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Quantum description of the orientational degrees of freedom in a biaxial nematic liquid

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Abstract

The quantum mechanical version of a classical model for studying the orientational degrees of freedom corresponding to a nematic liquid composed of biaxial molecules is presented. The effective degrees of freedom are described by operators carrying an SU(3) representation, which allows the explicit calculation of the partition function in the mean field approximation. The algebraic consistency conditions are solved numerically and the equilibrium phases of the system are determined. Phase diagrams corresponding to one extreme quantum case, together with the almost classical case are presented. The specific heat is also calculated for different choices of the constituent biaxial molecules. Our results reproduce the classical calculation in the limit of high temperatures and high quantum numbers. They present some interesting differences arising from the quantum behavior in the low-temperature limit. \bigcirc 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nematic liquids constitute a particular case of the phases denominated with the generic name of liquid crystals [1–5]. The molecules forming a liquid crystal can be roughly characterized as rod-like or disc-like, and the corresponding orientational

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symmetry is manifested by different types of local alignments of such molecules with respect to the director. In the case of a nematic liquid, the director is fixed in space and the molecules remain, on the average, parallel to it, though they can diffuse as in a normal liquid. The existence of a preferred direction makes this phase to exhibit birefringent properties. The energies involved in the transition from the liquid crystal phase to the isotropic liquid phase are normally small compared with the corresponding ones in the solid–liquid transition. This makes it possible to drastically change the response of liquid crystals by external agents, using relatively small amounts of energy. It is this property which mainly determines the numerous and important technological applications of liquid crystals¹ [6].

In this work we consider the quantum mechanical description of the orientational degrees of freedom of a nematic liquid consisting of biaxial molecules, in the mean field approximation. This system has been previously discussed in Ref. [7], where an exact calculation of the classical partition function, together with an extensive analysis of the corresponding phases, transition temperatures, thermodynamic quantities and order parameters, was made. We will refer to this work as the classical model. In this reference, the effective orientational degrees of freedom of the non-spherically symmetric molecules were described by an SU(3) invariant Hamiltonian constructed from the angular momentum operators L_i , i = 1, 2, 3 together with the traceless quadrupole tensor operator $Q_{\alpha\beta}$, $\alpha, \beta = 1, 2, 3$, which constitute a representation for the generators of SU(3). The interpretation of the model was performed in a coordinate system where the molecule is at rest, i.e. $L_i = 0$. In this system, the quadrupole operator $\bar{Q}_{\alpha\beta}$ relates to the inertia tensor of the molecule in such a way that the SU(3) Casimir operators, expressed through the eigenvalues of $\bar{Q}_{\alpha\beta}$, provide a description of the shape of the molecule.

The classical partition function in the mean field approximation was exactly calculated in Ref. [7], by first rewriting it as an integral over the space parameters of the SU(3) group, according to a theorem due to Macfarlane et al. [8,9]. This integral had been previously calculated by Harish-Chandra et al. [10,11]. The exact evaluation of the partition function, together with the fact that the consistency conditions consisted in two coupled algebraic equations, constituted an advantage over statistical theories [12–15] previously proposed in order to explain the isotropic \rightarrow uniaxial \rightarrow biaxial phase transitions discovered experimentally in nematic liquids [16–21]. The works included in [12–15] are generalizations of the Maier-Saupe theory, that was for some time the fullest existing statistical mechanical theory of the nematic state, which, nevertheless, did not include the biaxial phase [22,23].

Following an approach similar to most previous works, we only consider the orientational interaction energy among the molecules of the liquid, in such a way that the exact nature of the intermolecular forces need not be specified. Whether the liquid crystal state arises because of the hard core repulsive forces or the long range

¹ For a very readable and non technical introduction to liquid crystals and its applications see for example Ref. [6].

dispersive forces is a matter of indifference in the following. This approximation is expected to produce qualitatively reasonable results in the nematic case [12–15]. In this way, we are really calculating the excess thermodynamical properties of the ordered system, relative to those of the disordered one.

In this work we present a quantum description of the problem discussed in [7], which amounts to the generalization of the usual Heisenberg model describing the interaction of angular momentum operators (SU(2) case) to the situation where the interacting operators carry an SU(3) representation. Similarly to the classical case, we are able to exactly calculate the partition function in the mean field approximation. This is achieved by using the Weyl formula for the characters of SU(3) [24].

The paper is organized as follows. In Section 2 we introduce the model and apply the Weyl formula to calculate the partition function exactly. Section 3 describes the characterization of the constituents molecules of the liquid in terms of the irreducible representations of SU(3). The equilibrium phase is labeled in the same way as in Ref. [7], as briefly recalled in Section 4. Section 5 contains the self consistent equations of the corresponding mean field approximation. Section 6 describes the calculation of the equilibrium parameters, emphasizing those limiting cases that can be treated analytically. Some conclusions and comments are presented in Section 7.

2. The model

Following the work in Ref. [7], let us consider the effective Hamiltonian

$$H = -\frac{J}{N} \sum_{m \neq n} S_a^m S_a^n , \qquad (1)$$

which describes the orientational energy of the system. Here, the N independent operators S_a^m , m = 1, 2, 3, ..., N, a = 1, 2, 3, ..., 8 determine the degrees of freedom of each molecule of the liquid and carry an SU(3) representation, i.e.

$$[S_a^m, S_b^n] = \delta^{mn} i f_{abc} S_c^m , \qquad (2)$$

where f_{abc} are the SU(3) structure constants [25].

In the mean field (molecular field) approximation we replace (1) by

$$H = -JB_a \sum_{n=1}^N S_a^n , \qquad (3)$$

where the eight-dimensional vector $B_a = (1/N) \langle \sum_m S_a^m \rangle$, which represents the average field seen by each molecule, has to be determined consistently. In this approximation, the partition function Z is

$$Z = Tr e^{-\beta H} = Tr e^{\beta J B_a} \sum_n S_a^n = Z_0^N , \qquad (4)$$

where

$$Z_0 = Tr \,\mathrm{e}^{\beta J B_a S_a} \,. \tag{5}$$

As usual $1/\beta = k\mathcal{T}$, where k is the Boltzmann constant and \mathcal{T} is the temperature of the system.

The consistency equations for the mean field approximation reduce to

$$B_a = \frac{1}{\beta J} \frac{\partial}{\partial B_a} \ln Z_0 .$$
(6)

The basic problem now is to calculate such partition function for an arbitrary (p,q) irreducible representation of SU(3). The vector B_a lives in the adjoint representation of SU(3). It is always possible to select a reference frame where the vector has only two non-zero components. We choose them to be B_3 and B_8 . In this way, the partition function reduces to

$$Z_0 = Tr \,\mathrm{e}^{\beta J(B_3 S_3 + B_8 S_8)} \,. \tag{7}$$

The partition function (5) is the character of the operator $e^{-\beta H}$. In this way, to calculate Z_0 for an arbitrary representation (p,q) of SU(3), we can use the Weyl formula for the characters, which leads to [24]

$$Z_{0} = \frac{1}{(\Lambda_{1} - \Lambda_{2})(\Lambda_{1} - \Lambda_{3})(\Lambda_{2} - \Lambda_{3})} \begin{vmatrix} \Lambda_{1}^{(p+q+2)} & \Lambda_{1}^{(q+1)} & 1 \\ \Lambda_{2}^{(p+q+2)} & \Lambda_{2}^{(q+1)} & 1 \\ \Lambda_{3}^{(p+q+2)} & \Lambda_{3}^{(q+1)} & 1 \end{vmatrix},$$
(8)

in the case of SU(3). Here, p + q is the number of boxes in the first row of the corresponding Young tableau, while q is the number of boxes in the second row of the tableau. The eigenvalues Λ_i , i = 1, 2, 3 are

$$\Lambda_i = \mathrm{e}^{\beta J \boldsymbol{B} \cdot \boldsymbol{w}_i} \,, \tag{9}$$

where w_i are the weights of the fundamental representation

$$w_1 = \left(\frac{1}{2}, \frac{1}{2\sqrt{3}}\right), \quad w_2 = \left(-\frac{1}{2}, \frac{1}{2\sqrt{3}}\right), \quad w_3 = \left(0, -\frac{1}{\sqrt{3}}\right).$$
 (10)

They satisfy the condition $\Lambda_1 \Lambda_2 \Lambda_3 = 1$. In a more convenient notation

$$\rho = \frac{1}{2}\beta JB_3, \quad \sigma = \frac{1}{2\sqrt{3}}\beta JB_8 \,, \tag{11}$$

we have

$$\Lambda_1 = e^{\rho + \sigma}, \quad \Lambda_2 = e^{-\rho + \sigma}, \quad \Lambda_3^{-1} = \Lambda_1 \Lambda_2 = e^{2\sigma}.$$
 (12)

The partition function is given by

$$Z_0^{(p,q)} = \frac{1}{\sinh 2\rho - 2\sinh \rho \cosh 3\sigma} (-e^{(p+2q+3)\sigma} \sinh(p+1)\rho + e^{(p-q)\sigma} \sinh(p+q+2)\rho - e^{-(q+2p+3)\sigma} \sinh(q+1)\rho).$$
(13)

3. Specification of the constituent molecules

The orientational degrees of freedom of the molecules are described by the eight operators S_a , which can be reinterpreted as the angular momentum L_i , i = 1, 2, 3, and the quadrupole moment Q_{ij} operators, according to [7].

The molecules forming the liquid will be characterized by the representation (p,q) of SU(3). To this end we consider the two Casimir operators of the group

$$\mathbf{C}_2 = S_a S_a = I_2 \mathbf{I}, \quad \mathbf{C}_3 = d_{abc} S_a S_b S_c = I_3 \mathbf{I}$$
(14)

which take the following values in each irreducible representation (p,q), [26]

$$I_2 = \frac{p^2 + q^2 + pq + 3(p+q)}{3},$$
(15)

$$I_3 = \frac{1}{18}(p-q)(p+2q+3)(2p+q+3).$$
(16)

Motivated by the classical description and in order to compare with it, we rewrite the above invariants in terms of the eigenvalues μ_i , i = 1, 2, 3, with the restriction $\mu_1 + \mu_2 + \mu_3 = 0$. In the classical situation one defines $I_3 = \frac{3}{2}\mu_1\mu_2\mu_3$, which can be reproduced in our case by choosing

$$\mu_1 = -\frac{1}{3}(p+2q+3), \quad \mu_2 = -\frac{1}{3}(p-q), \quad \mu_3 = \frac{1}{3}(2p+q+3), \quad (17)$$

according to the relation (16). Following the analogy, we calculate what used to be the quadratic Casimir operator, obtaining

$$-(\mu_1\mu_2 + \mu_1\mu_3 + \mu_2\mu_3) = I_2 + 1, \qquad (18)$$

where I_2 is given by Eq. (15). The choice (17) implies the ordering $\mu_1 \leq \mu_2 \leq \mu_3$, for arbitrary values of p and q. The eigenvalues (17) satisfy the cubic equation

$$\mu^3 - (I_2 + 1)\mu - \frac{2}{3}I_3 = 0, \qquad (19)$$

and thus can be written as

$$\mu_1 = \mu \cos\left(\psi + \frac{2\pi}{3}\right), \quad \mu_2 = \mu \cos\left(\psi - \frac{2\pi}{3}\right), \quad \mu_3 = \mu \cos\psi, \quad (20)$$

which is consistent with the ordering introduced in (17). Here

$$\mu = \pm 2\sqrt{\frac{(I_2+1)}{3}}, \quad \cos 3\psi = \pm \frac{\sqrt{3}I_3}{(I_2+1)^{3/2}},$$
(21)

in complete analogy with the classical case. The order relation for the eigenvalues, dictated by Eq. (17), leads to the following correlations between ψ and μ :

$$\mu > 0 \leftrightarrow 0 < \psi < \frac{\pi}{3}, \quad \mu < 0 \leftrightarrow \pi < \psi < \pi + \frac{\pi}{3}$$
(22)

for arbitrary p and q. Given μ and ψ , we obtain the corresponding values of p and q according to

$$q = \sqrt{3}\mu\sin\psi - 1, \quad p = \sqrt{3}\mu\sin\left(\psi + \frac{2\pi}{3}\right) - 1.$$
 (23)

The physical interpretation associated to the (p,q) characterization of the individual molecules is made through the classical connection

$$a_i^2 = \frac{1}{3}(a_1^2 + a_2^2 + a_3^2) + \frac{1}{2}\mu_i , \qquad (24)$$

which relates the μ -values (17) with the shape corresponding to a molecule described by a mass distribution defined by six equal masses at distances $\pm a_1, \pm a_2, \pm a_3$ from the center [7]. The correspondence is

$$\mu_{1} = \mu_{2} = \mu_{3} \quad \text{(spherically symmetric molecule)},$$

$$\mu_{1} = \mu_{2} < 0, \quad \mu_{3} > 0 \quad \text{(rod molecule)},$$

$$\mu_{1} < 0, \quad \mu_{2} = \mu_{3} > 0 \quad \text{(disc molecule)},$$

$$\frac{1}{2}(\mu_{1} + \mu_{3}) > \mu_{2} \quad \text{(rod-like molecule)},$$

$$\frac{1}{2}(\mu_{1} + \mu_{3}) < \mu_{2} \quad \text{(disc-like molecule)}.$$

(25)

Expressions (17) together with the classification (25), imply that in the quantum case we do not have at our disposal either spherically symmetric or uniaxial molecules to begin with. The description used allows only biaxial molecules which are rod-like (p > q) or disc-like (p < q).

4. The equilibrium phases

The equilibrium state of the system is characterized by the vector B_a in the frame where its only components are B_3 and B_8 . Again, an SU(3) invariant description of such phase will be given by the corresponding vector invariants, in the adjoint representation

$$\bar{I}_2 = B_a B_a = B_3^2 + B_8^2, \quad \bar{I}_3 = d_{abc} B_a B_b B_c = \frac{1}{\sqrt{3}} (-B_8^3 + 3B_8 B_3^2) .$$
 (26)

From Eqs. (26), we can verify that B_8 satisfies the cubic equation

$$B_8^3 - \bar{I}_2 B_8 - \frac{2}{3} \bar{I}_3 = 0 \tag{27}$$

and consequently can be expressed in any of the forms (20). A convenient choice is made by considering that the relevant variable is the matrix $B_a \lambda_a$ in the fundamental representation, whose eigenvalues are

$$\mu_{1} \cdot \boldsymbol{B} = \lambda_{1} = \frac{1}{2}B_{3} + \frac{1}{2\sqrt{3}}B_{8} := \lambda \cos\left(\phi + \frac{2\pi}{3}\right) ,$$

$$\mu_{2} \cdot \boldsymbol{B} = \lambda_{2} = -\frac{1}{2}B_{3} + \frac{1}{2\sqrt{3}}B_{8} := \lambda \cos\left(\phi - \frac{2\pi}{3}\right) ,$$

$$\mu_{3} \cdot \boldsymbol{B} = \lambda_{3} = -\frac{1}{\sqrt{3}}B_{8} := \lambda \cos\phi .$$
(28)

In this way we identify

$$B_8 = -\sqrt{3}\,\lambda\cos\phi, \quad B_3 = -\sqrt{3}\,\lambda\sin\phi \;. \tag{29}$$

The equilibrium phase is described by the variables λ , ϕ , which can be translated in a geometrical language regarding the average shape of the equilibrium states via the relations (25) and (28), in terms of the eigenvalues λ_i .

5. Calculation of the equilibrium parameters

In the coordinates chosen so far, the consistency equations in the mean field approximation are given by

$$B_3 = \frac{1}{\beta J} \frac{\partial}{\partial B_3} \ln Z_0^{(p,q)}, \quad B_8 = \frac{1}{\beta J} \frac{\partial}{\partial B_8} \ln Z_0^{(p,q)}, \quad (30)$$

where the partition function $Z_0^{(p,q)}$ is written in Eq. (13). The original expression

$$B_a = \frac{1}{Z_0} Tr(S_a e^{\beta J(B_3 S_3 + B_8 S_8)}), \quad a = 3, 8 , \qquad (31)$$

for the consistency conditions, allows us to see that we will always have the solution $B_3 = 0 = B_8$, $(\lambda = 0)$ corresponding to the isotropic phase. In this case, the partition function is $Z_0 = \frac{1}{2}(p+1)(q+1)(p+q+2)$, independent of the variable ϕ , which we choose as $\phi = 0$ to describe the isotropic phase. Nevertheless, this phase will not always be the stable one.

Let us introduce the following adimensional variables:

$$T = \frac{4}{\beta J}, \quad y = \frac{4\sqrt{3}}{T}\lambda , \qquad (32)$$

in terms of which we can write relations (11) as

$$\rho = -\frac{y}{2}\sin\phi, \quad \sigma = -\frac{y}{2\sqrt{3}}\cos\phi . \tag{33}$$

The temperature T_c used in Ref. [7] is related to our definition by

$$T_c = \frac{1}{3\mu^2}T , \qquad (34)$$

where μ is given by Eq. (21). In the sequel we will refer to T_c as the classical temperature.

In terms of the variables y and ϕ , the equilibrium equations reduce to

$$\frac{1}{4}yT = \frac{\partial}{\partial y}\ln Z_0^{(p,q)}, \quad 0 = \frac{\partial}{\partial \phi}\ln Z_0^{(p,q)}.$$
(35)

The free energy F of the system is

$$\beta F = -\ln Z_0^{(p,q)} + \frac{T}{2}\rho^2 + \frac{3T}{2}\sigma^2 = -\ln Z_0^{(p,q)} + \frac{1}{8}Ty^2 , \qquad (36)$$

which has to be an absolute local minimum, according to Eqs. (35), in order to determine the equilibrium state of the system. The thermodynamic properties are given by

$$\frac{S}{k} = -\frac{1}{4}y^2T + \ln Z_0^{(p,q)}, \quad \frac{U}{J} = -\frac{1}{32}T^2y^2, \quad \frac{C}{k} = -\frac{1}{8}\frac{d}{dT}(y^2T^2), \quad (37)$$

where S is the entropy per particle due to the orientational order, U is the energy per particle and C is the specific heat. They correspond to the same expressions used in Ref. [7].

The symmetries of the partition function allow us to restrict the initial interval $-\pi < \phi < \pi$ to $0 < \phi < \frac{\pi}{3}$. Furthermore, we have the following relations among the different values of Λ_i :

$$0 < \Lambda_1 < \Lambda_2 < 1 < \Lambda_3, \quad 0 < \phi < \frac{\pi}{6}, \\ 0 < \Lambda_1 < 1 < \Lambda_2 < \Lambda_3, \quad \frac{\pi}{6} < \phi < \frac{\pi}{3},$$
(38)

which reduce to

$$\Lambda_1 = e^{(1/\sqrt{3})y\cos(\phi + 2\pi/3)}, \quad \Lambda_2 = e^{(1/\sqrt{3})y\cos(\phi - 2\pi/3)}, \quad \Lambda_3 = e^{(1/\sqrt{3})y\cos\phi}.$$
(39)

Their ratios are

$$\frac{\Lambda_1}{\Lambda_3} = e^{-y\sin(\phi + \pi/3)}, \quad \frac{\Lambda_2}{\Lambda_3} = e^{-y\sin(\pi/3 - \phi)}, \quad \frac{\Lambda_1}{\Lambda_2} = e^{-y\sin\phi}.$$
(40)

6. The phases of the system

The free energy βF of the system, given by Eq. (36), is a function of five variables; $\beta F = \beta F(T, p, q, y, \phi)$. The absolute minimum conditions (35), which correspond to two equations in our case, allow us to find y = y(T, p, q) and $\phi = \phi(T, p, q)$ for equilibrium, thus selecting the particular phase which is energetically favorable. This calculation is made numerically, and these results determine all the remaining thermodynamic properties of the system. The entropy, energy and specific heat can be subsequently calculated by using the expressions (37). The general behavior of the specific heat, as a function of the temperature is presented in Fig. 1. Here we have labeled by T_b , T_u , the transition temperatures between the biaxial–uniaxial phases and the uniaxial–isotropic phases, respectively.

6.1. The $T \to 0 (y \to \infty)$ case

Let us consider the interval $0 < \phi < \frac{\pi}{3}$ in such a way that all the ratios (40) tend to zero exponentially. For $p, q \ge 1$, the corresponding limit in the partition function (8) is

$$\ln Z_0^{(p,q)} = (p+q) \ln \Lambda_3 + q \ln \Lambda_2 + \frac{\Lambda_1}{\Lambda_3} + \frac{\Lambda_2}{\Lambda_3} + \frac{\Lambda_1}{\Lambda_2} .$$
(41)

In order to determine which of the last three terms in the above expression dominates, we still have to consider the further intervals $0 < \phi < \frac{\pi}{6}$, where $\sin \phi < \sin(\frac{\pi}{3} - \phi) < \sin(\frac{\pi}{3} + \phi)$, together with $\frac{\pi}{6} < \phi < \frac{\pi}{3}$, where $\sin(\frac{\pi}{3} - \phi) < \sin \phi < \sin(\frac{\pi}{3} + \phi)$. In the first case, the free energy reduces to

$$\beta F = -(p+q)\frac{y}{\sqrt{3}}\cos\phi - q\frac{y}{\sqrt{3}}\cos\left(\phi - \frac{2\pi}{3}\right) - e^{-y\sin\phi} + \frac{1}{8}Ty^2.$$
(42)



Fig. 1. General form of the specific heat as a function of temperature, for the different phases.

Introducing the notation

$$A(\phi) = \frac{p+q}{\sqrt{3}}\cos\phi + \frac{q}{\sqrt{3}}\cos\left(\phi - \frac{2\pi}{3}\right) ,$$

$$B(\phi) = \frac{p+q}{\sqrt{3}}\sin\phi + \frac{q}{\sqrt{3}}\sin\left(\phi - \frac{2\pi}{3}\right) ,$$
(43)

the solutions that minimize the free energy are

$$\phi = \phi_0 - \frac{\cos \phi_0}{A(\phi_0)} e^{-(4A(\phi_0)/T)\sin \phi_0}, \quad \tan \phi_0 = \frac{\sqrt{3q}}{2p+q},$$

$$y = \frac{4}{T} (A(\phi_0) - \sin \phi_0 e^{-(4A(\phi_0)/T)\sin \phi_0}).$$
(44)

This limit corresponds to the biaxial equilibrium phase since $\lambda \neq 0$, $\phi \neq 0$. For the case $0 < \phi < \frac{\pi}{6}$, we obtain the following expression for the specific heat:

$$\frac{C}{k} = \left(\frac{2q}{T}\right)^2 e^{-2q/T} , \qquad (45)$$

where there is a mass gap given by 2q. The prediction (45) has to be compared with the classical case, where the specific heat goes like $C/k = 3 + 3T/(\mu \sin 3\psi)^2$ in that limit. Moreover, Eq. (45) signals a peculiar behavior for the cases q=0, $p \neq 0$, which will be separately discussed in Section 6.4.

The analogous solution in the interval $\pi/6 \leq \phi \leq \pi/3$ leads to

$$\frac{C}{k} = \left(\frac{2p}{T}\right)^2 e^{-2p/T} .$$
(46)

This is consistent with the symmetry $p \leftrightarrow q$ which connects the corresponding two intervals of ϕ .

6.2. Biaxial-uniaxial phase transition

The uniaxial phase is characterized by $y \neq 0$, $\phi = 0$. In order to determine the transition temperature T_b , we expand the free energy $F(T, y, \phi)$ in powers of ϕ and find the corresponding minimum. The expression is

$$\beta F(T, y, \phi) = \frac{Ty^2}{8} + G_0(y) + G_2(y) \phi^2 + O(\phi^4) , \qquad (47)$$

where the functions G_0, G_2 are explicitly known. To determine the transition temperature we approach from the biaxial phase and look for the corresponding minimum of (47) having $y \neq 0$ and $\phi \neq 0$, but small. The conditions are

$$0 = \frac{\partial F}{\partial \phi} = 2\phi G_2(y) + \mathcal{O}(\phi^3) , \qquad (48)$$

$$0 = \frac{\partial F}{\partial y} = \frac{Ty}{4} + \frac{\partial G_0}{\partial y} + \mathcal{O}(\phi^2) .$$
(49)

From Eq. (48) we obtain $G_2(y) = 0$, whose numerical solution determines \bar{y} . Substituting this result in Eq. (49), the transition temperature is

$$T_b = -4\left(\frac{1}{y}\frac{\partial G_0}{\partial y}\right)\Big|_{\bar{y}}$$
(50)

6.3. Uniaxial-isotropic phase transition

As we keep increasing the temperature we go from the uniaxial phase to the isotropic phase, characterized by $\phi = 0$, y = 0. To determine the transition temperature T_u we proceed in complete analogy to the previous section. Now we expand the free energy of the uniaxial phase in the vicinity of y = 0,

$$\beta F(y,\phi=0,T) = -\ln Z_0^{(p,q)} + \frac{1}{8}Ty^2 = \frac{1}{8}Ty^2 - \frac{1}{16}I_2y^2 - \frac{\sqrt{3}}{240}I_3y^3 - \ln \frac{(p+1)(q+1)(p+q+2)}{2} + \frac{1}{2560}I_2(I_2+2)y^4 + \frac{\sqrt{3}}{8960}I_2I_3y^5 + O(y^6).$$
(51)

In this case, the equilibrium condition is given by the inflection points of the free energy, i.e. $\partial F/\partial y = 0$, $\partial^2 F/\partial y^2 = 0$.

Keeping up to fourth-order terms in (51), the above system is solved by

$$y^* = 4\sqrt{3} \frac{I_3}{I_2(I_2+2)}, \quad T^* = \frac{1}{2}I_2 + \frac{3}{10} \frac{I_3^2}{I_2(I_2+2)}.$$
 (52)

This solution is a good approximation whenever y^* is small.

Nevertheless, for a range of temperatures below T^* , we can verify that the uniaxial phase does not provide an absolute minimum for the free energy of the system. In fact, the calculated free energy is higher than the one corresponding to the isotropic phase, which makes the uniaxial phase metastable. In this way, the true transition temperature T_u between the uniaxial and the isotropic phase is obtained by the minimum condition together with the requirement that $\beta F = \beta F|_{isotropic} = -\ln \frac{1}{2}(p+1)(q+1)(p+q+2)$. In the same approximation as the one used in Eq. (52), these new conditions provide

$$y_u = 4\sqrt{3} \frac{4I_3}{3I_2(I_2+2)}, \quad T_u = \frac{1}{2}I_2 + \frac{4}{15}\frac{I_3^2}{I_2(I_2+2)},$$
 (53)

which confirm that $T_u < T^*$, together with the fact that the metastable region is small indeed. A further discussion of the metastability region can be found in Section 4.5 of Ref. [5].

We can calculate the limit of the specific heat when we approach T_u from the left, in the case when $I_3 \rightarrow 0$ ($p \rightarrow q$). To this end we have to find y = y(T), which we obtain by requiring $\partial F/\partial y = 0$ in Eq. (51). We get

$$y = 4\sqrt{3} \frac{1}{I_2(I_2+2)} \left(I_3 + \sqrt{I_3^2 + \frac{10}{3}I_2(I_2+2)\left(\frac{I_2}{2} - T\right)} \right) .$$
 (54)

From the above equation we can verify that if we substitute the value for T_u given by Eq. (53), we recover the value y_u written in the same equation. Next, we use the expression (37) for the specific heat to obtain

$$\left. \frac{C}{k} \right|_{T \to T_u} = 20 \frac{I_2}{I_2 + 2} + \mathcal{O}(I_3^2) \,. \tag{55}$$

This expression has the correct classical limit given by $C/k|_{T \to T_u} = 20$.

6.4. The $q = 0, p \neq 0$ case

According to Eqs. (23), q=0 corresponds to the lower bound of ψ , $\sin \psi_{\min} = 1/\sqrt{3\mu}$, for a given value of μ . There is also a maximun value of ψ , given by the condition p=0. The classical case corresponds to $\mu \to \infty$, which set these limits in $\psi_{\min} = 0$ and $\psi_{\max} = \frac{\pi}{3}$, respectively. Thus, the quantum version of the model contrains the range of ψ in the phase diagram accordingly, as shown in Figs. 4 and 5. Similarly as in the classical case, these boundaries present only an isotropic–uniaxial transition and the biaxial phase is not present at all.

Let us consider the limit $T \to 0$ within the range $0 \le \phi \le \frac{\pi}{6}$ in expression (8) for the exact partition function. As before, $\Lambda_1, \Lambda_2 \to 0$ while $\Lambda_3 \to \infty$ in such a way that the expansion of the partition function up to second-order terms leads to

$$\ln Z_0^{(p,q=0)} = p \ln \Lambda_3 + \frac{\Lambda_1}{\Lambda_3} + \frac{\Lambda_2}{\Lambda_3} - \frac{1}{2} \left(\frac{\Lambda_1}{\Lambda_3}\right)^2 - \frac{1}{2} \left(\frac{\Lambda_2}{\Lambda_3}\right)^2 + \cdots .$$
 (56)

The above expression differs from the q = 0 restriction of Eq. (41), in the absence of the previously dominating term Λ_1/Λ_2 . It is enough to consider (56) to first order,

which leads to

$$\beta F = -\frac{p}{\sqrt{3}} y \cos \phi - e^{-y \sin(\pi/3 - \phi)} - e^{-y \sin(\pi/3 + \phi)} + \frac{1}{8} T y^2 .$$
(57)

Since we are interested in solutions near $\phi = 0$, we have to keep both exponentials, which are of the same order now. The equilibrium conditions lead to $\phi = 0$, i.e. we remain in the uniaxial phase for low temperatures, with no transition to the biaxial one. We also obtain

$$y = \frac{4}{T\sqrt{3}}(p - 3e^{-2p/T}).$$
(58)

The above expression leads to a specific heat given by

$$\frac{C}{k} = \frac{8p^2}{T^2} e^{-2p/T} , (59)$$

in the $T \to 0, y \to \infty$ limit.

The absence of the biaxial phase in this case can also be verified from the general discussion of Section 6.2, by looking at the expansion of the free energy in powers of ϕ . It is possible to verify numerically that the coefficient of the power ϕ^2 in Eq. (47) cannot be made zero, unless y = 0. That is to say, there can be no transition to the biaxial phase when q = 0, $p \neq 0$.

The angle ψ is given by

$$\cos 3\psi = \frac{p(p+3)(2p+3)}{2(p^2+3p+3)^{3/2}},$$
(60)

which reduces to the classical value $\cos 3\psi = 1$, i.e. $\psi = 0$, in the limit $p \to \infty$. Recalling the phase diagram of Ref. [7], we verify that in this regime we have only the uniaxial and isotropic phases.

6.5. The p = q case

Here $I_2 = p(p+2)$, $I_3 = 0$. At low temperatures the equilibrium points correspond to the biaxial phase and, exactly as in the classical situation, the phase transition is directly to the isotropic one. In order to better understand the limiting values of the transition temperature, together with the resulting specific heats, we will take the corresponding limit starting from the uniaxial phase, with $I_3 = 0$. In this case Eq. (54), valid for any point in this phase, reduces to

$$y = 4\sqrt{\frac{10}{I_2(I_2+2)}} \left(\frac{I_2}{2} - T\right).$$
(61)

From Eqs. (53) we see that, in this limit, the uniaxial phase merges into the isotropic one, with y = 0, at the transition temperature $T_b = T_u = \tilde{T} = I_2/2$. In the conventions of Ref. [7], this temperature corresponds to

$$\tilde{T}_c = \frac{1}{8} \frac{I_2}{I_2 + 1} , \qquad (62)$$

which reproduces the value $\tilde{T}_c = \frac{1}{8}$ for high quantum numbers. The specific heat at the transition is

$$\frac{C}{k}\Big|_{\tilde{T}} = 5\frac{I_2}{I_2 + 2} = 5\frac{(p+1)^2 - 1}{(p+1)^2 + 1}.$$
(63)

The above result reproduces the classical prediction.

7. Final comments

We have presented a quantum mechanical description of the orientational degrees of freedom of a biaxial nematic liquid in the mean field approximation, thus extending the classical approach proposed in Ref. [7].

The fact that the dynamical variables carry a representation of SU(3) allows again for an exact calculation of the quantum partition function, this time in terms of the Weyl formula for the characters of the group. In this way, the consistent equations of the mean field approximation reduce to two coupled algebraic equations, in a manner similar to the case in Ref. [7]. As expected Ref. [27,28], the classical behavior is recovered in the high temperature, high quantum numbers regime.

The phase structure of the system includes a biaxial phase in the range $0 < T < T_b$, a uniaxial phase in the range $T_b < T < T_u$, $T_b < T_u$, and an isotropic phase for $T > T_u$. The latter phase acts here as a reference, because the model does not include a description of translational degrees of freedom of the liquid. This structure is exhibited in Figs. 1 and 3 for the specific heat, as well as in the phase diagrams shown in Figs. 4 and 5.

Generally speaking, the quantum calculation introduces the following modifications with respect to the classical situation: (i) a correct description of the thermodynamic quantities in the limit $T \rightarrow 0$ is predicted, which is absent in the classical case, (ii) a systematic decrease in the transition temperatures T_u, T_b is found, and (iii) a three-dimensional phase diagram is obtained.

In the low temperature limit $T \to 0$, the quantum calculation of the specific heat leads to the result $C/k \sim 1/T^2 e^{-\alpha/T}$, according to Eqs. (45) and (46), signaling a mass gap characteristic of the quantum spectra. The classical limit in this regime is C/k = 3. Also, the quantum calculation is consistent with the Nernst postulate for the entropy in the $T \to 0$ limit. Representative curves of the specific heat are shown in Figs. 2 and 3, for different choices of p, q. Each figure includes the classical prediction for comparison.

Deviations from the above general picture appear in two cases: (i) The region p = q, $(\psi = \pi/3)$ presents a direct transition from the biaxial to the isotropic phase, in complete analogy with the classical situation. This can be seen in Fig. 2. (ii) The region q = 0, $p \neq 0$, corresponding to $\psi = \psi_{\min}$ (p = 0, $q \neq 0$, corresponding to $\psi = \psi_{\max}$) does not support the biaxial phase and only allows for a uniaxial-isotropic phase transition.



Fig. 2. Specific heat for different values of p = q, ($\psi = 30^{\circ}$ and different values of μ). The upper curve is the classical result. The temperature T is in classical units.



Fig. 3. Specific heat for p = 1, q = 2, $(\mu = 2.9, \psi = 36.6^{\circ})$ and p = 27, q = 41, $(\mu = 40.7, \psi = 36.6^{\circ})$. The upper curve is the classical result. The temperature T is in classical units.

In the quantum regime, the free energy of the system is a function of the variables μ , ψ , y, ϕ , T_c , as opposed to the classical case where μ and y enter through the combination $x = (\sqrt{3}T_c/8)\mu y$. This means that our phase diagram is three-dimensional



Fig. 4. Phase Diagram for $\mu = 2$. The temperature *t* is in classical units $\times 1000$. The phases are denoted by: I (Isotropic), U (Uniaxial) and B (Biaxial). The region inside the two horizontal lines is the allowed domain of ψ .



Fig. 5. Phase Diagram for $\mu = 15$. The temperature *t* is in classical units $\times 1000$. The phases are denoted by: I (Isotropic), U (Uniaxial) and B (Biaxial). The region inside the two horizontal lines is the allowed domain of ψ .

instead. In order to provide a smooth comparison with the classical case, we have chosen to construct the phase diagram in terms of μ , ψ and T_c . In Figs. 4 and 5 we present the two-dimensional sections corresponding to $\mu = 2$ and $\mu = 15$, respectively, employing the same coordinate scales in both cases. The latter is almost classical, while the former is purely quantal. The over-all shape of both diagrams is the same, and the corresponding domain of the angle ψ is restricted by the condition p, q > 0. Nevertheless, the μ -dependence is clearly exhibited, showing the lowering of the transition temperatures, as commented above. These diagrams have been obtained by assuming that p and q are continuous, instead of discrete, variables. The physical points, corresponding to integers p, q correspond to a subset in such diagrams, which becomes denser as long as p, q increase. The interpolation between $\mu = 2$ and 15 is smooth, as verified for a number of intermediate values of the parameter.

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