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Molecular theory of nematic liquid crystals viewed as effect of collective excitation in ferromagnetic systems*

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We develop a microscopic theory of the nematic phase with consideration of the effect of the collective excitation on properties of nematic liquid crystals. The model is based on the Heisenberg's exchange model of the ferromagnetic materials. Since the orientation of the molecular long axis and the angular momentum of the molecule rotating around its long axis have the same direction, operators can be introduced to research the nematic liquid crystals. Using the lattice model and the Holstein–Primakoff transformation, the Hamiltonian of the system can be obtained, which has the same form as that of the ferromagnetic substance. The relation between the order parameter and reduced temperature can be gotten. It is in good agreement with the experimental results in the low temperature region, the accordance is better than that of the molecular field theory and the computer simulation. In high temperature region close to the transition point, by considering the effect of the higher-order terms in the Hamiltonian, theoretical prediction is in better agreement with the experiment. That indicates the many-body effect is important to nematic liquid crystals.

Keywords: nematic liquid crystals, collective excitation, order parameters
PACC: 6130, 6130C, 6470M

1. Introduction

As far as the microscopic theoretical description of the nematic liquid crystals (NLC)[1−7] is concerned, two aspects should be included: one is the micromechanism which result in the molecular orientational order, the other is the statistical method. Since the pioneering work of Onsager and Ann,[8] Flory[9] and Maier–Saupe,[10,11] a large number of molecular theories of nematic order have been proposed, and all but a very few of them fall into one of the following two groups: (1) The Maier–Saupe theory and its extensions and variants, which assume that nematic long-range order results primarily from orientation-dependent intermolecular attractions. (2) The hard-rod and van der Waals theories, in which the nematic order is assumed to result from the orientation-dependence of the very short-ranged intermolecular repulsion. The method adopted in the Maier–Saupe theory resembles the one treating the mean field in the ferromagnetic theory. The method of cluster expansion of the imperfect gas statistic theory is adopted in the hard-rod theory, and the two-particle group is considered only. Certainly, the development of the microscopic theory of NLC should include the above two aspects, such as Rajan and Woo who adopted the method of Born–Green–Yvon in liquid theory.[12] But this modification cannot reflect sufficiently the influence of the collective excitation. The collective excitation is a kind of many-body effect, which deals with the correlation of the molecular motion. We know that the coulomb potential between electrons in metal will be shielded owning to the collective effect, and liquid helium shows the superfluid phenomenon due to the collective effect. Because NLC is the many-body system that contains a large number of molecules, we believe that for NLC, collective effect should be considered, which can influence the molecular orientational

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order.

Spin wave theory was proposed in 1930 by Bloch. There is a kind of the significant elementary excitations in solid-state theory arising from the interactions between local spins. For a spin system composed of N lattice points, only considering the exchange interactions of the nearest neighbour lattices and assuming that the exchange integrals J are the same, then the interaction of the spins can be expressed as $V = -2J \sum\limits_{(i,j)} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j = -2 \sum\limits_{(i,j)} V_{ij}$, where $\sum\limits_{(i,j)}$ denotes the sum over all nearest pairs of molecules. That is Heisenberg's exchange model.[13] Using the model, the correlation of the molecular motion can be included and the intermolecular interaction potential of NLC can be obtained. A five-dimensional vector is introduced to denote the order parameter tensor in the second part of this paper. Every component of the five-dimensional vector can be expressed using the angular momentum operators. Then, let the operators act on the orientational quantum state $|n\rangle = |l, m\rangle$ and make the Holstein–Primakoff transformation,[14] the two-body interaction potential can be expressed with the creation operator and the annihilation operator. For researching the influence of the collective excitation on the system properties, expression of the creation operator and the annihilation operator in momentum space can be gotten using the Fourier transformation. These operators can operate on all the lattice point and represent the collective coordinates. By using Bose–Einstein statistics and numerical calculation, the relation of the order parameter and the reduced temperature can be obtained. The results we obtained by our theory are in good agreement with those of the experiment, especially in the low temperature region. Next, by considering the influence of the higher-order items, the modified relation of the order parameter and the reduced temperature can be gotten. It is shown that in high temperature region, the numerical results approach the experimental points. Our results fall between the results of Maier–Saupe and HJL, and the tendency of the curve is the same as theirs. That indicates the many-body effect is important to NLC. At last, the molecular field is used to solve the transition point in high temperature region. By calculating a self-consistent equation that the order parameters satisfy, we obtain that the order parameter is 0.4111 at the transition point, which is close to the Maier–Saupe's result of 0.4289.

2. Operator expression of the order parameter tensor in NLC

2.1. Intermolecular interaction potential and operator expression of the order parameter tensor

For the rod-like nematic molecules, only considering the interactions of the nearest neighbours, the interaction potential between the ith and the jth molecules can be expressed as

$$\begin{aligned} V_{ij} =& U(r_{ij}) P_2(\cos\theta_{ij}) = U(r_{ij}) P_2(\Omega_i \cdot \Omega_j) \\ =& U(r_{ij}) \left[\frac{3}{2} \cos^2 \theta_{ij} - \frac{1}{2} \right], \end{aligned} \tag{1}$$

where $U(r_{ij})$ is only related to the molecular centre-of-mass position, so it is called the radial interaction potential; $P_2(\cos\theta_{ij})$ is the second Legendre polynomial, it is only related to the molecular orientation; Ω_i and Ω_j are orientation unit vectors of the molecular i and j, respectively; θ_{ij} is the angle between Ω_i and Ω_j.

Usually, the order parameter tensor is defined as

$$Q = \begin{pmatrix} \left\langle \frac{3}{2}\Omega_x^2 - \frac{1}{2} \right\rangle & \left\langle \frac{3}{2}\Omega_x\Omega_y \right\rangle & \left\langle \frac{3}{2}\Omega_x\Omega_z \right\rangle \\ \left\langle \frac{3}{2}\Omega_y\Omega_x \right\rangle & \left\langle \frac{3}{2}\Omega_y^2 - \frac{1}{2} \right\rangle & \left\langle \frac{3}{2}\Omega_y\Omega_z \right\rangle \\ \left\langle \frac{3}{2}\Omega_z\Omega_x \right\rangle & \left\langle \frac{3}{2}\Omega_z\Omega_y \right\rangle & \left\langle \frac{3}{2}\Omega_z^2 - \frac{1}{2} \right\rangle \end{pmatrix}, \tag{2}$$

where $\Omega_x = \sin\theta\cos\varphi$, $\Omega_y = \sin\theta\sin\varphi$, $\Omega_z = \cos\theta$, $< \ldots >$ represents statistical average. Using additive formula of spherical function and substituting into Eq.(1), we have

$$V_{ij} = \frac{2}{3} U(r_{ij}) \sum_{\mu\nu} Q_{\mu\nu}(i) Q_{\mu\nu}(j). \tag{3}$$

For the rigid rod-like molecule, the unit vector of

the molecular long axis is defined as orientation Ω. Assuming that the molecule rotates around its long axis, the direction of angular momentum $\boldsymbol{L}$ also lies along the long axis, therefore Ω and $\boldsymbol{L}$ have the same direction, as shown in Fig.1.

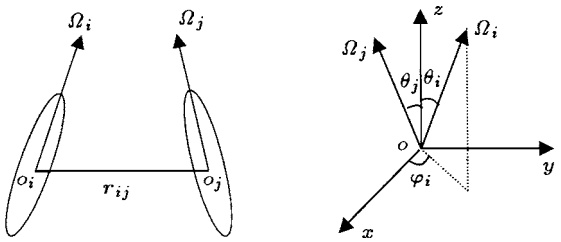


Fig.1. Sketch of the rod-like molecule.

We define the orientation operator

$$\hat{\Omega} = \frac{\hat{\boldsymbol{L}}}{|\boldsymbol{L}|} = \frac{\hat{\boldsymbol{L}}}{\sqrt{l(l+1)}\hbar}, \tag{4}$$

$$\hat{\Omega}_x = \frac{\hat{L}_x}{\sqrt{l(l+1)}\hbar}, \quad \hat{\Omega}_y = \frac{\hat{L}_y}{\sqrt{l(l+1)}\hbar},$$
$$\hat{\Omega}_z = \frac{\hat{L}_z}{\sqrt{l(l+1)}\hbar}. \tag{5}$$

In this way, the unit vector Ω can be expressed with operators, which is very crucial in our theory. Then the solid-state quantum theory can be used to research NLC. Substituting Eq.(5) into Eq.(2) and making it symmetrical, the order parameter tensor Q can be written as

$$Q = \frac{1}{l(l+1)\hbar^2} \begin{pmatrix} \frac{3}{2}\hat{L}_x^2 - \frac{1}{2}l(l+1)\hbar^2 & \frac{3}{4}(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x) & \frac{3}{4}(\hat{L}_x\hat{L}_z + \hat{L}_z\hat{L}_x) \\ \frac{3}{4}(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y) & \frac{3}{2}\hat{L}_y^2 - \frac{1}{2}l(l+1)\hbar^2 & \frac{3}{4}(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y) \\ \frac{3}{4}(\hat{L}_z\hat{L}_x + \hat{L}_x\hat{L}_z) & \frac{3}{4}(\hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z) & \frac{3}{2}\hat{L}_z^2 - \frac{1}{2}l(l+1)\hbar^2 \end{pmatrix}. \tag{6}$$

Obviously, as shown in the definition Eq.(6), the order parameter tensor is symmetric and traceless, i.e. $Q_{\mu\nu} = Q_{\nu\mu}, \mathrm{Tr}\boldsymbol{Q} = 0$.

2.2. τ vector and its operator expression

Because the order parameter tensor $\boldsymbol{Q}$ is a symmetric and traceless second rank tensor, it can be denoted by the five-dimensional column vector $\boldsymbol{\tau}$ as follows:

$$\tau_0 = \sqrt{\frac{3}{2}}Q_{33}, \quad \tau_{-1} = -\mathrm{i}Q_{23} + Q_{31}, \quad \tau_{+1} = \tau_{-1}^*,$$

$$\tau_{-2} = \frac{1}{2}(Q_{11} - Q_{22}) + \mathrm{i}Q_{12}, \quad \tau_{+2} = \tau_{-2}^*. \tag{7}$$

We introduce the step operators $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$. For convenience, the origin of coordinates is chosen at the molecular centre-of-mass, and then we can get the relations

$$[\hat{L}_x, \hat{L}_y] = -\mathrm{i}\hbar\hat{L}_z,$$
$$[\hat{L}_z, \hat{L}_\pm] = \mp\hbar\hat{L}_\pm, \quad [\hat{L}_+, \hat{L}_-] = -2\hbar\hat{L}_z,$$
$$\hat{L}_\pm\hat{L}_\mp = \hat{L}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z,$$
$$\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x = \frac{1}{2\mathrm{i}}(\hat{L}_+^2 - \hat{L}_-^2),$$
$$\hat{L}_x^2 - \hat{L}_y^2 = \frac{1}{2}(\hat{L}_+^2 + \hat{L}_-^2),$$
$$\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-), \quad \hat{L}_y = \frac{1}{2\mathrm{i}}(\hat{L}_+ - \hat{L}_-). \tag{8}$$

From Eqs.(6)–(8), the operator expression of τ_k $(k = 0, \pm1, \pm2)$ can be obtained:

$$\hat{\tau}_0 = \frac{\sqrt{\frac{3}{2}}[\frac{3}{2}\hat{L}_z^2 - \frac{1}{2}l(l+1)\hbar^2]}{l(l+1)\hbar^2},$$
$$\hat{\tau}_{-1} = \frac{\frac{3}{4}(\hat{L}_z\hat{L}_- + \hat{L}_-\hat{L}_z)}{l(l+1)\hbar^2},$$
$$\hat{\tau}_{+1} = \frac{\frac{3}{4}(\hat{L}_z\hat{L}_+ + \hat{L}_+\hat{L}_z)}{l(l+1)\hbar^2},$$
$$\hat{\tau}_{-2} = \frac{\frac{3}{4}\hat{L}_+^2}{l(l+1)\hbar^2},$$
$$\hat{\tau}_{+2} = \frac{\frac{3}{4}\hat{L}_-^2}{l(l+1)\hbar^2}. \tag{9}$$

This definition satisfies the equation $\sum_{\mu\nu} Q_{\mu\nu}Q_{\mu\nu} =$

$\boldsymbol{\tau}^{\dagger}\cdot\boldsymbol{\tau}$, thus Eq.(3) can be written as

$$\begin{aligned}V_{ij}=&\frac{2}{3}U(r_{ij})[\boldsymbol{\tau}(i)]^{\dagger}\cdot[\boldsymbol{\tau}(j)]\\=&\frac{2}{3}U(r_{ij})[\hat{\tau}_{+2}(i)\hat{\tau}_{-2}(j)\\&+\hat{\tau}_{+1}(i)\hat{\tau}_{-1}(j)+\hat{\tau}_{0}(i)\hat{\tau}_{0}(j)\\&+\hat{\tau}_{-1}(i)\hat{\tau}_{+1}(j)+\hat{\tau}_{-2}(i)\hat{\tau}_{+2}(j)].\end{aligned}\tag{10}$$

Supposing the orientational quantum state $\{|l,m_i\rangle |l,m_j\rangle\}$ is a set of eigenvectors in $(\hat{L}^2,\hat{L}_z)$ representation, using $\hat{L}_z|l,m\rangle = m\hbar|l,m\rangle$, $\hat{L}_{\pm}|l,m\rangle = \hbar C_{\pm}^{lm}|l,m\mp1\rangle$, $C_{\pm}^{lm}=[(l\pm m)(l\mp m+1)]^{\frac{1}{2}}$, we have,

$$\begin{aligned}\hat{\tau}_0|l,m\rangle&=\frac{\sqrt{\frac{3}{2}}[\frac{3}{2}m^2-\frac{1}{2}l(l+1)]}{l(l+1)}|l,m\rangle,\\\hat{\tau}_{-1}|l,m\rangle&=\frac{3}{4}\frac{(2m+1)C_{-}^{lm}}{l(l+1)}|l,m+1\rangle,\\\hat{\tau}_{+1}|l,m\rangle&=\frac{3}{4}\frac{(2m-1)C_{+}^{lm}}{l(l+1)}|l,m-1\rangle,\\\hat{\tau}_{-2}|l,m\rangle&=\frac{\sqrt{\frac{1}{2}}\frac{3}{2}C_{-}^{lm}C_{-}^{l,m+1}}{l(l+1)}|l,m+2\rangle,\\\hat{\tau}_{+2}|l,m\rangle&=\frac{\sqrt{\frac{1}{2}}\frac{3}{2}C_{+}^{lm}C_{+}^{l,m-1}}{l(l+1)}|l,m-2\rangle.\end{aligned}\tag{11}$$

2.3. Holstein–Primakoff transformation

$|l,m\rangle$ represents a orientational quantum state, where l is invariable, m is variable. Let $n=l-m$, then the single molecule orientational quantum state can also be expressed as $|n\rangle = |l,l-n\rangle$. Creation operator and annihilation operator are introduced as follows:

$$\begin{aligned}&\hat{a}|n\rangle=\sqrt{n}|n-1\rangle,\\&\hat{a}^{\dagger}|n\rangle=\sqrt{n+1}|n+1\rangle,\\&[\hat{a},\hat{a}^{\dagger}]=1,\quad \hat{a}^{\dagger}\hat{a}|n\rangle=n|n\rangle,\end{aligned}\tag{12}$$

where $\hat{a}^{\dagger}$ is the quasi-particle creation operator, $\hat{a}$ is the quasi-particle annihilation operator, $\hat{a}^{\dagger}\hat{a}$ is the quasi-particle number operator. Applying these operators to the orientational quantum state, we have

$$\begin{aligned}\hat{a}|n\rangle=&\hat{a}|l,l-n\rangle=\hat{a}|l,m\rangle\\=&\sqrt{l-m}|l,l-(n-1)\rangle=\sqrt{l-m}|l,m+1\rangle,\\\hat{a}^{\dagger}|n\rangle=&\hat{a}^{\dagger}|l,l-n\rangle=\hat{a}^{\dagger}|l,m\rangle\\=&\sqrt{l-m+1}|l,l-(n+1)\rangle\\=&\sqrt{l-m+1}|l,m-1\rangle.\end{aligned}\tag{13}$$

So $\hat{\tau}_k$ can be expressed by $\hat{a}^{\dagger}$ and $\hat{a}$,

$$\begin{aligned}\hat{\tau}_0&=\frac{1}{2}\sqrt{\frac{3}{2}}\frac{1}{l(l+1)}[l(2l-1)-3(2l-\hat{a}^{\dagger}\hat{a})\hat{a}^{\dagger}\hat{a}],\\\hat{\tau}_{-1}&=\frac{3}{4}\frac{2l-1-2\hat{a}^{\dagger}\hat{a}}{l(l+1)}\sqrt{2l-\hat{a}^{\dagger}\hat{a}}\hat{a},\\\hat{\tau}_{+1}&=\frac{3}{4}\frac{2l+1-2\hat{a}^{\dagger}\hat{a}}{l(l+1)}\sqrt{2l-\hat{a}^{\dagger}\hat{a}+1}\hat{a}^{\dagger},\\\hat{\tau}_{-2}&=\frac{3}{2}\sqrt{\frac{1}{2}}\frac{1}{l(l+1)}\sqrt{2l-\hat{a}^{\dagger}\hat{a}-1}\sqrt{2l-\hat{a}^{\dagger}\hat{a}}\hat{a}\hat{a},\\\hat{\tau}_{+2}&=\frac{3}{2}\sqrt{\frac{1}{2}}\frac{1}{l(l+1)}\sqrt{2l-\hat{a}^{\dagger}\hat{a}+2}\sqrt{2l-\hat{a}^{\dagger}\hat{a}+1}\hat{a}^{\dagger}\hat{a}^{\dagger}.\end{aligned}\tag{14}$$

Equation (10), the intermolecular interaction potential, can be rewritten with the creation operator and the annihilation operator as

$$\begin{aligned}V_{ij}=&\frac{2}{3}U(r_{ij})\Big[\frac{9}{2l^2}(\hat{a}_i^{\dagger}\hat{a}_i^{\dagger}\hat{a}_j\hat{a}_j+\hat{a}_i\hat{a}_i\hat{a}_j^{\dagger}\hat{a}_j^{\dagger})\\&+\frac{9}{2l}(\hat{a}_i^{\dagger}\hat{a}_j+\hat{a}_i\hat{a}_j^{\dagger})\\&+\frac{3}{2l^2}(l-3\hat{a}_i^{\dagger}\hat{a}_i)(l-3\hat{a}_j^{\dagger}\hat{a}_j)\Big].\end{aligned}\tag{15}$$

3. System Hamiltonian in lattice model

3.1. System Hamiltonian in primary approximation

It can be estimated that $l\gg1$. This estimation can be proved as follows: for $\boldsymbol{L}=I\boldsymbol{\omega}$, rotational kinetic energy can be expressed as $\overline{\frac{1}{2}I\omega^2}=\frac{1}{2}k_{\mathrm{B}}T$, where I is rotational inertia of the molecule. So we have $\overline{L^2}=Ik_{\mathrm{B}}T$, $\overline{l(l+1)\hbar^2}=Ik_{\mathrm{B}}T$. Using approximation, when l is comparatively large, the formula can be approximated as $\bar{l}=\frac{1}{\hbar}(Ik_{\mathrm{B}}T)^{\frac{1}{2}}$. For NLC molecules, I approximately equals to $10^{-43}\sim10^{-47}\mathrm{kg\cdot m^2}$,[15] at room-temperature, taking numerical estimation we can get $l\approx10\sim10^2$. So the assumption $l\gg1$ is reasonable. With this estimation, we have $\frac{n}{l}\ll1$, and using Eq.(14), $\hat{\tau}_k$ can be approximately expressed as

$$\begin{aligned}&\hat{\tau}_0\approx\sqrt{\frac{3}{2}}\frac{1}{l}(l-3\hat{a}^{\dagger}\hat{a}),\\&\hat{\tau}_{-1}\approx\frac{3}{\sqrt{2l}}\hat{a},\quad\hat{\tau}_{+1}\approx\frac{3}{\sqrt{2l}}\hat{a}^{\dagger},\\&\hat{\tau}_{-2}\approx\sqrt{\frac{1}{2}}\frac{3}{l}\hat{a}\hat{a},\quad\hat{\tau}_{+2}\approx\sqrt{\frac{1}{2}}\frac{3}{l}\hat{a}^{\dagger}\hat{a}^{\dagger}.\end{aligned}\tag{16}$$

Thus, the intermolecular interaction potential func-

tion of Eq. (15) can be expressed approximately as

$$V_{ij} \approx \frac{2}{3}U(r_{ij})[\frac{9}{2l}(\hat{a}_i^\dagger \hat{a}_j + \hat{a}_i \hat{a}_j^\dagger) + \frac{3}{2l}(l - 3\hat{a}_i^\dagger \hat{a}_i - 3\hat{a}_j^\dagger \hat{a}_j)]. \quad (17)$$

The lattice model is adopted in our theory. Supposing NLC system is composed of N lattice points. There is a molecule at each lattice point. Only considering their nearest neighbours, using Eqs.(10) and (16), the Hamiltonian of the system can be written as

$$\begin{aligned}\hat{H}_0 \approx & \frac{1}{2}U(r_{ij})\frac{2}{3}{\sum_{i,\delta}}' \left[\frac{9}{2l}(\hat{a}_i^\dagger \hat{a}_{i+\delta} + \hat{a}_i \hat{a}_{i+\delta}^\dagger) + \frac{3}{2l}(l - 3\hat{a}_i^\dagger \hat{a}_i - 3\hat{a}_{i+\delta}^\dagger \hat{a}_{i+\delta})\right] \\ = & \frac{1}{2}ZNU(r_{ij}) - 3\frac{U(r_{ij})}{l}Z\sum_i \hat{a}_i^\dagger \hat{a}_i + \frac{3U(r_{ij})}{2l}{\sum_{i,\delta}}'(\hat{a}_i^\dagger \hat{a}_{i+\delta} + \hat{a}_i \hat{a}_{i+\delta}^\dagger), \end{aligned} \quad (18)$$

where we suppose that the molecules between two lattices have the same $U(r_{ij})$; N is number of molecules of the liquid crystal system, the factor $\frac{1}{2}$ is required to avoid counting intermolecular interactions twice, ${\sum_{i,\delta}}'$ represents that the summation is exclusive of the terms with $\delta = 0$. Because of $U(r_{ij}) < 0$, replacing $U(r_{ij})$ by $-|U|$, then Eq.(18) can be rewritten as

$$\begin{aligned}\hat{H}_0 = & E_0 + 3Z\frac{|U|}{l}\sum_i \hat{a}_i^\dagger \hat{a}_i - \frac{3|U|}{2l}{\sum_{i,\delta}}'(\hat{a}_i^\dagger \hat{a}_{i+\delta} + \hat{a}_i \hat{a}_{i+\delta}^\dagger), \end{aligned} \quad (19)$$

where $E_0 = -ZN|U|/2$. In spin wave theory, the Hamiltonian of ferromagnetism is

$$\begin{aligned}\hat{H}_0 = & -ZN|J|S^2 + 2Z|J|S\sum_l \hat{a}_l^\dagger \hat{a}_l - |J|S{\sum_{l,\delta}}'(\hat{a}_l^\dagger \hat{a}_{l+\delta} + \hat{a}_l \hat{a}_{l+\delta}^\dagger). \end{aligned} \quad (20)$$

It is clear that the forms of Eq.(19) and Eq.(20) are in good agreement. Transferring Eq.(19) from coordinate space to momentum space, the Hamiltonian can be rewritten as

$$\begin{aligned}\hat{H}_0 = & E_0 + 3Z\frac{|U|}{l}\sum_i \frac{1}{N}\sum_{k,k'}\exp\left(\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{R}_i\right)\hat{b}_{k'}^\dagger \hat{b}_k \\ & - \frac{3|U|}{2l}{\sum_{i,\delta}}'\frac{1}{N}\sum_{k,k'}(\exp\left(-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{R}_i\right)\exp\left(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{i+\delta}\right)\hat{b}_{k'}^\dagger \hat{b}_k + \exp\left(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_i\right)\exp\left(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{i+\delta}\right)\hat{b}_k \hat{b}_{k'}^\dagger) \\ = & E_0 + \sum_k \hbar\omega_k \hat{b}_k^\dagger \hat{b}_k, \end{aligned} \quad (21)$$

where $\hbar\omega_k = 3Z\frac{|U|}{l}(1-\gamma_k)$, $\gamma_k = \frac{1}{Z}\sum_\delta \exp\left(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\delta}\right) = \gamma_{-k}$.

Crystals have the property of inversion symmetry. Different crystals have different γ_k, so the relation between frequency of spin wave and wave vector $\boldsymbol{k}$ can be calculated by combining the symmetry of the crystal in ferromagnetic theory. Under low temperature circumstances, by using long wave condition to expand γ_k, we can solve $\hbar\omega_k$. Because the long wave dispersion relation of sc, bcc and fcc are the same, we have

$$\hbar\omega_k = 3\frac{|U|}{l}\left(Z - \sum_\delta \exp\left(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\delta}\right)\right) \approx \frac{3}{2}\frac{|U|}{l}\sum_\delta (\boldsymbol{k}\cdot\boldsymbol{\delta})^2 = 3\frac{|U|}{l}a^2k^2, \quad (22)$$

where a is the lattice constant.

3.2. The modification to the Hamiltonian by considering the higher-order items

From the Eq.(14), for $\frac{n}{l} \ll 1$, using the Taylor expansion and saving to the higher order item $\left(\frac{n}{l}\right)^2$, i.e. $\frac{\hat{a}^\dagger \hat{a} \hat{a}^\dagger \hat{a}}{l^2}$, we can obtain the two-body interaction potential

$$
\begin{aligned}
V_{ij} =& -\frac{2}{3}|U|[\hat{\tau}_{+2}(i)\hat{\tau}_{-2}(j)+\hat{\tau}_{+1}(i)\hat{\tau}_{-1}(j)+\hat{\tau}_0(i)\hat{\tau}_0(j)+\hat{\tau}_{-1}(i)\hat{\tau}_{+1}(j)+\hat{\tau}_{-2}(i)\hat{\tau}_{+2}(j)] \\
\approx& -\frac{2}{3}|U|\Big\{\Big[\frac{3}{2}+\frac{9}{2l}(\hat{a}_i^\dagger\hat{a}_j+\hat{a}_i\hat{a}_j^\dagger-\hat{a}_i^\dagger\hat{a}_i-\hat{a}_j^\dagger\hat{a}_j)\Big]+\frac{9}{2l^2}(\hat{a}_i^\dagger\hat{a}_i^\dagger\hat{a}_j\hat{a}_j+\hat{a}_i\hat{a}_i\hat{a}_j^\dagger\hat{a}_j^\dagger) \\
&+\frac{9}{4l^2}(\hat{a}_i^\dagger\hat{a}_i\hat{a}_i^\dagger\hat{a}_i+\hat{a}_j^\dagger\hat{a}_j\hat{a}_j^\dagger\hat{a}_j)-\frac{45}{8l^2}(\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_j\hat{a}_j+\hat{a}_i^\dagger\hat{a}_i\hat{a}_i^\dagger\hat{a}_j+\hat{a}_i\hat{a}_j^\dagger\hat{a}_j\hat{a}_j^\dagger+\hat{a}_i^\dagger\hat{a}_i\hat{a}_i\hat{a}_j^\dagger) \\
&+\frac{27}{2l^2}\hat{a}_i^\dagger\hat{a}_i\hat{a}_j^\dagger\hat{a}_j\Big\}. \qquad (23)
\end{aligned}
$$

Only considering the interaction of the nearest neighbours ($j=i+\delta$), the Hamiltonian of the system can be written as

$$
\begin{aligned}
\hat{H} =& \hat{H}_0+\hat{H}_1 \\
=& -\frac{1}{3}|U|{\sum_{i,\delta}}'\Big\{\Big[\frac{3}{2}+\frac{9}{2l}(\hat{a}_i^\dagger\hat{a}_{i+\delta}+\hat{a}_i\hat{a}_{i+\delta}^\dagger-\hat{a}_i^\dagger\hat{a}_i-\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta})\Big] \\
&+\frac{9}{2l^2}(\hat{a}_i^\dagger\hat{a}_i^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}+\hat{a}_i\hat{a}_i\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}^\dagger)+\frac{9}{4l^2}(\hat{a}_i^\dagger\hat{a}_i\hat{a}_i^\dagger\hat{a}_i+\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}) \\
&-\frac{45}{8l^2}(\hat{a}_i^\dagger\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}+\hat{a}_i^\dagger\hat{a}_i\hat{a}_i^\dagger\hat{a}_{i+\delta}+\hat{a}_i\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}^\dagger+\hat{a}_i^\dagger\hat{a}_i\hat{a}_i\hat{a}_{i+\delta}^\dagger)+\frac{27}{2l^2}\hat{a}_i^\dagger\hat{a}_i\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\Big\}, \qquad (24)
\end{aligned}
$$

where

$$
\hat{H}_0=-\frac{1}{3}|U|{\sum_{i,\delta}}'\Big[\frac{3}{2}+\frac{9}{2l}(\hat{a}_i^\dagger\hat{a}_{i+\delta}+\hat{a}_i\hat{a}_{i+\delta}^\dagger-\hat{a}_i^\dagger\hat{a}_i-\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta})\Big], \qquad (25)
$$

$$
\begin{aligned}
\hat{H}_1 =& -\frac{1}{3}|U|{\sum_{i,\delta}}'\Big[\frac{9}{2l^2}(\hat{a}_i^\dagger\hat{a}_i^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}+\hat{a}_i\hat{a}_i\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}^\dagger)+\frac{9}{4l^2}(\hat{a}_i^\dagger\hat{a}_i\hat{a}_i^\dagger\hat{a}_i+\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}) \\
&-\frac{45}{8l^2}(\hat{a}_i^\dagger\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}+\hat{a}_i^\dagger\hat{a}_i\hat{a}_i^\dagger\hat{a}_{i+\delta}+\hat{a}_i\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\hat{a}_{i+\delta}^\dagger+\hat{a}_i^\dagger\hat{a}_i\hat{a}_i\hat{a}_{i+\delta}^\dagger)+\frac{27}{2l^2}\hat{a}_i^\dagger\hat{a}_i\hat{a}_{i+\delta}^\dagger\hat{a}_{i+\delta}\Big]. \qquad (26)
\end{aligned}
$$

Transferring Eq.(26) from coordinate space to momentum space, then

$$
\hat{H}_1=\frac{3}{4}|U|\frac{Z}{Nl^2}\sum_{k,k',q}[5(\gamma_{k-q}+\gamma_{k'})-6\gamma_{k-k'-q}-2-4\gamma_{k+k'}]\hat{b}_{k-q}^\dagger\hat{b}_{k'+q}^\dagger\hat{b}_{k'}\hat{b}_k, \qquad (27)
$$

where we use $\frac{1}{N}\sum_{\delta}\exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{\delta}]=\delta_{kk'}$, $\sum_k\gamma_k=0$. Eq.(27) represents the interaction between the quasi-particles, the quantum of $\boldsymbol{k}$ and $\boldsymbol{k}'$ are annihilated, the quantum of $\boldsymbol{k}-\boldsymbol{q}$ and $\boldsymbol{k}'+\boldsymbol{q}$ are created, which is the typical interaction between the quasi-particles. The interactions between the quasi-particles have modified effect on $\hbar\omega_k$.

From $\hat{H}=\hat{H}_0+\hat{H}_1$, the motion equation of $\hat{b_k}$ can be established:

$$
\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{b}_k=[\hat{b}_k,\hat{H}_0]+[\hat{b}_k,\hat{H}_1]=\hbar\omega_k(T)\hat{b}_k, \qquad (28)
$$

using the expression of the $\hat{H}_0$ and $\hat{H}_1$, Eqs.(21) and (27), and the commutation relations $[\hat{b}_k,\hat{b}_{k'}^\dagger]=\delta_{k,k'}$, $[\hat{b}_k,\hat{b}_{k'}]=0$, $[\hat{b}_k^\dagger,\hat{b}_{k'}^\dagger]=0$, we can get

$$
[\hat{b}_k,\hat{H}_0]=3Z\frac{|U|}{l}(1-\gamma_k)\hat{b}_k, \qquad (29)
$$

$$
\begin{aligned}
[\hat{b}_k,\hat{H}_1]=&\frac{3}{4}\frac{Z|U|}{Nl^2}\Big\{\sum_{k',q}[5(\gamma_k+\gamma_{k'})-6\gamma_{k-k'}-2 \\
&-4\gamma_{k+k'+q}]\hat{b}_{k'+q}^\dagger\hat{b}_{k'}\hat{b}_{k+q} \\
&+\sum_{k',q}[5(\gamma_{k-q}+\gamma_{k'-q})-6\gamma_{k-k'}-2 \\
&-4\gamma_{k+k'-q}]\hat{b}_{k'-q}^\dagger\hat{b}_{k-q}\hat{b}_{k'}\Big\}. \qquad (30)
\end{aligned}
$$

Taking the linear approximation and using the formula $\sum_{k'}\gamma_{k-k'}<\hat{n}_{k'}>_{\mathrm{T}}=\gamma_k\sum_{k'}\gamma_{k'}<\hat{n}_{k'}>_{\mathrm{T}}$, Eq.(30)

can be rewritten as

$$[\hat{b}_k, \hat{H}_1] = -\frac{Z|U|}{N}\frac{15}{l^2}(1-\gamma_k) \times \sum_{k'}(1-\gamma_{k'}) < \hat{b}^{\dagger}_{k'}\hat{b}_{k'} >_{\mathrm{T}} \hat{b}_k. \quad (31)$$

Substituting Eqs.(29) and (31) into Eq.(28), we get

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{b}_k = 3Z\frac{|U|}{l}(1-\gamma_k) \times \left\{1 - \frac{5}{Nl}\sum_{k'}(1-\gamma_{k'}) < \hat{b}^{\dagger}_{k'}\hat{b}_{k'} >_{\mathrm{T}}\right\}\hat{b}_k. \quad (32)$$

Comparing Eq.(28) with Eq.(32), we get

$$\hbar\omega_k(T) = 3Z\frac{|U|}{l}(1-\gamma_k)\left[1 - \frac{5}{l}e(T)\right], \quad (33)$$

where $e(T)$ is the renormalization factor,

$$e(T) = \frac{1}{N}\sum_{k'}(1-\gamma_{k'}) < \hat{b}^{\dagger}_{k'}\hat{b}_{k'} >_{\mathrm{T}} = \frac{1}{N}\sum_{k'}(1-\gamma_{k'}) < \hat{n}_{k'} >_{\mathrm{T}}. \quad (34)$$

4. Result and discussion

4.1. The relation of the order parameter and the reduced temperature

Choosing z-axis as the preferred direction of the molecules in NLC, from Eq.(2) we have

$$Q = \begin{pmatrix} -\frac{S}{2} & 0 & 0 \\ 0 & -\frac{S}{2} & 0 \\ 0 & 0 & S \end{pmatrix}, \quad (35)$$

where S is the order parameter, and $S = \langle\hat{Q}_{33}\rangle_{\mathrm{T}} = \langle P_2(\cos\theta)\rangle_{\mathrm{T}}$. From $\hat{\tau}_0 = \sqrt{\frac{3}{2}}Q_{33}$, we can get

$$S = \langle\hat{Q}_{33}\rangle_{\mathrm{T}} = \sqrt{\frac{2}{3}}\langle\hat{\tau}_0\rangle_{\mathrm{T}}, \quad (36)$$

under the primary approximation, we have

$$S = \sqrt{\frac{2}{3}}\left\langle\sqrt{\frac{3}{2}}\frac{1}{l}(l - 3\hat{a}^{\dagger}_i\hat{a}_i)\right\rangle_{\mathrm{T}} = 1 - \frac{3}{l}\sum_i\left\langle\frac{1}{N}\sum_{kk'}\exp(-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{R}_i)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_i)\hat{b}^{\dagger}_{k'}\hat{b}_k\right\rangle_{\mathrm{T}} = 1 - \frac{3}{l}\frac{1}{N}\sum_k\langle\hat{b}^{\dagger}_k\hat{b}_k\rangle_{\mathrm{T}}, \quad (37)$$

according to the Bose–Einstein statistic relation, we can get

$$\langle\hat{b}^{\dagger}_k\hat{b}_k\rangle_{\mathrm{T}} = \langle\hat{n}_k\rangle = \frac{1}{\mathrm{e}^{\frac{\hbar\omega_k}{k_{\mathrm{B}}T}} - 1}, \quad (38)$$

then,

$$\sum_k\langle\hat{n}_k\rangle = \frac{V}{(2\pi)^3}\int\frac{4\pi k^2}{\mathrm{e}^{\beta\hbar\omega} - 1}\mathrm{d}k = \frac{N}{8f}\left(\frac{k_{\mathrm{B}}Tl}{3\pi|U|}\right)^{\frac{3}{2}}\xi\left(\frac{3}{2}\right). \quad (39)$$

Thus, the relation of the order parameter and the reduced temperature can be expressed as

$$S = 1 - \frac{3}{8lf}\left(\frac{k_{\mathrm{B}}Tl}{3\pi|U|}\right)^{\frac{3}{2}}\xi\left(\frac{3}{2}\right) \approx 1 - CT_{\mathrm{R}}^{\frac{3}{2}}, \quad (40)$$

where $C = \frac{3}{8lf}\left(\frac{l}{3\pi}\right)^{\frac{3}{2}}2.612$, $V = \frac{Na^3}{f}$, $T_{\mathrm{R}} = \frac{k_{\mathrm{B}}T}{|U|}$, and f is the structural coefficient(for the structure of simple cubic, $f = 1$). When $l = 200$, the relation of the order parameters to the reduced temperature T_{R} can be obtained, which is shown in Fig.2.

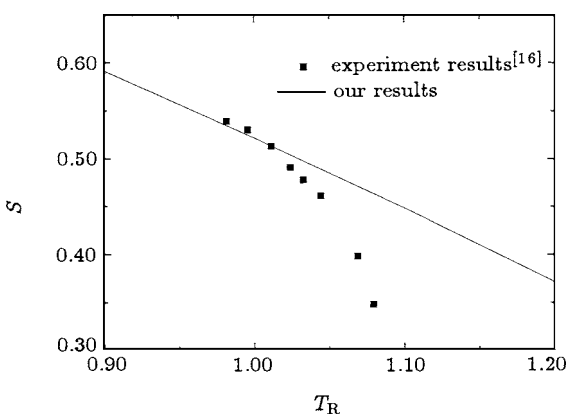


Fig.2. Dependence of the order parameters on the reduced temperature.

It can be seen from Fig.2 that the order parameter S decreases as the reduced temperature increases, which shows that the order degree of the system is destroyed by heat motion of the molecules as the temperature increases. The results we get are in good agreement with those of the experiments,[16] especially in the low temperature region. It is the first time that the quantum theory is applied to research NLC. For review articles and books dealing with this subject, we may mention that most of the theories about NLC have solved the order problems close to the transition point, but in the low temperature region these theories do not hold. The collective excitation theory of

NLC we proposed can solve the problem. Just as in ferromagnetic theory, in order to discuss the relation between spontaneous magnetization and temperature, the theory of molecular field and high temperature expansion approximation method are adopted at high temperature region close to the Curie point; spin wave theory is adopted in low temperature region.

When considering the higher-order items, under the long wave approximation, combining with Eqs.(33), (34), (37) and (38), the self-consistent equation which the order parameter satisfies can be obtained, and the order parameter depends on reduced temperature. Thus, the relation of the order parameter to the reduced temperature can be calculated numerically, which is shown in Fig.3.

It can be seen from Fig.3 that the higher-order terms have almost no effect on the relation of the order parameter and the reduced temperature in the low temperatures, but at high temperatures region, the slope of the curve increases remarkably and our results approach the experimental points. Although the results of Ref.[17] agree well with experimental ones, there are adjustable parameters in it. Figure 3 also shows that our results fall between the results of Maier–Saupe[11] and HJL,[17] and the tendency of the curve is the same as theirs. That shows the many-body effect is important to NLC.

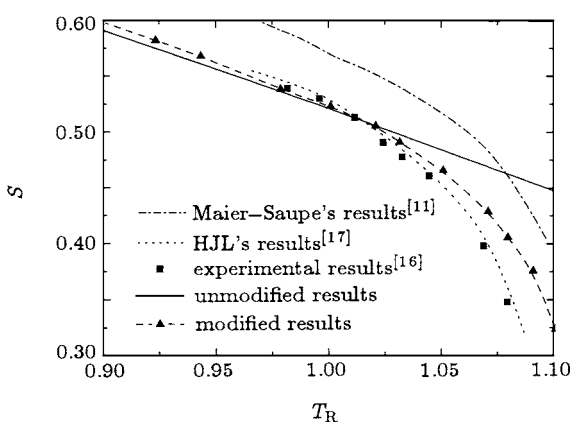


Fig.3. Dependence of the order parameters on the reduced temperature when considering the higher-order terms.

4.2. Calculation of the nematic-isotropic transition point

We use the theory of molecular field[18,19] to calculate the nematic-isotropic transition point in the high temperature region close to the transition point. From Eqs.(10) and (36), we have

$$\hat{H} = -\frac{1}{2}|U|\frac{2}{3}\sum_{i=1}^{N}\{\hat{\tau}_0(i)[Z\langle\hat{\tau}_0\rangle_{\mathrm{T}}]\}$$
$$= -\frac{1}{2}|U|\sqrt{\frac{2}{3}}SZ\sum_{i=1}^{N}\hat{\tau}_0(i). \tag{41}$$

Equation (41) shows that the system energy is the summation of the molecule interaction potentials. In Eq.(41), we adopt a approximation of substituting $\hat{\tau}_k(j)$ for $\langle\hat{\tau}_k\rangle_{\mathrm{T}}$ which is the statistical average of $\hat{\tau}_k$.

The Hamiltonian of a single molecule can be expressed as

$$\hat{H}_i = -\frac{1}{2}|U|\sqrt{\frac{2}{3}}SZ\hat{\tau}_0, \tag{42}$$

the statistical average of $\hat{\tau}_0$ is

$$\langle\hat{\tau}_0\rangle = \frac{\sum_{m=-l}^{l}\frac{\sqrt{\frac{3}{2}}\left[\frac{3}{2}m^2-\frac{1}{2}l(l+1)\right]}{l(l+1)}\mathrm{e}^{-\beta E_m}}{\sum_{m=-l}^{l}\mathrm{e}^{-\beta E_m}}, \tag{43}$$

where

$$E_m = -\frac{1}{2}|U|\sqrt{\frac{2}{3}}SZ\frac{\sqrt{\frac{3}{2}}\left[\frac{3}{2}m^2-\frac{1}{2}l(l+1)\right]}{l(l+1)}. \tag{44}$$

Defining $\xi = -\frac{3}{4}Z\frac{|U|}{k_{\mathrm{B}}T}$, then

$$S = \frac{\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left\{\frac{3}{2}\frac{m^2}{l(l+1)}\mathrm{e}^{\frac{-\xi Sm^2}{l(l+1)}}\right\}}{\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathrm{e}^{\frac{-\xi Sm^2}{l(l+1)}}} - \frac{1}{2}. \tag{45}$$

Obviously, $S = 0$ is a solution of Eq.(45), and none zero solution must exist. By numerical calculation, we can find that the order parameter is 0.4111 at the transition point, which is close to Maier–Saupe's result of 0.4289.[15]

In the microscopic theory of NLC put forward in the paper, quantum theory[20,21] is adopted, and the effect of the collective effect on the molecular orientational order is explored. As is well known, liquid crystal is considered to be a kind of classical fluid, the quantum effect do not exist. But the quantum effect in NLC is proved in our work. The mass of the liquid crystal molecule is about three or four times as that of the atom U^{238}, which is comparatively large. When considering the molecular orientational order, the corresponding effective mass should be calculated. We use Eq.(22) to estimate the effective mass m_{eff} of the molecule. We could have $\hbar\omega_k = 3\frac{|U|}{l}a^2k^2 = \frac{\hbar^2k^2}{2m_{\mathrm{eff}}}$,

so $m_{\text{eff}} = \dfrac{\hbar^2 l}{6|U|a^2}$. m_{eff} can be very small, its order is about 10^{-27}kg, so it is not strange for the NLC to show quantum effect.

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