}_2) + \cdots\ , \\ \Delta K_{22}/\overline{K} &= -2\Delta - \Delta'(\overline{P}_4/\overline{P}_2) + \cdots\ , \\ \Delta K_{33}/\overline{K} &= \Delta + 4\Delta'(\overline{P}_4/\overline{P}_2) + \cdots\ . \end{aligned} \tag{26}$$

The quantities Δ and Δ' depend on the details of the molecules. There is at present no way of calcalculating them. Equation (26) predicts that in the limit that $\overline{P}_4 \ll \overline{P}_2$, which is expected to be the case in the limit of small $\overline{P}_2$, $K_{11} = K_{33}$. It also predicts that the departure from this equality is related in a simple way to the ratio $\overline{P}_4/\overline{P}_2$. If the temperature dependence of these moments of the distribution function were known independently it would be possible to evaluate Δ and Δ' from the data on the Frank elastic constants and check Eq. (26). Unfortunately it has not been possible to measure $\overline{P}_4$.[6] Calculations of this moment depend sensitively on the type of intermolecular interaction used. For this reason it is not possible to make an unambiguous check of Eq. (26).

It is possible to verify that Δ and Δ' are positive as required if the experimentally observed ordering of the elastic constants ($K_{33} > K_{11} > K_{22}$) is to be obtained. The radial integrals in Eq. (22) heavily weight terms which are large at large values of u. It is expected that $f_{j'j''j}(j', j'', j \neq 0)$ will be of longer range than $\rho_{k'k''k}(k', k'', k \neq 0)$. This is the case because the intermolecular interaction is anisotropic even if the molecules cannot overlap for any orientations but the anisotropy in the c.m. distribution function is expected to be most pronounced for values of the c.m. separation such that the molecules can overlap for some orientations. For this reason only contributions of Eq. (22) with $k' = k'' = 0$ will be considered for the purpose of this argument. The only contributing terms are f_{222} and f_{422}. In both cases it is easy to decide the sign. The most anisotropic aspect of the intermolecular interaction is the difference between the following two configurations; molecules 1 and 2 at right angles to each other with r_{12} in the plane defined by their orientations. By requiring that the second configuration be the preferred one, we find that $f_{222} > 0$ and $f_{422} < 0$. For both cases we find Δ and Δ' positive.

III. EXPLICIT RESULTS FOR SPHEROCYLINDERS

For the case of hard spherocylinders (cylinders capped with hemispheres at both ends) it is possible to explicitly evaluate Δ and Δ'. Here, of course, it is the translational entropy term which completely determines the elastic constants. In the limit of no volume change, the mean-field expression for the translational entropy can be written[7]

$$-TS_t/N = \tfrac{1}{2}(4.541)kT_c \int\!\!\int d\Omega_1\, d\Omega_2\, h(\Omega_1) h(\Omega_2) B(\theta_{12})\ , \tag{27}$$

where B_{12} is the second virial coefficient,

$$B(\theta_{12}) = \tfrac{2}{3}\pi a^3 + \pi a^2 l + a^2 l\,|\sin\theta_{12}|\ .$$

The obvious generalization of this result is

$$\begin{aligned} -TS_t/N &= \tfrac{1}{4}(4.541)kT_c \\ &\times \int\!\!\int\!\!\int d\Omega_1\, d\Omega_2\, d^3r\, h(\Omega_1) h(\Omega_2)\, \delta(\vec{r}, \Omega_1, \Omega_2)\ . \end{aligned} \tag{28}$$

Here $\vec{r}$ is the vector joining the centers of mass of molecules 1 and 2, $\delta(\vec{r}, \Omega_1, \Omega_2)$ is unity if the molecules overlap and zero if they do not. In principle this calculation could be done by expressing δ as a sum of terms as was done for the intermolecular interaction. In practice this does not prove to be convenient. For this reason the calculation will be done in another way. The results of the previous section can be used as a partial check on the method. As in Sec. II, the method of the calculation will be to evaluate changes in Eq. (28) caused by three types of distortions. Also as discussed in the previous section, a local coordinate system such that the direction between the preferred direction and the z' axis is given by

$$
\begin{aligned}
&\vec{q} \parallel \hat{x} \ \text{(splay)} && \Delta\theta_n = q r_x - q^2 r_x r_z \,, \\
&\vec{q} \parallel \hat{y} \ \text{(torsion)} && \Delta\theta_n = q r_y \,, \\
&\vec{q} \parallel \hat{z} \ \text{(bending)} && \Delta\theta_n = q r_z + q^2 r_x r_z \,,
\end{aligned}
\tag{29}
$$

can be chosen for these three distortions. The Frank elastic energies corresponding to these three distortions are $\frac{1}{2}Vq^2K_{11}$, $\frac{1}{2}Vq^2K_{22}$, and $\frac{1}{2}Vq^2K_{33}$, respectively. For the purposes of this calculation the series expansion of the orientational distribution function will be exploited. At the point $\vec{r}=0$ we have

$$
\begin{aligned}
h(\Omega_1) &= \frac{1}{4\pi}\sum_n a_n P_n(\cos\theta_1) \\
&= \frac{1}{4\pi}\sum_n (2n+1)\overline{P}_n P_n(\cos\theta_1) \,.
\end{aligned}
\tag{30}
$$

For $r \neq 0$, the spherical addition theorem may be used to write

$$
h(\Omega_2) = \frac{1}{4\pi}\Big[1 + 4\pi\overline{P}_2 \sum_m Y_{2,m}(\Omega_2) Y^*_{2,m}(\Delta\theta_n, 0) + \cdots\Big] \,. \tag{31}
$$

For small q the $Y^*_{n,m}(\Delta\theta_n, 0)$ may be expanded in a power series in q. As before, a term of order q^0 will be neglected because it gives rise to the undistorted result. There are no terms of order q which contribute to the final result. The terms of order q^2 are

$$
\begin{aligned}
\frac{-TS_t}{N} = {}& \tfrac{1}{4}(4.541)kT_c \iint d\Omega_1\, d\Omega_2 \int d^3r\, q^2\, \delta(r, \Omega_1, \Omega_2) \sum_n \overline{P}_n \\
&\times \left[b_{n2}\big(Y_{n,2}(\Omega_2) + Y_{n,-2}(\Omega_2)\big) \begin{pmatrix} r_x^2 \\ r_y^2 \\ r_z^2 \end{pmatrix} + b_{n0} Y_{n,0}(\Omega_2) \begin{pmatrix} r_x^2 \\ r_y^2 \\ r_z^2 \end{pmatrix} + b_{n1}\big(Y_{n,1}(\Omega_2) - Y_{n,-1}(\Omega_2)\big) \begin{pmatrix} r_x r_z \\ 0 \\ -r_x r_z \end{pmatrix} \right] \\
&\times \sum_{n'} \frac{2n'+1}{4\pi} \overline{P}_{n'} P_{n'}(\cos\theta_1) \,.
\end{aligned}
\tag{32}
$$

Here

$$
\begin{aligned}
b_{n0} &= -\tfrac{1}{4} n(n+1) \left(\frac{2n+1}{4\pi}\right)^{1/2} , \\
b_{n1} &= \tfrac{1}{2} n(n+1) \left(\frac{(n-1)!}{(n+1)!}\right)^{1/2} \left(\frac{2n+1}{4\pi}\right)^{1/2} , \\
b_{n2} &= \tfrac{1}{8}(n-1)n(n+1)(n+2) \left(\frac{(n-2)!}{(n+2)!}\right)^{1/2} \left(\frac{2n+1}{4\pi}\right)^{1/2} .
\end{aligned}
$$

The top entry in the column vectors of Eq. (32) is to be used for the case of the splay distortion, the second entry for torsion, and the last for bending.

The function δ may be visualized in the following manner. The locus of points where δ changes from one to zero describes a closed surface. Inside the surface $\delta = 1$, outside $\delta = 0$. There are three mutually perpendicular planes containing the origin which are mirror planes for the surface. Consider two spherocylinders A and B. The center of A is at the origin. We introduce a primed coordinate system such that the long axis of A is perpendicular to the z' axis and at an angle $\frac{1}{2}\theta_{12}$ with the x' axis. The long axis of B is perpendicular to $\hat{z}'$ and makes an angle $-\frac{1}{2}\theta_{12}$ with the x' axis. The surface is the surface traced out by the center of B as it is moved to all points such that the surfaces of the two spherocylinders are tangent to each other. It is clear that the mirror planes are the planes perpendicular to $\hat{x}'$, $\hat{y}'$, and $\hat{z}'$. More concretely, the surface may be constructed by placing at the origin a prism of height $2a$ with rhomboidal base of side l and angle θ_{12}. The base is oriented such that the diagonal joining the angles θ_{12} is parallel to the x' axis. The other diagonal is parallel to the y' axis. The rest of the surface is made up by placing all of the sections of a cylinder of height $2l$ and radius a, and of a sphere of radius a on the four nonbasal faces of the prism to form a smooth curvilinear surface. There is only one way in which this may be done. Here, as above, a and $a+l$ are the width and length of the spherocylinders, respectively. An exploded diagram is presented in Fig. 2.

The construction described above gives a very easy way of calculating the second virial coefficient for hard spherocylinders $B(\theta_{12})$. This quantity was first calculated by Onsager.[8] It is just one-half of the volume enclosed by the surface discussed above:

$$
B(\theta_{12}) = \tfrac{1}{2}\left(2al^2\sin\theta_{12} + 2l\pi a^2 + \tfrac{4}{3}\pi a^3\right) .
$$

The relationship between the primed and unprimed coordinate systems is given by the transformation matrix equation:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \dfrac{x_1+x_2}{2\cos(\frac{1}{2}\theta_{12})} & \dfrac{x_1-x_2}{2\sin(\frac{1}{2}\theta_{12})} & \dfrac{y_1z_2-y_2z_1}{\sin(\theta_{12})} \\ \dfrac{y_1+y_2}{2\cos(\frac{1}{2}\theta_{12})} & \dfrac{y_1-y_2}{2\sin(\frac{1}{2}\theta_{12})} & \dfrac{z_1x_2-z_2x_1}{\sin(\theta_{12})} \\ \dfrac{z_1+z_2}{2\cos(\frac{1}{2}\theta_{12})} & \dfrac{z_1-z_2}{2\sin(\frac{1}{2}\theta_{12})} & \dfrac{x_1y_2-x_2y_1}{\sin(\theta_{12})} \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} .$$

Here (x_1, y_1, z_1) are the coordinates of a unit vector parallel to Ω_1, (x_2, y_2, z_2) are the coordinates of a unit vector parallel to Ω_2, and θ_{12} is the angle between molecules 1 and 2.

An inspection of Eq. (32) reveals that it is necessary to calculate the integrals over r of the product of δ and one of the following: r_x^2, r_y^2, r_z^2, and r_xr_z. These integrals can most easily be done by transforming to the primed coordinate system to take advantage of the symmetry of δ. We have

$$r_x^2 = \frac{(x_1+x_2)^2}{4\cos^2(\frac{1}{2}\theta_{12})}(r_x')^2 + \frac{(x_1-x_2)^2}{4\sin^2(\frac{1}{2}\theta_{12})}(r_y')^2 + \frac{(y_1z_2-y_2z_1)^2}{\sin^2(\theta_{12})}(r_z')^2 + \text{cross terms} . \tag{33}$$

There are corresponding expressions for r_y^2, r_z^2, and r_xr_z. In the primed coordinate system δ has reflection symmetry in the three coordinate planes so the cross terms in the expression above do not contribute to the integral. For this reason the only quantities which need be calculated are

$$\begin{aligned} R_{xx} &\equiv \int d^3r'(r_x')^2\,\delta(r', \Omega_1, \Omega_2) , \\ R_{yy} &\equiv \int d^3r'(r_y')^2\,\delta(r', \Omega_1, \Omega_2) , \\ R_{zz} &\equiv \int d^3r'(r_z')^2\,\delta(r', \Omega_1, \Omega_2) . \end{aligned} \tag{34}$$

These integrals can be evaluated in a straightforward but tedious manner using the construction of the surface discussed above. The results are

$$\begin{aligned} R_{zz} &= \tfrac{1}{3}[a^2][2al^2\sin(\theta_{12}) + \tfrac{3}{2}\pi la^2 + \tfrac{4}{5}\pi a^3] \\ R_{yy} &= \tfrac{1}{3}al^4\sin(\theta_{12})\sin^2(\tfrac{1}{2}\theta_{12}) + \tfrac{2}{3}\pi a^2l^3\sin^2(\tfrac{1}{2}\theta_{12}) \\ &\quad + \tfrac{4}{3}a^3l^2\sin(\theta_{12}) + \tfrac{1}{2}\pi a^4l\cos^2(\tfrac{1}{2}\theta_{12}) \\ &\quad + \tfrac{4}{3}a^3l^2\theta_{12}\sin^2(\tfrac{1}{2}\theta_{12}) + \pi a^4l\sin^2(\tfrac{1}{2}\theta_{12}) \\ &\qquad + \tfrac{4}{15}\pi a^5 , \\ R_{xx}(\theta_{12}) &= R_{yy}(\pi-\theta_{12}) . \end{aligned} \tag{35}$$

All that remains is a complicated integration over Ω_1 and Ω_2. A typical term is proportional to

$$J' = \iint d\Omega_1\, d\Omega_2 (Y_{n,2}(\Omega_2) + Y_{n,-2}(\Omega_2)) \frac{(x_1+x_2)^2}{4\cos^2(\frac{1}{2}\theta_{12})} \times R_{xx}(\theta_{12})P_{n'}(\cos\theta_1)\overline{P}_n\overline{P}_{n'} . \tag{36}$$

For any reasonable model of the nematic state $\overline{P}_n$ decreases rapidly as n increases. (This is most true near T_c.) Hence the dominant contributions to the elastic constants are given by the lowest values of $(n+n')$ in Eq. (36). Of course, as we have seen, the terms where either n or n' is zero do not contribute to the elastic constants. Hence, the dominant terms in Eq. (32) are those with $n = 2 = n'$. Next in importance are those with $n=2$, $n'=4$ or $n=4$, $n'=2$. The integrals necessary to construct these terms are evaluated in the Appendix. Terms with $n+n' > 6$ are neglected.

Collecting the results of the Appendix and substituting into Eq. (32), we obtain the results:

$$-TS_t = (V/v_0)\tfrac{1}{4}(4.541)kT_cq^2a^5\tfrac{1}{280}\pi \times \left\{ \tfrac{25}{24}(\overline{P}_2)^2 \left[(7R^4+20R^2) + \begin{pmatrix} 2R^4 & -2R^2 \\ -4R^4 & +4R^2 \\ 2R^4 & -2R^2 \end{pmatrix} \right] + \tfrac{225}{128}\overline{P}_2\overline{P}_4 \begin{pmatrix} -3R^4+8R^2 \\ -R^4(\frac{8}{3})R^2 \\ 4R^4-(\frac{32}{3})R^2 \end{pmatrix} \right\} . \tag{37}$$

Here $R = l/a$. The elastic constants are obtained from this expression by dividing by $\frac{1}{2}Vq^2$; the top entry in the column vectors is to be used for K_{11} etc. We have

$$\begin{aligned} \Delta K_{11}/\overline{K} &= \frac{2R^2 - 2 + 27(\overline{P}_4/\overline{P}_2)(-\frac{3}{16}R^2 + \frac{1}{2})}{7R^2+20} , \\ \Delta K_{22}/\overline{K} &= \frac{-4R^2 + 4 + 27(\overline{P}_4\overline{P}_2)(-\frac{1}{16}R^2 + \frac{1}{6})}{7R^2+20} , \end{aligned} \tag{38}$$

$$\Delta K_{33}/\overline{K} = \frac{2R^2 - 2 + 27(\overline{P}_4\overline{P}_2)(\frac{1}{4}R^2 - \frac{2}{3})}{7R^2+20} .$$

This form of the elastic constants is consistent with the form of Sec. II. The values of Δ and Δ' are

$$\begin{aligned} \Delta &= (2R^2-2)/(7R^2+20) , \\ \Delta' &= 27(\tfrac{1}{16}R^2 - \tfrac{1}{6})/(7R^2+20) . \end{aligned} \tag{39}$$

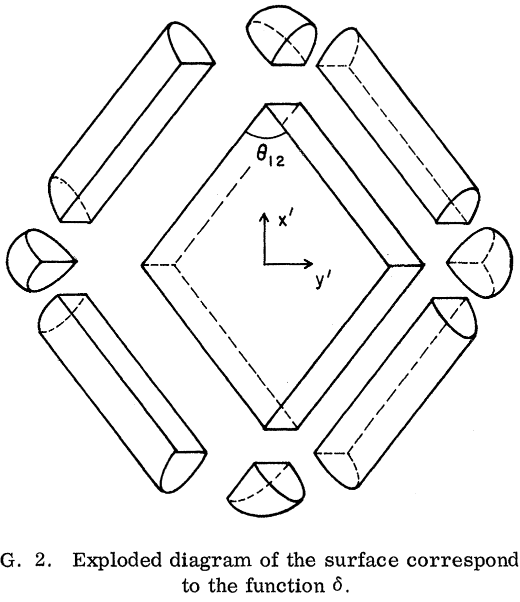

FIG. 2. Exploded diagram of the surface corresponding to the function δ.

IV. COMPARISON WITH EXPERIMENT

There is one result of this theory which is model independent. This is the prediction that in the limit of small $\overline{P}_2$, $K_{11} = K_{33}$ and that all three elastic constants are proportional to $\overline{P}{}_2^2$. This result was derived for the case of London dispersion forces by Nehring and Saupe.[9] This work has extended it to arbitrary intermolecular interactions. The early experiments of Zwetkoff[10] and Saupe[11] are in agreement with the prediction that the elastic constants of *p*-azoxyanisole (PAA) are proportional to $\overline{P}{}_2^2$. However, they found K_{33} to be much larger than K_{11}. Recent experiments by Gruler[12] for PAA and Shtrikmann *et al.*[13] for *N*-*p*-methoxybenzylidene (MBBA) indicate that K_{33} is not substantially larger than K_{11} near $T = T_c$.

The values of the elastic constants at the transitions for PAA and MBBA are[12,13]

PAA:

$$\Delta K_{11}/\overline{K} = 0.02\ , \quad \Delta K_{22}/\overline{K} = -0.42\ , \quad \Delta K_{33}/\overline{K} = 0.41\ , \tag{40}$$

MBBA:

$$\Delta K_{11}/\overline{K} = 0.15\ , \quad \Delta K_{22}/\overline{K} = -0.41\ , \quad \Delta K_{33}/\overline{K} = 0.26\ .$$

The corresponding values of Δ and Δ' are

$$\begin{aligned} &\text{PAA: } \Delta = 0.18\ , \quad \Delta' = 0.054\ , \\ &\text{MBBA: } \Delta = 0.20\ , \quad \Delta' = 0.016\ . \end{aligned} \tag{41}$$

The detailed temperature dependence of the elastic constants of MBBA has not been observed. The theory predicts that there should be little departure from the temperature dependence of $\overline{P}{}_2^2$. The experimental observations of PAA indicate that K_{11} and K_{22} are nearly proportional to $\overline{P}{}_2^2$ but that K_{33} is a much faster decreasing function of the temperature than is $\overline{P}{}_2^2$. Since PAA is a relatively inflexible molecule, it is possible to apply the model of Sec. III. The best fit to the data is obtained with a length-to-breadth ratio of 3.4 and a value of the ratio $\overline{P}_4/\overline{P}_2$ of 0.5. With these numbers the values of Δ and Δ' were reproduced to order 1%. The value of the length-to-breadth ratio is almost in exact agreement with the actual dimensions of the molecule (17×7×2 Å). The value of the ratio $\overline{P}_4/\overline{P}_2$ is in good agreement with the theoretical value obtained if the model intermolecular interaction is taken to be proportional to $|\sin\theta_{12}|$.[14] The only disagreement between theory and experiment is on the temperature dependence of K_{11}. The departure from proportionality to $\overline{P}{}_2^2$ should be nearly as great for K_{11} as for K_{33} but of the opposite sign according to Eq. (26). It is possible that higher-order terms in this series tend to interfere destructively in the case of the intermediate elastic constant K_{11} and constructively in the case of the largest K_{33}. It would be very useful to have an experimental result for $\overline{P}_4$. If this quantity were known, it would be possible to have a definite answer for this question.

It should be noted that for temperatures much lower than T_c the variations in the elastic constants may reflect the onset of a smectic phase, a possibility neglected here.

APPENDIX

There are 12 terms in Eq. (32) which must be evaluated. Nine of them are of the form

$$J = \int\int d\Omega_1\, d\Omega_2 \big[b_{n2}\big(Y_{n,2}(\Omega_2) + Y_{n,-2}(\Omega_2)\big) + b_{n0} Y_{n,0}(\Omega_2)\big]\, I P_{n'}(\cos\theta_1)\ , \tag{A1}$$

with correspondences given in Table II. Three of them are of the form

$$J = \int\int d\Omega_1\, d\Omega_2 b_{n1}\big(Y_{n,1}(\Omega_2) - Y_{n,-1}(\Omega_2)\big)$$

TABLE II. Terms of the form given in Eq. (A1).

J	I
$X+$	$(x_1+x_2)^2\, R_{xx}(\theta_{12})/\ 4\cos^2(\tfrac{1}{2}\theta_{12})$
$X-$	$(x_1-x_2)^2\, R_{yy}(\theta_{12})/\ 4\sin^2(\tfrac{1}{2}\theta_{12})$
$Y+$	$(y_1+y_2)^2\, R_{xx}(\theta_{12})/\ 4\cos^2(\tfrac{1}{2}\theta_{12})$
$Y-$	$(y_1-y_2)^2\, R_{yy}(\theta_{12})/\ 4\sin^2(\tfrac{1}{2}\theta_{12})$
$Z+$	$(z_1+z_2)^2\, R_{xx}(\theta_{12})/\ 4\cos^2(\tfrac{1}{2}\theta_{12})$
$Z-$	$(z_1-z_2)^2\, R_{yy}(\theta_{12})/\ 4\sin^2(\tfrac{1}{2}\theta_{12})$
XY	$(x_1y_2-x_2y_1)\, R_{zz}(\theta_{12})/\ \sin^2(\theta_{12})$
XZ	$(x_1z_2-x_2z_1)\, R_{zz}(\theta_{12})/\ \sin^2(\theta_{12})$
YZ	$(y_1z_2-y_2z_1)\, R_{zz}(\theta_{12})/\ \sin^2(\theta_{12})$

TABLE III. Terms of the form given in Eq. (A2).

J	I
$C+$	$(x_1+x_2)\ (z_1+z_2)\ R_{xx}(\theta_{12})/\ 4\ \cos^2(\frac{1}{2}\theta_{12})$
$C-$	$(x_1-x_2)\ (z_1-z_2)\ R_{yy}(\theta_{12})/\ 4\ \sin^2(\frac{1}{2}\theta_{12})$
CC	$(y_1z_2-y_2z_1)\ (x_1y_2-x_2y_1)\ R_{zz}(\theta_{12})/\ \sin^2(\theta_{12})$

$$\times IP_{n'}(\cos\theta_1)\ , \qquad \text{(A2)}$$

with correspondences given in Table III. As discussed in Sec. III, the contribution to the elastic constants of a given order of $\overline{P}_n\overline{P}_{n'}$ is proportional to

$$\begin{aligned} K_{11}&:\ (X+)+(X-)+YZ+(C+)+(C-)+CC\ ,\\ K_{22}&:\ (Y+)+(Y-)+XZ\ , \qquad \text{(A3)}\\ K_{33}&:\ (Z+)+(Z-)+XY-C+)-(C-)-CC. \end{aligned}$$

The most complex part of the integrands of the integrals J is the dependence on θ_{12}. This suggests that the integrals be expanded as

$$J=\sum_{ll'mm'}\iint d\Omega_1\, d\Omega_2\, g^J(ll'mm')Y_{l',m'}(\Omega_2) \times Y_{l,m}(\Omega_1)f(\theta_{12})\ . \qquad \text{(A4)}$$

All of the explicit dependence on θ_{12} is represented by the function f. This integral may be reduced to a one-dimensional integral. The result is

$$J=\sum_{lm} g^J(llm-m)2\pi(-1)^m\int P_l(\cos\theta_{12})f(\theta_{12})\,d\theta_{12}\ . \qquad \text{(A5)}$$

The coefficients $g^J(llm-m)$ will be shortened to $g^J(lm)$. These coefficients depend on n and n', but this will not be reflected in the notation in the interest of avoiding cumbersome subscripting. The g coefficients have been worked out for the cases of $n=2$ and $n'=0$, 2, 4. The case of $n=0$ gives no contribution because b_{0m} is zero. Note that there is no net contribution to the elastic constants from the case $n=2$, $n'=0$ and that the contributions to K_{11} and K_{33} are the same for the case of $n=2$, $n'=2$. The contributions from the cases $n=2$, $n'=4$, and $n=4$, $n'=2$ are the same so only the coefficients for the former are recorded here. The coefficients $g^J(lm)$ are given in Tables IV–VI. Note that $g^J(lm)=g^J(l-m)$.

TABLE IV. The coefficents $g^J(lm)$ for the case $n=2$, $n'=0$.

l	m	$g^{X\pm}$	$g^{Y\pm}$	$g^{Z\pm}$	g^{XY}	g^{XZ}	g^{YZ}	$g^{C\pm}$	g^{CC}
2	2	$\frac{1}{4}$	$-\frac{1}{4}$	0	$-\frac{2}{7}$	$\frac{1}{28}$	$-\frac{1}{28}$	0	$-\frac{1}{7}$
2	1	0	0	0	0	0	$-\frac{1}{7}$	$\frac{1}{2}$	0
2	0	$\frac{1}{2}$	$\frac{1}{2}$	-1	$\frac{5}{21}$	$-\frac{1}{14}$	$\frac{5}{42}$	0	$-\frac{1}{21}$
1	1	± 1	0	0	0	0	0	$\pm\frac{1}{2}$	0
1	0	0	0	$-\pm 2$	0	0	0	$-\pm 1$	0
0	0	1	0	-1	$\frac{1}{3}$	0	$-\frac{1}{3}$	-1	$\frac{1}{3}$

TABLE V. The coefficients $g^J(lm)$ for the case $n=2$, $n'=2$.

l	m	$g^{X\pm}$	$g^{Y\pm}$	$g^{Z\pm}$	g^{XY}	g^{XZ}	g^{YZ}	$g^{C\pm}$	g^{CC}
4	2	0	0	0	$\frac{3}{49}$	$\frac{1}{98}$	$\frac{-1}{98}$	0	$\frac{-2}{49}$
4	1	0	0	0	0	$\frac{-7}{98}$	$\frac{-5}{98}$	0	0
4	0	0	0	0	$\frac{-12}{245}$	$\frac{26}{245}$	$\frac{22}{245}$	0	$\frac{8}{245}$
3	1	$\frac{\pm 3}{10}$	$\frac{\pm 3}{14}$	$\frac{-\pm 27}{35}$	0	0	0	$\frac{\pm 6}{35}$	0
3	0	0	0	0	0	0	0	$\frac{\pm 9}{35}$	0
2	2	$\frac{-1}{14}$	$\frac{1}{14}$	0	$\frac{4}{49}$	$\frac{-1}{98}$	$\frac{1}{98}$	0	$\frac{2}{49}$
2	1	0	0	0	0	0	$\frac{-1}{49}$	$\frac{1}{14}$	0
2	0	$\frac{-6}{7}$	$\frac{-4}{7}$	$\frac{-11}{7}$	$\frac{-25}{147}$	$\frac{-22}{49}$	$\frac{-44}{147}$	$\frac{-1}{7}$	$\frac{5}{147}$
1	1	$\frac{\pm 1}{5}$	0	0	0	0	0	$\frac{-\pm 1}{10}$	0
1	0	0	0	$-\pm\frac{4}{5}$	0	0	0	$\frac{-\pm 2}{5}$	0
0	0	0	0	0	$\frac{-1}{15}$	$\frac{1}{5}$	$\frac{1}{15}$	0	$\frac{-1}{15}$

When the sums of Eq. (A5) are carried out, the results are as given below. In these expressions $x=\cos\theta_{12}$. For $n=2$, $n'=0$

$$\begin{aligned} &X+=\int_{-1}^{1}2\pi\,\tfrac{1}{2}\,(\tfrac{3}{2}\,x+\tfrac{1}{2})\,R_{xx}(\theta_{12})\,dx\ ,\\ &X-=\int_{-1}^{1}\ 2\pi\,\tfrac{1}{2}\,(-\tfrac{3}{2}x+\tfrac{1}{2})\,R_{yy}(\theta_{12})\,dx\ ,\\ &Y+=0\ ,\quad Y-=0\ ,\quad Z+=-X+\ ,\quad Z-=-X-\ ,\qquad \text{(A6)}\\ &XY=\int_{-1}^{1}2\pi\,\tfrac{1}{2}\,R_{zz}(\theta_{12})\,dx\ ,\quad XZ=0\ ,\quad YZ=-XY\ ,\\ &C+=-X+\ ,\quad C-=-X-\ ,\quad CC=XY\ . \end{aligned}$$

For $n=2$, $n'=2$

$$X+=2\pi\int_{-1}^{1}-\tfrac{1}{2}\,(\tfrac{3}{2}x^2-\tfrac{1}{2})R_{xx}(\theta_{12})\,dx\ ,$$

$$X-=2\pi\int\tfrac{1}{2}(-\tfrac{3}{2}\,x^{2}+\tfrac{1}{2})R_{yy}(\theta_{12})\,dx\ ,$$

TABLE VI. The coefficients $g^J(lm)$ for the case $n=2$, $n'=4$.

l	m	$g^{X\pm}$	$g^{Y\pm}$	$g^{Z\pm}$	g^{XY}	g^{XZ}	g^{YZ}	$g^{C\pm}$	g^{CC}
4	2	0	0	0	$\frac{-30}{539}$	$\frac{-5}{539}$	$\frac{5}{539}$	0	$\frac{20}{539}$
4	1	0	0	0	0	$\frac{-5}{462}$	$\frac{-25}{3234}$	0	0
4	0	$\frac{1}{6}$	$\frac{5}{42}$	$\frac{-2}{7}$	$\frac{114}{1617}$	$\frac{15}{1078}$	$\frac{-11}{1078}$	$\frac{4}{21}$	$\frac{-76}{1617}$
3	1	$\frac{-\pm 1}{6}$	$\frac{-\pm 5}{42}$	0	0	0	0	$\frac{-\pm 2}{21}$	0
3	0	0	0	$\frac{-\pm 4}{7}$	0	0	0	$\frac{\pm 4}{21}$	0
2	2	$\frac{1}{84}$	$\frac{-1}{84}$	0	$\frac{-2}{147}$	$\frac{1}{588}$	$\frac{-1}{588}$	0	$\frac{-1}{147}$
2	1	0	0	0	0	0	$\frac{4}{147}$	$\frac{-2}{21}$	0
2	0	$\frac{1}{7}$	$\frac{1}{7}$	$\frac{-2}{7}$	$\frac{10}{147}$	$\frac{1}{49}$	$\frac{5}{147}$	0	$\frac{-2}{147}$

$$
\begin{aligned}
Y+ &= 2\pi \int \tfrac{3}{14}\left(-\tfrac{5}{2}x^2 + x + \tfrac{1}{2}\right) R_{xx}(\theta_{12})\, dx \,, \\
Y- &= 2\pi \int \tfrac{3}{14}\left(-\tfrac{5}{2}x^2 - x + \tfrac{1}{2}\right) R_{yy}(\theta_{12})\, dx \,, \\
Z+ &= 2\pi \int \tfrac{1}{14}\left(-\tfrac{27}{2}x^2 - 3x + \tfrac{11}{2}\right) R_{xx}(\theta_{12})\, dx \,, \\
Z- &= 2\pi \int \tfrac{1}{14}\left(-\tfrac{27}{2}x^2 + 3x + \tfrac{11}{2}\right) R_{yy}(\theta_{12})\, dx \,, \qquad \text{(A7)} \\
XY &= 2\pi \int \tfrac{1}{7}\left(-\tfrac{9}{4}x^2 - \tfrac{1}{4}\right) R_{zz}(\theta_{12})\, dx \,, \\
XZ &= 2\pi \int \tfrac{1}{7}\left(-\tfrac{33}{4}x^2 + \tfrac{15}{4}\right) R_{zz}(\theta_{12})\, dx \,, \\
YZ &= 2\pi \int \left(-\tfrac{3}{4}x^2 + \tfrac{1}{4}\right) R_{zz}(\theta_{12})\, dx \,, \\
C+ &= 2\pi \int \tfrac{1}{14}\left(-\tfrac{3}{2}x^2 - \tfrac{3}{2}x + 1\right) R_{xx}(\theta_{12})\, dx \,, \\
C- &= 2\pi \int \tfrac{1}{14}\left(-\tfrac{3}{2}x^2 + \tfrac{3}{2}x + 1\right) R_{yy}(\theta_{12})\, dx \,, \\
CC &= 2\pi \int \tfrac{1}{7}\left(\tfrac{3}{2}x^2 - 1\right) R_{zz}(\theta_{12})\, dz \;.
\end{aligned}
$$

For $n=2,\ n'=4$

$$
\begin{aligned}
X+ &= 2\pi \int_{-1}^{1} \tfrac{1}{12}\left(\tfrac{35}{8}x^3 + \tfrac{5}{8}x^2 - \tfrac{23}{8}x - \tfrac{1}{8}\right) R_{xx}(\theta_{12})\, dx \,, \\
X- &= 2\pi \int \tfrac{1}{12}\left(-\tfrac{35}{8}x^3 + \tfrac{5}{8}x^2 + \tfrac{23}{8}x - \tfrac{1}{8}\right) R_{xx}(\theta_{12})\, dx \,, \\
Y+ &= \tfrac{5}{7}X+ \,, \quad Y- = \tfrac{5}{7}X- \,, \quad Z+ = -\tfrac{12}{7}X+ \,, \\
Z- &+ -\tfrac{12}{7}X- \,, \qquad \text{(A8)} \\
XY &= 2\pi \int -\tfrac{2}{49}\left(-\tfrac{35}{8}x^2 + \tfrac{7}{8}\right) R_{zz}(\theta_{12})\, dx \,, \\
XZ &= -\tfrac{5}{12}XY \,, \quad YZ = -\tfrac{7}{12}XY \,, \\
C+ &= \tfrac{8}{7}X+ \,, \quad C- = \tfrac{8}{7}X- \,, \quad CC = -\tfrac{2}{3}XY \,.
\end{aligned}
$$

The one-dimensional integrals which appear in these expressions are easy to evaluate. The results are

$$
\begin{aligned}
\int_{-1}^{1} R_{xx}(\theta_{12})\, dx &= \int R_{yy}(\theta_{12})\, dx \\
&= \tfrac{1}{12}\pi a l^4 + \tfrac{2}{3}\pi a^2 l^3 + 3\pi a^3 l^2 + \tfrac{3}{2}\pi a^4 l + \tfrac{8}{15}\pi a^5 \,, \\
\int R_{xx}(\theta_{12}) x\, dx &= -\int R_{yy}(\theta_{12}) x\, dx \\
&= \tfrac{1}{48}\pi a l^4 + \tfrac{2}{9}\pi a^2 l^3 + \tfrac{7}{18}\pi a^3 l^2 + \tfrac{1}{6}\pi a^4 l \,, \qquad \text{(A9)} \\
\int_{-1}^{1} R_{xx}(\theta_{12}) x^2\, dx &= \int R_{yy}(\theta_{12}) x^2\, dx \\
&= \tfrac{1}{48}\pi a l^4 + \tfrac{2}{9}\pi a^2 l^3 + \tfrac{71}{144}\pi a^3 l^2 \\
&\quad + \tfrac{1}{2}\pi a^4 l + \tfrac{8}{45}\pi a^5 \,, \\
\int R_{xx}(\theta_{12}) x^3\, dx &= -\int R_{yy}(\theta_{12}) x^3\, dx \\
&= \tfrac{1}{96}\pi a l^4 + \tfrac{2}{15}\pi a^2 l^3 + \tfrac{19}{80}\pi a^3 l^2 + \tfrac{1}{10}\pi a^4 l \,, \\
\int R_{zz}(\theta_{12})\, dx &= \tfrac{1}{3}\pi a^3 l^2 + \pi a^4 l + \tfrac{8}{15}\pi \,, \\
\int R_{zz}(\theta_{12}) x^2\, dx &= \tfrac{1}{12}\pi a^3 l^2 + \tfrac{1}{3}\pi a^4 l + \tfrac{8}{45}\pi \;.
\end{aligned}
$$

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[1] C. W. Oseen, Trans. Faraday Soc. **29**, 883 (1933); F. C. Frank, Discuss. Faraday Soc. **25**, 19 (1958); J. L. Erickson, Arch. Ration. Mech. Anal. **10**, 189 (1962).

[2] R. Priest, thesis (University of Pennsylvania, 1972) (University Microfilm, Ann Arbor, Michigan).

[3] W. Maier and A. Saupe, Z. Naturforsch. **13A**, 564 (1958); Z. Naturforsch. **14A**, 882 (1959); Z. Naturforsch. **15A**, 287 (1960).

[4] M.Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1967).

[5] R. Priest, Mol. Cryst. Liq. Cryst. **17**, 129 (1972).

[6] It is possible to measure $\bar{P}_4$ in principle. See, for example, R. Callender and P. S. Pershan, Phys. Rev. Lett. **23**, 947 (1972).

[7] R. Alben, Mol. Cryst. Liq. Cryst. **13**, 193 (1971).

[8] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).

[9] J. Nehring and A. Saupe, J. Chem. Phys. **56**, 5527 (1972).

[10] V. Zwetkoff, Acta Physicochim. URSS **6**, 865 (1937), as corrected for the magnetic anisotropy data according to V. Zwetkoff [Acta Physicochim. URSS **18**, 358 (1943)].

[11] A. Saupe, Z. Naturforsch. **15A**, 810 (1960); Z. Naturforsch. **15A**, 815 (1960).

[12] H. Gruler (unpublished).

[13] S. Shtrikmann, E. P. Wohlfarth, and Y. Wand, Phys. Lett. **37A**, 369 (1971).

[14] G. Lasher, J. Chem. Phys. **53**, 4141 (1970).