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Theory of nine elastic constants of biaxial nematics*

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In this paper, a rotational invariant of interaction energy between two biaxial-shaped molecules is assumed and in the mean field approximation, nine elastic constants for simple distortion patterns in biaxial nematics are derived in terms of the thermal average $\langle D^{(l)}_{mn}\rangle\langle D^{(l')}_{m'n'}\rangle$, where $D^{(l)}_{mn}$ is the Wigner rotation matrix. In the lowest order terms, the elastic constants depend on coefficients Γ, Γ', λ, order parameters $\bar{Q}_0 = Q_0\langle D^{(2)}_{00}\rangle + Q_2\langle D^{(2)}_{02} + D^{(2)}_{0-2}\rangle$ and $\bar{Q}_2 = Q_0\langle D^{(2)}_{20}\rangle + Q_2\langle D^{(2)}_{22} + D^{(2)}_{2-2}\rangle$. Here Γ and Γ' depend on the function form of molecular interaction energy $v_{j'j''j}(r_{12})$ and probability function $f_{k'k''k}(r_{12})$, where r_{12} is the distance between two molecules, and λ is proportional to temperature. Q_0 and Q_2 are parameters related to multiple moments of molecules. Comparing these results with those obtained from Landau–de Gennes theory, we have obtained relationships between coefficients, order parameters used in both theories. In the special case of uniaxial nematics, both results are reduced to a degenerate case where $K_{11} = K_{33}$.

Keywords: biaxial nematic liquid crystal, elastic theory
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1. Introduction

In biaxial nematics, there are two preferred molecular orientations perpendicular to each other ($\hat{a}$ and $\hat{b}$). For the convenience of description, a third direction ($\hat{c}$) perpendicular to the former two can be chosen and they form a triad of orthogonal director fields.[1] Following closely the classical formalism used in solid state, Saupe[1] obtained a free energy density depending on the distortions of directors $\hat{a}$, $\hat{b}$, and $\hat{c}$. Considering all possible rotational invariants of partial derivatives of directors $\hat{a}$, $\hat{b}$, and $\hat{c}$, Govers and Vertogen[2] derived an equivalent form of elastic energy density. In both Saupe's, and Govers–Vertogen's theories, fifteen independent elastic constants are present: nine for simple distortion patterns (called pure modes), three for coupled modes, three for surface terms. The equivalence of two sets of elastic constants is shown and their relationships are given in Ref.[3]. Generally, the elastic energy for uniaxial or biaxial nematics should not only depend on the distortions of director fields,[4,5] but also on the molecular orientation orders around the preferred axes. One attempt to derive such an expression is to use Landau–de Gennes's theory, and expand the elastic energy into a power series of rotational invariant of order parameter matrix.[3] However, in this derivation, only the macroscopic symmetry of order parameter matrix is involved, the molecular interactions are not considered. In order to obtain an elastic energy based on molecular interactions, we consider, in this paper, a rotational invariant of interaction energy between biaxial-shaped molecules, and by using mean field approximation, expressions of elastic constants for nine pure modes are derived. The results will be analysed and compared with those derived in Landau–de Gennes's theory.

2. Interaction energy density

The molecular interaction between molecules 1 and 2 should be a rotational invariant. Generally, the energy satisfying this requirement has the form

$$V_{12} = \sum_{jj'j''} V_{jj'j''}(|\boldsymbol{r}_{12}|) \sum_{mM} (-1)^M \times C(j'j''j; m, M-m) Q_{j',m}(\Omega_1) \times Q_{j'',M-m}(\Omega_2) Y_{j,-M}(\hat{r}_{12}), \quad (1)$$

where $\boldsymbol{r}_{12} = r_{12}\hat{r}_{12}$ is the vector between centres of mass of molecules 1 and 2, $C(j'j''j; m, M-m)$ is

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Clebsch–Gordan coefficient, Ω_1 and Ω_2 are the Euler angles of molecules 1 and 2 in the laboratory frame respectively. In a frame fixed on molecule, suppose the multiple moment of molecule is Q_{lm}, where $l = 0, 1, 2, \ldots$, $m = 0, \pm1, \pm2, \ldots, \pm l$. Moment $Q_{l,m}(\Omega)$ can be obtained by a rotation transformation,

$$Q_{j',m}(\Omega_1) = \sum_n D^{(j')}_{mn}(\Omega_1) Q_{j'n},$$
$$Q_{j'',M-m}(\Omega_2) = \sum_n D^{(j'')}_{M-m,n}(\Omega_2) Q_{j''n}, \quad (2)$$

where $\Omega_i = (\alpha_i, \beta_i, \gamma_i)$ is the Euler angle for the ith molecule ($i = 1, 2$). Quantity $D^{(j')}_{mn}$ is the Wigner rotation matrix element.[6] The dipole–dipole interaction is given by $(j', j'', j) = (1, 1, 2)$ term, the induced dipole–induced-dipole and quadrupole–quadrupole interactions are given by $(j', j'') = (2, 2)$, $j = 0, 2, 4$ terms. Odd value terms for j' or j'' will vanish for centrosymmetric molecules (such odd-parity terms can occur in the cholesteric state). In the Cartesian coordinate system, the quadrupole moment matrix of a centrosymmetric molecule $Q_{ij}(i, j = 1, 2, 3)$ is real, symmetric and can be chosen as traceless.[7] When it is diagonalized, there are only two independent diagonal elements. Transforming these matrix elements into spherical components, we have $Q_{2,\pm1} = 0$, $Q_{2,2} = Q_{2,-2} = Q^*_{2,2} = Q^*_{2,-2}$. Two independent nonzero elements can be chosen as $Q_{2,0}$ and $Q_{2,2}$.

The probability of finding molecule 2 with orientation Ω_2 at position $\boldsymbol{r}_2$ when molecule 1 is at $\bar{r}_1$ with orientation Ω_1 should also be a rotational invariant, i.e.

$$f = \sum_{k'k''k} f_{k'k''k}(r_{12}) \sum_{pP} (-1)^P \times C(k'k''k; p, P-p) Q_{k',p}(\Omega_1) \times Q_{k'',P-p}(\Omega_2) Y_{k.-P}(\hat{r}_{12}). \quad (3)$$

Combining Eqs.(1) and (3), the interaction energy between molecules 1 and 2 becomes

$$E_{12} = \iiiint V_{12}(\Omega_1, \Omega_2, \boldsymbol{r}_{12}) \times f(\Omega_1, \Omega_2, \boldsymbol{r}_{12}) \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_{12}. \quad (4)$$

For a N-molecule system, the energy density in a volume V is

$$E = \frac{1}{2V} \sum_{i \neq j} \sum_{j=1}^{N} E_{ij} \approx \frac{N^2}{2V} E_{12}. \quad (5)$$

Substituting Eqs.(1) and (3) into Eq.(5), and choosing $V_{j'j''j} = v_{j'j''j}/N$, we have

$$E = \frac{N}{2V} \iiiint \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_{12} \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 \times \sum_{j'j''j} v_{j'j''j}(r_{12}) \sum_{k'k''k} f_{k'k''k}(r_{12}) \times \sum_{mpMP} (-1)^{M+P} C(j'j''j; m, M-m) \times C(k'k''k; p, P-p) Q_{j',m}(\Omega_1) Q_{k',p}(\Omega_1) \times Q_{j'',M-m}(\Omega_2) Q_{k'',P-p}(\Omega_2) \times Y_{j,-M}(\hat{r}_{12}) Y_{k,-P}(\hat{r}_{12}). \quad (6)$$

From Eq.(2) we have

$$Q_{j',m}(\Omega_1) Q_{k',p}(\Omega_1) = \sum_{m'} \sum_{p'} Q_{j',m'} Q_{k',p'} D^{(j')}_{m,m'}(\Omega_1) D^{(k')}_{p,p'}(\Omega_1).$$

Expanding the coupled rotational matrices $D^{(j')}_{m,m'}(\Omega_1) D^{(k')}_{p,p'}(\Omega_1)$ into linear combination of $D^{(j)}_{m,n}$s, we have

$$Q_{j',m}(\Omega_1) Q_{k',p}(\Omega_1) = \sum_{m'p'} Q_{j',m'} Q_{k',p'} \sum_{l'} C(j'k'l'; m, p) C(j'k'l'; m', p') \times D^{(l')}_{m+p,m'+p'}(\Omega_1). \quad (7a)$$

Similarly,

$$Q_{j'',M-m}(\Omega_2) Q_{k'',P-p}(\Omega_2) = \sum_{m''p''} Q_{j'',m''} Q_{k'',p''} \sum_{l''} C(j''k''l''; M-m, P-p) \times C(j''k''l''; m'', p'') D^{(l'')}_{M+P-m-p,m''+p''}(\Omega_2). \quad (7b)$$

For the convenience of writing, we change symbols $\boldsymbol{r}_1$ to $\boldsymbol{R}$, $\boldsymbol{r}_{12}$ to $\boldsymbol{r}$, and write Ω_1, Ω_2 as Ω_R, Ω_{R+r} respectively. Because the interaction energy is rotationally invariant, we choose $\{\hat{a}(\boldsymbol{R}), \hat{b}(\boldsymbol{R}), \hat{c}(\boldsymbol{R})\}$ as a frame (called the primed frame) where the interaction energy is calculated. In this frame, the angle Ω_{R+r} is obtained by

(1) Rotating molecule 2 by an Euler angle $\Delta\Omega = (\Delta\alpha, \Delta\beta, \Delta\gamma)$ from $\{\hat{a}(\boldsymbol{R}), \hat{b}(\boldsymbol{R}), \hat{c}(\boldsymbol{R})\}$ to $\{\hat{a}(\boldsymbol{R}+\boldsymbol{r}), \hat{b}(\boldsymbol{R}+\boldsymbol{r}), \hat{c}(\boldsymbol{R}+\boldsymbol{r})\}$;

(2) Rotating molecule 2 by an Euler angle $\Omega_r = (\alpha_r, \beta_r, \gamma_r)$ from $\{\hat{a}(\boldsymbol{R}+\boldsymbol{r}), \hat{b}(\boldsymbol{R}+\boldsymbol{r}), \hat{c}(\boldsymbol{R}+\boldsymbol{r})\}$ to Ω_{R+r}.

The rotation matrix is

$$D^{(l'')}_{M+P-m-p,m''+p''}(\Omega_{R+r}) = \sum_s D^{(l'')}_{M+P-m-p,s}(\Delta\Omega) D^{(l'')}_{s,m''+p''}(\Omega_r). \quad (8)$$

Substituting Eq.(7) into Eq.(6), and using Eq.(8), we have

$$
\begin{aligned}
E =&\frac{N}{2V}\iiiint \mathrm{d}\Omega_r\mathrm{d}\Omega_R\mathrm{d}\boldsymbol{R}\mathrm{d}\boldsymbol{r}\sum_{j'j''j}\sum_{k'k''k}v_{j'j''j}(r)f_{k'k''k}(r)\\
&\times\sum_{mpMP}(-1)^{M+P}C(j'j''j;m,M-m)C(k'k''k;p,P-p)\\
&\times\sum_{m'p'}Q_{j',m'}Q_{k',p'}\sum_{l'}C(j'k'l';m,p)C(j'k'l';m',p')D^{(l')}_{m+p,m'+p'}(\Omega_R)\\
&\times\sum_{m''p''}Q_{j'',m''}Q_{k'',p''}\sum_{l''}C(j''k''l'';M-m,P-p)C(j''k''l'';m'',p'')\\
&\times\sum_{s}D^{(l'')}_{M+P-m-p,s}(\Delta\Omega)D^{(l'')}_{s,m''+p''}(\Omega_r)Y_{j,-M}(\hat{r})Y_{k,-P}(\hat{r}).
\end{aligned}\tag{9}
$$

Using mean field approximation, the orientations of molecules in the local director frames at $\boldsymbol{R}$ and $\boldsymbol{R}+\boldsymbol{r}$ are averaged to $\langle D^{(j')}_{m+p,m'+p'}(\Omega_R)\rangle_{\Omega_R}$ and $\langle D^{(l'')}_{s,m''+p''}(\Omega_r)\rangle_{\Omega_r}$. Taking integration of $\int \mathrm{d}\Omega_R\int\mathrm{d}\Omega_r$ and absorbing the result into $v_{j'j''j}f_{k'k''k}$ for the sake of simplicity, Eq.(9) becomes

$$
\begin{aligned}
E =&\frac{N}{2V}\iint \mathrm{d}\boldsymbol{R}\mathrm{d}\boldsymbol{r}\sum_{j'j''j}\sum_{k'k''k}v_{j'j''j}(r)f_{k'k''k}(r)\\
&\times\sum_{mpMP}(-1)^{M+P}C(j'j''j;m,M-m)C(k'k''k;p,P-p)\\
&\times\sum_{m'p'}Q_{j',m'}Q_{k',p'}\sum_{l'}C(j'k'l';m,p)C(j'k'l';m',p')\langle D^{(l')}_{m+p,m'+p'}(\Omega_R)\rangle\\
&\times\sum_{m''p''}Q_{j'',m''}Q_{k'',p''}\sum_{l''}C(j''k''l'';M-m,P-p)C(j''k''l'';m'',p'')\\
&\times\sum_{s}D^{(l'')}_{M+P-m-p,s}(\Delta\Omega)\langle D^{(l'')}_{s,m''+p''}(\Omega_r)\rangle Y_{j,-M}(\hat{r})Y_{k,-P}(\hat{r}).
\end{aligned}\tag{10}
$$

3. Calculations of elastic constants for pure modes

In Saupe's theory,[1] neglecting surface terms, the elastic energy density for biaxial nematics is written as

$$
\begin{aligned}
E_s =&\frac{1}{2}\sum_a\{K_{aa}[(\hat{a}\cdot\nabla\hat{b})\cdot\hat{c}]^2\\
&+K_{ab}[(\hat{a}\cdot\nabla\hat{a})\cdot\hat{b}]^2+K_{ac}[(\hat{a}\cdot\nabla\hat{a})\cdot\hat{c}]^2\\
&+2C_{ab}(\hat{a}\times\nabla\times\hat{a})\cdot(\hat{b}\times\nabla\times\hat{b})\},
\end{aligned}\tag{11}
$$

where $\sum\limits_a$ means a cyclic permutation over a, b, and c. For example, for an arbitrary function $f(a,b,c)$, $\sum\limits_a f(a,b,c)=f(a,b,c)+f(b,c,a)+f(c,a,b)$.

In Eq.(1), there are twelve elastic constants: nine for pure modes (Ks), three for coupled modes(Cs). In order to derive expressions of elastic constants for pure modes, we consider the following distortions:

$$
\text{(A)}\qquad
\begin{aligned}
&\hat{a}(\boldsymbol{r})=\hat{x},\\
&\hat{b}(\boldsymbol{r})=\cos\theta_a\hat{y}+\sin\theta_a\hat{z},\\
&\hat{c}(\boldsymbol{r})=-\sin\theta_a\hat{y}+\cos\theta_a\hat{z},
\end{aligned}\tag{12a}
$$

where $\theta_a=\Delta_a\sin(\boldsymbol{q}\cdot\boldsymbol{r})$;

$$
\text{(B)}\qquad
\begin{aligned}
&\hat{a}(\boldsymbol{r})=\cos\theta_b\hat{x}-\sin\theta_b\hat{z},\\
&\hat{b}(\boldsymbol{r})=\hat{y},\\
&\hat{c}(\boldsymbol{r})=\sin\theta_b\hat{x}+\cos\theta_b\hat{z},
\end{aligned}\tag{12b}
$$

where $\theta_b(\boldsymbol{r})=\Delta_b\sin(\boldsymbol{q}\cdot\boldsymbol{r})$;

$$
\text{(C)}\qquad
\begin{aligned}
&\hat{a}(\boldsymbol{r})=\cos\theta_c\hat{x}+\sin\theta_c\hat{y},\\
&\hat{b}(\boldsymbol{r})=-\sin\theta_c\hat{x}+\cos\theta_c\hat{y},\\
&\hat{c}(\boldsymbol{r})=\hat{z},
\end{aligned}\tag{12c}
$$

where $\theta_c=\Delta_c\sin(\boldsymbol{q}\cdot\boldsymbol{r})$.

Substituting $\hat{a}(\boldsymbol{r})$, $\hat{b}(\boldsymbol{r})$, $\hat{c}(\boldsymbol{r})$ in distortion patterns A, B and C into Eq.(11), we obtain

$$
\begin{aligned}
E_1 =& \frac{1}{2}K_{aa}q_x^2\Delta_a^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}) + \frac{1}{2}K_{bc}(q_y\cos\theta_a + q_z\sin\theta_a)^2\Delta_a^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}) \\
&+ \frac{1}{2}K_{cb}(q_y\sin\theta_a - q_z\cos\theta_a)^2\Delta_a^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}), \\
E_2 =& \frac{1}{2}K_{bb}q_y^2\Delta_b^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}) + \frac{1}{2}K_{ca}(q_x\sin\theta_b + q_z\cos\theta_b)\Delta_b^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}) \\
&+ \frac{1}{2}K_{ac}(-q_x\cos\theta_b + q_z\sin\theta_b)^2\Delta_b^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}), \\
E_3 =& \frac{1}{2}K_{cc}q_z^2\Delta_c^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}) + \frac{1}{2}K_{ab}(q_x\cos\theta_c + q_y\sin\theta_c)^2\Delta_c^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}) \\
&+ \frac{1}{2}K_{ba}(q_x\sin\theta_c - q_y\cos\theta_c)^2\Delta_c^2\cos^2(\boldsymbol{q}\cdot\boldsymbol{r}). \qquad (13)
\end{aligned}
$$

For small angle approximation, i.e. $\Delta_a \ll 1$, $\Delta_b \ll 1$, $\Delta_c \ll 1$, E_i $(i = 1, 2, 3)$ may be expanded into the power series of Δ_a, Δ_b, Δ_c. Keeping only the quadratic terms and integrating over the entire volume V, we have

$$
\begin{aligned}
E_1 &= \frac{1}{4}\Delta_a^2 V(K_{aa}q_x^2 + K_{bc}q_y^2 + K_{cb}q_z^2), \\
E_2 &= \frac{1}{4}\Delta_b^2 V(K_{bb}q_y^2 + K_{ca}q_z^2 + K_{ac}q_x^2), \\
E_3 &= \frac{1}{4}\Delta_c^2 V(K_{cc}q_z^2 + K_{ab}q_x^2 + K_{ba}q_y^2). \qquad (14)
\end{aligned}
$$

For the three distortions above, interaction energy in Eq.(10) will also give similar forms under mean field approximation. By comparing the corresponding coefficients, nine elastic constants for pure modes can be derived.

In distortion patterns A, B and C, the Euler angles between directors $\{\hat{a}(\boldsymbol{R}),\ \hat{b}(\boldsymbol{R}),\ \hat{c}(\boldsymbol{R})\}$ and $\{\hat{a}(\boldsymbol{R}+\boldsymbol{r}),\ \hat{b}(\boldsymbol{R}+\boldsymbol{r}),\ \hat{c}(\boldsymbol{R}+\boldsymbol{r})\}$ are, $\Delta\Omega_1 = (-\pi/2, \Delta\theta_a, \pi/2)$, $\Delta\Omega_2 = (0, \Delta\theta_b, 0)$, $\Delta\Omega_3 = (\Delta\theta_c, 0, 0)$ respectively. In power series of $\boldsymbol{q}$, $\Delta\theta_a$, $\Delta\theta_b$, $\Delta\theta_c$ can be expanded as

$$
\begin{aligned}
\Delta\theta_\alpha &\equiv \theta_\alpha(\boldsymbol{R}+\boldsymbol{r}) - \theta_\alpha(\boldsymbol{R}) \\
&= \Delta_\alpha[\boldsymbol{q}\cdot\boldsymbol{r}\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}(\boldsymbol{q}\cdot r)^2\sin(\boldsymbol{q}\cdot\boldsymbol{R})], \qquad (15)
\end{aligned}
$$

where $\alpha = a, b, c$.

In the primed frame (corresponding to rotation pattern A), the position vector $\boldsymbol{r}$ is

$$
\begin{aligned}
x &= x', \\
y &= y'\cos\theta_a - z'\sin\theta_a, \\
z &= y'\sin\theta_a + z'\cos\theta_a. \qquad (16)
\end{aligned}
$$

Substituting the above transformation into Eq.(5), expanding it into power series of Δ_a and keeping only the linear and quadratic terms, we have for

$$
\begin{aligned}
&\boldsymbol{q}||\hat{x}, \quad \Delta\theta_a = \Delta_a\left[qx'\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2x'^2\sin(\boldsymbol{q}\cdot\boldsymbol{R})\right]; \\
&\boldsymbol{q}||\hat{y}, \quad \Delta\theta_a = \Delta_a\left\{q[y' - z'\Delta_a\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2[y'^2 - 2y'z'\Delta_a\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\sin(\boldsymbol{q}\cdot\boldsymbol{R})\right\}; \\
&\boldsymbol{q}||\hat{z}, \quad \Delta\theta_a = \Delta_a\left\{q[z' + y'\Delta_a\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2[z'^2 + 2z'y'\Delta_a\sin(\boldsymbol{q}\cdot R)]\sin(\boldsymbol{q}\cdot\boldsymbol{R})\right\}.
\end{aligned}
$$

Similarly, for distortions B and C,

$$
\begin{aligned}
&\boldsymbol{q}||\hat{x}, \quad \Delta\theta_b = \Delta_b\left\{q[x' + z'\Delta_b\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2[x'^2 + 2x'z'\Delta_b\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\sin(\boldsymbol{q}\cdot\boldsymbol{R})\right\}; \\
&\boldsymbol{q}||\hat{y}, \quad \Delta\theta_b = \Delta_b\left[qy'\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2y'^2\sin(\boldsymbol{q}\cdot\boldsymbol{R})\right]; \\
&\boldsymbol{q}||\hat{z}, \quad \Delta\theta_b = \Delta_b\left\{q[z' - x'\Delta_b\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2[z'^2 - 2z'x'\Delta_b\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\sin(\boldsymbol{q}\cdot\boldsymbol{R})\right\}.
\end{aligned}
$$

$$\begin{aligned}
&\boldsymbol{q}||\hat{x}, \quad \Delta\theta_c = \Delta_c\Big\{q[x' - y'\Delta_c\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2[x'^2 - 2x'y'\Delta_c\sin(\boldsymbol{q}\cdot\boldsymbol{R})]\sin(\boldsymbol{q}\cdot\boldsymbol{R})\Big\};\\
&\boldsymbol{q}||\hat{y}, \quad \Delta\theta_c = \Delta_c\Big\{q[x'\Delta_c\sin(\boldsymbol{q}\cdot\boldsymbol{R}) + y']\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2[2x'y'\Delta_c\sin(\boldsymbol{q}\cdot\boldsymbol{R}) + y'^2]\sin(\boldsymbol{q}\cdot\boldsymbol{R})\Big\};\\
&\boldsymbol{q}||\hat{z}, \quad \Delta\theta_c = \Delta_c\Big[qz'\cos(\boldsymbol{q}\cdot\boldsymbol{R}) - \frac{1}{2}q^2z'^2\sin(\boldsymbol{q}\cdot\boldsymbol{R})\Big]. \qquad (17)
\end{aligned}$$

Notice that here $\boldsymbol{q}$ is still in the laboratory frame (unprimed system).

Expanding rotation matrix $D^{(l'')}_{M+P-m-p,s}(\Delta\Omega)$ into the power series of $\Delta\theta_a$, $\Delta\theta_b$, $\Delta\theta_c$ and keeping only linear and quadratic terms, we find that terms like $\sin(\boldsymbol{q}\cdot\boldsymbol{R})$, $\cos(\boldsymbol{q}\cdot\boldsymbol{R})$. $\sin(\boldsymbol{q}\cdot\boldsymbol{R})\cos(\boldsymbol{q}\cdot\boldsymbol{R})$ will be zeros after integration over $\mathrm{d}\boldsymbol{R}$ and terms like $\sin^2(\boldsymbol{q}\cdot\boldsymbol{R})$, $\cos^2(\boldsymbol{q}\cdot\boldsymbol{R})$ will be $V/2$. So by simply setting

$$\begin{aligned}
\boldsymbol{q}||\hat{x}, \quad &\Delta\theta_a = \Delta_a qx',\\
&\Delta\theta_b = \Delta_b qx' - (\Delta_b q)^2x'z',\\
&\Delta\theta_c = \Delta_c qx' + (\Delta_c q)^2x'y',\\
\boldsymbol{q}||\hat{y}, \quad &\Delta\theta_a = \Delta_a qy' + (\Delta_a q)^2y'z',\\
&\Delta\theta_b = \Delta_b qy',\\
&\Delta\theta_c = \Delta_c qy' - (\Delta_c q)^2x'y',\\
\boldsymbol{q}||\hat{z}, \quad &\Delta\theta_a = \Delta_a qz' - (\Delta_a q)^2y'z',\\
&\Delta\theta_b = \Delta_b qz' + (\Delta_b q)^2x'z',\\
&\Delta\theta_c = \Delta_c qz', \qquad (18)
\end{aligned}$$

and absorbing $1/\sqrt{2}$ into coefficient $v_{j'j''j}$, we will obtain same integration results.

In geometry A, B and C the expansions of $D^{(l'')}_{M+P-m-p,s}(\Delta\Omega)$ for $\boldsymbol{q}||\hat{x}$, $\boldsymbol{q}||\hat{y}$, $\boldsymbol{q}||\hat{z}$ are

$$\begin{aligned}
&D^{(l'')}_{M+P-m-p,s}(\Delta\Omega)\\
=&\Delta_\alpha^2q^2r^2\Big[K^{(l''\alpha)}_{m+p,s}\delta_{M+P,0} + D^{(\alpha i)}_{l''s}(M+P, m+p)\\
&\times\sqrt{\frac{4\pi}{2l''+1}}Y_{2,M+P}(\hat{r})\Big], \qquad (19)
\end{aligned}$$

where $\alpha = a, b, c$, $i = x, y, z$. Here the q^0 term and $Y_{2,m'}$ $(m' \neq M+P)$ in q^2 order are neglected since the former one will not contribute to the distortion energy and the latter will be zero after integration over $\hat{r}$. Coefficients $K^{(l''\alpha)}_{m+p,s}$, $D^{(\alpha i)}_{l''s}$ for $\alpha = a, b, c$, $i = x, y, z$ are given in Appendix A.

Substituting Eq.(19) into Eq.(10), one finds that the energy density has two terms. The one associated with $K^{(l''\alpha)}_{m+p,s}$ is denoted by E_1^α and has the form

$$\begin{aligned}
E_1^\alpha =&\frac{N}{2}\int\Delta_\alpha^2q^2r^4\mathrm{d}r\sum_{j'j''j}\sum_{k'k''k}v_{j'j''j}(r)f_{k'k''k}(r)\sum_{m'p'}Q_{j'm'}Q_{k'p'}\sum_{l'}C(j'k'l';m',p')\\
&\times\sum_{m''p''}Q_{j''m''}Q_{k''p''}\sum_{l''}C(j''k''l'';m'',p'')\sum_{qs}(-1)^qK^{(l''\alpha)}_{q,s}\langle D^{(l')}_{q,m'+p'}(\Omega_R)\rangle_{\Omega_R}\\
&\times\langle D^{(l'')}_{s,m''+p''}(\Omega_r)\rangle_{\Omega_r}\delta_{jk}\delta_{l'l''}\frac{(2j+1)(2l'+1)}{(2k'+1)}W(j'j''k'k'';j,l'), \qquad (20)
\end{aligned}$$

where $\alpha = a, b, c$, $W(j'j''k'k'';j,l')$ is Racah coefficient[6] and is defined as

$$\begin{aligned}
W(j'j''k'k'';j,l') =&\frac{1}{\sqrt{(2j+1)(2l'+1)}}\sum_{mM}C(j'j''j;m,M-m)C(jk''k';M,-M-p)\\
&\times C(j'l'k';m,-m-p)C(j''k''l';M-m,-M-p). \qquad (21)
\end{aligned}$$

The second term associated with $D^{(\alpha i)}_{l''s}(M+P, m+p)(\alpha = a, b, c,\ i = x, y, z)$ is denoted by $E_2^{\alpha i}$ and has the form

$$
\begin{aligned}
E_2^{\alpha i} =& \frac{N}{2}\int \Delta_\alpha^2 q^2 r^4 \mathrm{d}r \sum_{j'j''j}\sum_{k'k''k} v_{j'j''j}(r) f_{k'k''k}(r) C(jk2;0,0)\sum_{m'p'} Q_{j'm'}Q_{k'p'} \\
&\times \sum_{l'} (-1)^{l'} \sqrt{\frac{(2j+1)(2k+1)}{(2l'+1)(2l''+1)}} C(j'k'l';m',p') \sum_{m''p''} Q_{j''m''}Q_{k''p''} \\
&\times \sum_{l''} C(j''k''l'';m'',p'') X(j'k'l';j''k''l'';jk2) \\
&\times \sum_{qs} (-1)^q \langle D^{(l')}_{q,m'+p'}(\Omega_R)\rangle_{\Omega_R} \langle D^{(l'')}_{s,m''+p''}(\Omega_r)\rangle_{\Omega_r} D^{(\alpha i)}_{l''sl'}(q),
\end{aligned} \tag{22}
$$

where $D^{(\alpha i)}_{l''sl'}(q) = \sum\limits_x (-1)^x C(l''2l';x-q,-x) D^{(\alpha i)}_{l''s}(x,q)$,

$$
\begin{aligned}
X(j'j''j;k'k''k;l'l''2) =& \sum_{mpM} C(j'j''j;m,M-m) C(k'k''k;p,P-p) C(j'k'l';m,p) \\
&\times C(j''k''l'';M-m,P-p) C(jk2;M,P) C(l'l''2;m+p,M+P-m-p).
\end{aligned}
$$

For centrosymmetric molecule we have considered, the average values $\langle D^{(l')}_{q,m'+p'}(\Omega_R)\rangle_{\Omega_R}$, $\langle D^{(l'')}_{s,m''+p''}(\Omega_r)\rangle_{\Omega_r}$ will be zero when l', l'' are odd numbers. In order to express the total distortion energy in terms of orientation orders at both $\boldsymbol{R}+\boldsymbol{r}$ and $\boldsymbol{R}$ places, the lowest order terms are taken to be $l'=l''=2$. Further restricting ourselves to quadrupole moment interactions, we simplify Eqs.(20), (22) to obtain total energy as

$$
\begin{aligned}
E_1^{\alpha} =& \frac{N}{2}\int \Delta_\alpha^2 q^2 \{\Gamma[\bar{Q}_0^2 D^{(\alpha i)}_{202}(0) + \bar{Q}_0\bar{Q}_2 (D^{(\alpha i)}_{222}(0) + D^{(\alpha i)}_{2-22}(0) + D^{(\alpha i)}_{202}(2) + D^{(\alpha i)}_{202}(-2)) \\
&+ \bar{Q}_2^2 (D^{(\alpha i)}_{222}(2) + D^{(\alpha i)}_{2-22}(2) + D^{(\alpha i)}_{222}(-2) + D^{(\alpha i)}_{2-22}(-2))] \\
&+ \Gamma'[\bar{Q}_0^2 K^{(2\alpha)}_{00} + \bar{Q}_0\bar{Q}_2 (K^{(2\alpha)}_{02} + K^{(2\alpha)}_{20} + K^{(2\alpha)}_{0-2} + K^{(2\alpha)}_{-20}) \\
&+ \bar{Q}_2^2 (K^{(2\alpha)}_{22} + K^{(2\alpha)}_{2-2} + K^{(2\alpha)}_{-22} + K^{(2\alpha)}_{-2-2})]\},
\end{aligned} \tag{23}
$$

where $\alpha = a,b,c,\ \ i = x,y,z$,

$$
\begin{aligned}
\Gamma =& -\sqrt{\frac{2}{7}} N \int \sum_{jk} v_{22j}(r) f_{22k}(r) \\
&\times X(222;222;jk2) r^4 \mathrm{d}r, \\
\Gamma' =& N \int \sum_{j} v_{22j}(r) f_{22j}(r)(2j+1) \\
&\times W(2222;j,2) r^4 \mathrm{d}r, \\
\bar{Q}_0 =& Q_0 \langle D^{(2)}_{00}\rangle + Q_2 \langle D^{(2)}_{02} + D^{(2)}_{0-2}\rangle, \\
\bar{Q}_2 =& Q_0 \langle D^{(2)}_{20}\rangle + Q_2 \langle D^{(2)}_{22} + D^{(2)}_{2-2}\rangle, \\
Q_0 =& \sum_m C(222;m,-m) Q_{2m} Q_{2,-m} \\
=& \sqrt{\frac{2}{7}} (2Q_{2,2}^2 - Q_{2,0}^2), \\
Q_2 =& \sum_m C(222;m,2-m) Q_{2m} Q_{2,2-m} \\
=& 2\sqrt{\frac{2}{7}} Q_{2,0} Q_{2,2}.
\end{aligned} \tag{24}
$$

These definitions of $\bar{Q}_0$, $\bar{Q}_2$ are similar to those defined by Freiser.[7] Using the tables in Appendix A and comparing Eqs.(24) and (23), we have

$$
\begin{aligned}
K_{bb} =& -\left(\Gamma + \frac{1}{2}\Gamma'\right)\left(\bar{Q}_0 - \sqrt{\frac{2}{3}}\bar{Q}_2\right)^2, \\
K_{ac} = K_{ca} =& \frac{1}{2}(\Gamma - \Gamma')\left(\bar{Q}_0 - \sqrt{\frac{2}{3}}\bar{Q}_2\right)^2, \\
K_{cc} =& -\left(\Gamma + \frac{1}{2}\Gamma'\right)\frac{8}{3}\bar{Q}_2^2, \\
K_{ab} = K_{ba} =& \frac{1}{2}(\Gamma - \Gamma')\frac{8}{3}\bar{Q}_2^2, \\
K_{aa} =& -\left(\Gamma + \frac{1}{2}\Gamma'\right)\left(\bar{Q}_0 + \sqrt{\frac{2}{3}}\bar{Q}_2\right)^2, \\
K_{bc} = K_{cb} =& \frac{1}{2}(\Gamma - \Gamma')\left(\bar{Q}_0 + \sqrt{\frac{2}{3}}\bar{Q}_2\right)^2.
\end{aligned} \tag{25}
$$

In the uniaxial case, they become

$$
\begin{aligned}
K_{bb} =& -\left(\Gamma + \frac{1}{2}\Gamma'\right)\bar{Q}_0^2,\\
K_{ac} =& \frac{1}{2}(\Gamma - \Gamma')\bar{Q}_0^2,\\
K_{ca} =& \frac{1}{2}(\Gamma - \Gamma')\bar{Q}_0^2,\\
K_{ab} =& K_{ba} = K_{cc} = 0,\\
K_{aa} =& -\left(\Gamma + \frac{1}{2}\Gamma'\right)\bar{Q}_0^2,\\
K_{bc} =& \frac{1}{2}(\Gamma - \Gamma')\bar{Q}_0^2,\\
K_{cb} =& \frac{1}{2}(\Gamma - \Gamma')\bar{Q}_0^2. \qquad (26)
\end{aligned}
$$

Comparing these with Frank elastic constants, we have $K_{bb} = K_{aa} = K_{22}$, $K_{ac} = K_{bc} = K_{11}$, $K_{ca} = K_{ac} = K_{33}$ and $K_{11} = K_{33}$. In derivations above, we only considered the molecular interaction energy as free energy density. Generally, free energy density should be $F = E - TS$ where T is temperature, S is entropy. In uniaxial nematics, Priest[8] and Gelbart and Ben-Shaul[9] argued that entropy density can be written as $S_{\rm tot} = S_{\rm rot} + S_{\rm trans}$ where $S_{\rm rot}$ and $S_{\rm trans}$ are rotational and translational entropy density respectively. Since rotational entropy has the form of $\int f(\Omega)\ln f(\Omega)\mathrm{d}\Omega$ where Ω is the relative angle between the long axis of molecule and director $\hat{n}$, it makes no contribution to distortion energy. The translational entropy $S_{\rm trans}$ can also be written as a rotational invariant in a form similar to Eq.(6) with an additional constant λ. For the detailed derivation see Appendix B. In this case, all K's will be amplified by a factor $(1-\lambda)$, where $\lambda \equiv k_{\rm B}T\dfrac{g'(E_0)}{g(E_0)}$, $g'(E_0) \equiv \dfrac{\mathrm{d}g(E)}{\mathrm{d}E}|_{E=E_0}$, $g(E_0)$ is the microscopic state number density at non-distorted energy E_0.

According to Landau–de Gennes's theory, elastic energy density of biaxial nematics is

$$
\begin{aligned}
F_L =& \frac{L_1}{2}(\partial_i Q_{jk})(\partial_i Q_{jk})\\
&+ \frac{L_2}{2}(\partial_i Q_{ik})(\partial_j Q_{jk}), \qquad (27)
\end{aligned}
$$

where $Q_{ij} = S\left(c_i c_j - \dfrac{1}{3}\delta_{ij}\right) + \dfrac{1}{3}P(a_i a_j - b_i b_j)$.

Substituting Q_{ij} into Eq.(27), we have

$$
\begin{aligned}
K_{bb} =& 2L_1\left(S - \frac{1}{3}P\right)^2,\\
K_{ac} =& K_{ca} = (2L_1 + L_2)\left(S - \frac{1}{3}P\right)^2,\\
K_{cc} =& 2L_1\left(\frac{2}{3}P\right)^2,\\
K_{ab} =& K_{ba} = (2L_1 + L_2)\left(\frac{2}{3}P\right)^2,\\
K_{aa} =& 2L_1\left(S + \frac{1}{3}P\right)^2,\\
K_{bc} =& K_{cb} = (2L_1 + L_2)\left(S + \frac{1}{3}P\right)^2,\\
C_{ab} =& C_{bc} = C_{ca} = 0. \qquad (28)
\end{aligned}
$$

Comparing our results of elastic constants with those in Eq.(28), we have

$$
\begin{aligned}
&\bar{Q}_0 = S, \quad \bar{Q}_2 = \frac{\sqrt{6}}{6}P,\\
&(1-\lambda)\Gamma = \frac{2}{3}L_2,\\
&(1-\lambda)\Gamma' = -4(L_1 + \frac{1}{3}L_2).
\end{aligned}
$$

The two rotational invariants are

$$
\begin{aligned}
&\bar{Q}_0^2 + 2\bar{Q}_2^2 = S^2 + \frac{1}{3}P^2,\\
&\bar{Q}_0(\bar{Q}_0^2 - 6\bar{Q}_2^2) = S(S^2 - P^2).
\end{aligned}
$$

Notice that in simple distortion patterns we have considered, the coupled terms C_{ab}, C_{bc}, C_{ca} do not appear. In order to derive such terms, more complicated distortions need to be considered.

4. Conclusion

In this paper, we derive nine elastic constants for simple distortion patterns in biaxial nematics in terms of thermal average $\langle D^{(l)}_{mn}\rangle\langle D^{(l')}_{m'n'}\rangle$, where $D^{(l)}_{mn}$ is Wigner rotation matrix. In the lowest order l, l', the elastic constants depend on coefficients Γ, Γ' and λ, order parameters $\bar{Q}_0$ and $\bar{Q}_2$. Coefficients Γ and Γ' depend on the interaction energy function $v_{j'j''j}(r_{12})$ and probability function $f_{k'k''k}(r_{12})$ where r_{12} is the distance between two molecules. Coefficient λ depends on temperature and the microscopic state number density at the neighbourhood of non-distorted equilibrium energy. Q_0 and Q_2 are parameters related to multiple moments of molecules. Comparing our results with those obtained from Landau–de Gennes theory, relationships between coefficients, order parameters used in both theories are obtained. In the special case of uniaxial nematics, both results are reduced to a degenerate case where $K_{11} = K_{33}$.

Appendix A

Since $\langle D^{(l')}_{m+p,m'+p'}(\Omega_R)\rangle_{\Omega_R}$, $\langle D^{(l'')}_{s,m''+p''}(\Omega_r)\rangle_{\Omega_r}$ will be zero for odd $m+p$, s, values of $m+p$, s are taken to be 0, ± 2 for $l'=l''=2$. Tables 1–5 list all values of $D^{(\alpha i)}_{2s}(M+P,m+p)$ and $K^{(2i)}_{m+p,s}$ where $\alpha = a,b$, $i = x,y,z$. In distortion patterns A and B $D^{(ai)}_{2s}(M+P,-2) = D^{(ai)}_{2s}(-M-P,2)$, $D^{(bi)}_{2s}(M+P,-2) = D^{(bi)}_{2s}(-M-P,2)$. In distortion pattern C,

$$D^{(cx)}_{2-2}(0,2) = D^{(cx)}_{22}(0,-2) = \frac{2}{3},$$

$$D^{(cy)}_{2-2}(0,2) = D^{(cy)}_{22}(0,-2) = \frac{2}{3},$$

$$D^{(cz)}_{2-2}(0,2) = D^{(cz)}_{22}(0,-2) = -\frac{4}{3}.$$

The rests of $D^{(ci)}_{2s}(M+P,m+p)$ are zeros.

Table 1. Coefficients $D^{(ai)}_{2s}(M+P,0)(i=x,y,z)$ in Eq.(19).

$M+P=(-2,-1,0,1,2)$			
s	$D^{(ax)}_{2s}(M+P,0)$	$D^{(ay)}_{2s}(M+P,0)$	$D^{(az)}_{2s}(M+P,0)$
0	$\left(-\frac{1}{4},0,\frac{1}{2},0,-\frac{1}{4}\right)$	$\left(\frac{1}{4},-\frac{1}{2},\frac{1}{2},-\frac{1}{2},\frac{1}{4}\right)$	$\left(0,\frac{1}{2},-1,\frac{1}{2},0\right)$
2	$\left(0,0,\frac{\sqrt{6}}{12},0,-\frac{\sqrt{6}}{12}\right)$	$\left(0,0,\frac{\sqrt{6}}{12},-\frac{\sqrt{6}}{6},\frac{\sqrt{6}}{12}\right)$	$\left(0,0,-\frac{\sqrt{6}}{6},\frac{\sqrt{6}}{6},0\right)$
-2	$\left(-\frac{\sqrt{6}}{12},0,\frac{\sqrt{6}}{12},0,0\right)$	$\left(\frac{\sqrt{6}}{12},-\frac{\sqrt{6}}{6},\frac{\sqrt{6}}{12},0,0\right)$	$\left(0,\frac{\sqrt{6}}{6},-\frac{\sqrt{6}}{6},0,0\right)$

Table 2. Coefficients $D^{(ai)}_{2s}(M+P,2)(i=x,y,z)$ in Eq.(19).

$M+P=(-2,-1,0,1,2)$			
s	$D^{(ax)}_{2s}(M+P,2)$	$D^{(ay)}_{2s}(M+P,2)$	$D^{(az)}_{2s}(M+P,2)$
0	$\left(0,0,\frac{\sqrt{6}}{12},0,-\frac{\sqrt{6}}{4}\right)$	$\left(0,0,\frac{\sqrt{6}}{12},-\frac{1}{2},\frac{\sqrt{6}}{4}\right)$	$\left(0,0,-\frac{\sqrt{6}}{6},\frac{1}{2},0\right)$
2	$\left(0,0,0,0,-\frac{1}{4}\right)$	$\left(0,0,0,0,\frac{1}{4}\right)$	$(0,0,0,0,0)$
-2	$\left(0,0,\frac{1}{6},0,-\frac{1}{4}\right)$	$\left(0,0,\frac{1}{6},-\frac{\sqrt{6}}{6},\frac{1}{4}\right)$	$\left(0,0,-\frac{1}{3},\frac{\sqrt{6}}{6},0\right)$

Table 3. Coefficients $D^{(bi)}_{2s}(M+P,0)(i=x,y,z)$ in Eq.(19).

$M+P=(-2,-1,0,1,2)$			
s	$D^{(bx)}_{2s}(M+P,0)$	$D^{(by)}_{2s}(M+P,0)$	$D^{(bz)}_{2s}(M+P,0)$
0	$\left(\frac{1}{4},-\frac{1}{2},\frac{1}{2},-\frac{1}{2},\frac{1}{4}\right)$	$\left(-\frac{1}{4},0,\frac{1}{2},0,-\frac{1}{4}\right)$	$\left(0,\frac{1}{2},-1,\frac{1}{2},0\right)$
2	$\left(0,0,-\frac{\sqrt{6}}{12},\frac{\sqrt{6}}{6},-\frac{\sqrt{6}}{12}\right)$	$\left(0,0,-\frac{\sqrt{6}}{12},0,\frac{\sqrt{6}}{12}\right)$	$\left(0,0,\frac{\sqrt{6}}{6},-\frac{\sqrt{6}}{6},0\right)$
-2	$\left(-\frac{\sqrt{6}}{12},\frac{\sqrt{6}}{6},-\frac{\sqrt{6}}{12},0,0\right)$	$\left(\frac{\sqrt{6}}{12},0,-\frac{\sqrt{6}}{12},0,0\right)$	$\left(0,-\frac{\sqrt{6}}{6},\frac{\sqrt{6}}{6},0,0\right)$

Table 4. Coefficients $D^{(bi)}_{2s}(M+P,2)(i=x,y,z)$ in Eq.(19).

$M+P=(-2,-1,0,1,2)$			
s	$D^{(bx)}_{2s}(M+P,2)$	$D^{(by)}_{2s}(M+P,2)$	$D^{(bz)}_{2s}(M+P,2)$
0	$\left(0,0,-\frac{\sqrt{6}}{12},\frac{1}{2},-\frac{\sqrt{6}}{4}\right)$	$\left(0,0,-\frac{\sqrt{6}}{12},0,\frac{\sqrt{6}}{4}\right)$	$\left(0,0,\frac{\sqrt{6}}{6},-\frac{1}{2},0\right)$
2	$\left(0,0,0,0,\frac{1}{4}\right)$	$\left(0,0,0,0,-\frac{1}{4}\right)$	$(0,0,0,0,0)$
-2	$\left(0,0,\frac{1}{6},-\frac{\sqrt{6}}{6},\frac{1}{4}\right)$	$\left(0,0,\frac{1}{6},0,-\frac{1}{4}\right)$	$\left(0,0,-\frac{1}{3},\frac{\sqrt{6}}{6},0\right)$

Table 5. Coefficients $K^{(2i)}_{m+p,s}(i=a,b,c)$ in Eq.(19).

$m+p=(-2,0,2)$			
s	$K^{(2a)}_{m+p.,s}$	$K^{(2b)}_{m+p,s}$	$K^{(2c)}_{m+p,s}$
0	$\left(-\frac{\sqrt{6}}{12},-\frac{1}{2},-\frac{\sqrt{6}}{12}\right)$	$\left(\frac{\sqrt{6}}{12},-\frac{1}{2},\frac{\sqrt{6}}{12}\right)$	$(0,0,0)$
2	$\left(-\frac{1}{6},-\frac{\sqrt{6}}{12},0\right)$	$\left(-\frac{1}{6},\frac{\sqrt{6}}{12},0\right)$	$\left(-\frac{2}{3},0,0\right)$
-2	$\left(0,-\frac{\sqrt{6}}{12},-\frac{1}{6}\right)$	$\left(0,\frac{\sqrt{6}}{12},-\frac{1}{6}\right)$	$\left(0,0,-\frac{2}{3}\right)$

Appendix B

Consider a liquid crystal system contacting a heat reservoir of temperature T. Suppose the probability for molecule 1, 2, ..., N at position $\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N$ is $p(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,r_N)$. The corresponding entropy is

$$S_{\text{trans}}=-k_{\text{B}}\int p(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\times\ln p(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\ldots\mathrm{d}\boldsymbol{r}_N. \quad \text{(B1)}$$

Suppose the interaction energy between molecules 1, 2 at positions $\boldsymbol{r}_1,\boldsymbol{r}_2$ with orientations Ω_1,Ω_2 respectively is $V_{12}(\boldsymbol{r}_1,\boldsymbol{r}_2,\Omega_1,\Omega_2)$. Averaging over all possible orientations of Ω_1,Ω_2 gives the interaction energy between molecules 1, 2 depending on positions only, i.e.,

$$V_{12}(\boldsymbol{r}_1,\boldsymbol{r}_2)\equiv\langle V_{12}(\boldsymbol{r}_1,\boldsymbol{r}_2,\Omega_1,\Omega_2)\rangle_{\Omega_1,\Omega_2}. \quad \text{(B2)}$$

The total interaction energy of the system depending on positions $\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N$ is

$$V_t(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)=\frac{1}{2}\sum_{i\neq j}\sum_j V_{ij}(\boldsymbol{r}_i,\boldsymbol{r}_j). \quad \text{(B3)}$$

The probability function $p(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ is given by the Boltzmann distribution

$$p(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)=\frac{1}{Z}\exp\left[-\frac{V_{\text{t}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)}{k_{\text{B}}T}\right]. \quad \text{(B4)}$$

where partition function

$$Z=\int\exp\left[-\frac{V_t(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)}{k_{\text{B}}T}\right]\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\ldots\mathrm{d}\boldsymbol{r}_N.$$

Substitute Eqs.(B4) into Eq.(B1), we have the translational entropy

$$\begin{aligned}S_{\text{trans}}=&\frac{1}{T}\int p(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\\&\times V_{\text{t}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\ldots\mathrm{d}\boldsymbol{r}_N+k_{\text{B}}\ln Z\\=&\frac{1}{T}\langle V_{\text{t}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\rangle_{\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N}+k_{\text{B}}\ln Z\\=&\frac{1}{2T}\sum_{i\neq j}\sum_j\langle V_{ij}(\boldsymbol{r}_i,\boldsymbol{r}_j,\Omega_i,\Omega_j)\rangle_{\boldsymbol{r}_i,\boldsymbol{r}_j,\Omega_i,\Omega_j}\\=&\frac{1}{T}E+k_{\text{B}}\ln Z,\end{aligned} \quad \text{(B5)}$$

where E is the total internal energy of the system. Suppose in the energy interval $\mathrm{d}V_{\text{t}}$, the number of microscopic states is $g(V_{\text{t}})\mathrm{d}V_{\text{t}}$. The partition function can be rewritten as

$$Z=\int\exp[-\frac{V_{\text{t}}}{k_{\text{B}}T}]g(V_{\text{t}})\mathrm{d}V_{\text{t}}. \quad \text{(B6)}$$

According to the statistical theory, for a large-number-molecule system, integration function $\exp\left[-\frac{V_{\text{t}}}{k_{\text{B}}T}\right]g(V_{\text{t}})$ has a sharp peak value in a narrow energy interval ΔV_{t} at energy $\tilde{E}$. Consequently,

$$Z\approx\exp\left[-\frac{\tilde{E}}{k_{\text{B}}T}\right]g(\tilde{E})\Delta V_{\text{t}}. \quad \text{(B7)}$$

Hence $\ln Z\approx-\frac{\tilde{E}}{k_{\text{B}}T}+\ln(g(\tilde{E}))+\ln(\Delta V_{\text{t}})$. Compared with the first two terms, the last term $\ln(\Delta V_{\text{t}})$ can be neglected. So

$$\begin{aligned}S_{\text{trans}}=&\frac{1}{T}E+k_{\text{B}}\ln Z\\\approx&\frac{1}{T}E-\frac{1}{T}\tilde{E}+k_{\text{B}}\ln(g(\tilde{E})).\end{aligned} \quad \text{(B8)}$$

According to the statistical theory, $\tilde{E}=E$ where E is the internal energy of the state. So $S_{\text{trans}}=k_{\text{B}}\ln(g(E))$. Expanding E in the neighbourhood of uniform state energy E_0 (where there is no director distortion), we have

$$S_{\rm trans} = k_{\rm B}\ln(g(E_0)) + k_{\rm B}\frac{1}{g(E_0)}g'(E_0)E_{\rm t}^{\alpha}, \qquad \equiv(1-\lambda)E_{\rm t}^{\alpha}, \tag{B9}$$

where $E_{\rm t}^{\alpha} \equiv \Delta E = E - E_0$ is the distortion energy. The free energy density of the system is then

$$F = E - TS_{\rm trans} = E_{\rm t}^{\alpha}\left[1 - k_{\rm B}T\frac{g'(E_0)}{g(E_0)}\right]$$

where

$$\lambda \equiv k_{\rm B}T\frac{g'(E_0)}{g(E_0)}, \quad g'(E_0) \equiv \left.\frac{{\rm d}g(E)}{{\rm d}E}\right|_{E=E_0}.$$

References

[1] Saupe A 1981 *J. Chem. Phys.* **75** 5118

[2] Govers E and Vetogen G 1984 *Phys. Rev.* A **30** 1998

[3] Liu H 2000 *Acta Phys. Sin.* **49** 932 (in Chinese)

[4] de Gennes P G and Prost J 1993 *The Physics of Liquid Crystals* 2nd edn (Oxford: Clarendon)

[5] Guan R H, Wang C R, Yu H, Kang W X, Huai J X and Yang G C 2005 *Chin. Phys.* **14** 386

[6] Rose M 1967 *Elementary Theory of Angular Momentum* (New York: Wiley)

[7] Freiser M J 1971 *Mol. Cryst. Liq. Cryst.* **14** 165

[8] Priest R G 1973 *Phys. Rev.* A **7** 720

[9] Gelbart W M and Ben-Shaul A 1982 *J. Chem. Phys.* **77** 916