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A QUANTUM THEORY OF LIQUID CRYSTALS

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Abstract: A new approach towards an understanding of the basic excitations in the nematic liquid crystals is presented by exploring the pseudo-spin formalism. The hamiltonian of the system is explicitly written for spin 1 in terms of the boson creation and annihilation operators.
Using a method as developed in relation to the hydrogen-bonded ferroelectrics the spectrum of elementary excitations is calculated in two very important regions; one region being around the reciprocal lattice vector $\vec{q} = 0$, the other region being around the value $\vec{q}_0$ which coincides with the second maximum in a Fourier transform of the intermolecular potential. The former region corresponds to a linear part of the spectrum, whereas the latter region corresponds to a rotonic part of the spectrum.
In order to test the present results we have explicitly calculated the zero-sound velocity and the mass of the rotons.

1. Introduction

Liquid crystals discovered almost a century ago[1, 2] and classifield by Friedel[3, 4, 5] into three categories, namely, nematic, smectic and cholesteric, have been the subject of an extensive research[6, 7, 8]. A liquid crystal physically is a fluid with a molecular structure giving rise to a preferred direction at each point of the material. In smectic liquid crystals the large elongated molecules lie in layers with their long axes perpendicular to the planes of the layers and fluidity arises on account of the layers sliding over each other. On the other hand in nematic and cholesteric liquid crystals, the molecules are not confined in layers but are capable of random orientations in such a way as to make the orientations more or less continuous throughout

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the liquid. Furthermore nematic liquid crystals possess certain invariance properties under reflections, while this is not the case with the cholesteric liquids.

Existing theories for liquid crystals are classical consisting of a swarm[9] or a continuum model[10], so there should exist a need for a quantum theory. In the present paper we concentrate our attention to nematic liquid crystals. We suppose that a random orientation of large elongated rodlike molecules have a definite pattern in liquid state. In other words, we assume a definite ordering of molecules specifying their random orientation with the components of pseudospins which have been successfully explored to take quantum effects in ferroelectric hydrogen bonded crystals by De Gennes[11], Brout et al.[12] and Novaković[13]. At a nematic liquid — isotropic liquid transition temperature this ordering vanishes. This is the main subject in the present work. There is in literature a little different current concept of the ordering process[14, 15, 16]. Then we propose a general hamiltonian for nematic liquid crystals as discussed in Chapter 2. In Chapter 3 we consider the collective elementary excitations in such a system, whereas a possible effect of anharmonic terms is discussed in Chapter 4 together with the conclusion.

2. *General model*

In this Chapter we formulate a model hamiltonian for a nematic liquid crystal. Assuming that each long elongated rod-like molecule has n different orientations in such a way that these orientations are described by the components of a pseudo-spin S_j^z, where j labels the molecular sites, we propose the following hamiltonian of the system

$$H = -\sum_j \sum_{n=1}^{2S} \Omega_j (S_j^x)^n - \sum_{j,k} J_{jk} S_j^z S_k^z. \tag{1}$$

Here Ω_j are quantum parameters related to a transfer energy, whereas J_{jk} are ordinary parameters related to the intermolecular potential. It should be noted that this hamiltonian with $\Omega_1 \neq 0$ and $\Omega_n (n \geqslant 2) = 0$ is identical with the hamiltonian of a KDP type. However, J_{jk} are completely different in the two cases. At present J_{jk} is continuously varying function for a fluid, $J_{jk} = f(|\vec{r}|), \vec{r} = \vec{r}_j - \vec{r}_k$, which is not the case for solids like KDP.

The above hamiltonian is thus very general, so we simplify it a bit further by letting $n = 1, 2$. Physically, we imagine a molecular structure of a nematic liquid crystal in which all rod-like molecules are capable of 3 possible orientations. This is only a mathematical simplification and there is no physical restriction of the general model. However, the treatment and results to be

obtained would essentially be identical for general S. Thus the hamiltonian simplifies to

$$H = -\Omega_1 \sum_i S_i^x - \Omega_2 \sum_j (S_j^x)^2 - \sum_{j,k} J_{jk} S_j^z S_k^z, \tag{2}$$

where $S = 1$. Now, we rotate the spin system through an angle φ, i. e.,

$$\begin{aligned} S_i^x &= \cos\varphi\, S_i^{x'} + \sin\varphi\, S_i^{z'}, \\ S_i^z &= -\sin\varphi\, S_i^{x'} + \cos\varphi\, S_i^{z'}. \end{aligned} \tag{3}$$

Further, we define a spin-raising (lowering) operator S_i^+ as $S_i^- = (S_j^{x'} \pm \pm i S_j^{y'})/2$ by assuming a bosonic character for these operators as follows

$$\begin{aligned} S_j^+ &= \sqrt{2S}\,(1 - \varepsilon\, b_j^+ b_j)\, b_j + \ldots \\ S_j^- &= \sqrt{2S}\, b_j^+ (1 - \varepsilon\, b_j^+ b_j) + \ldots \\ S_j^{z'} &= S - b_j^+ b_j, \end{aligned} \tag{4a}$$

where the parameter ε depends on the representation used. Using a set of ideal bosons we obtain (see Ref. [17])

$$\varepsilon = 1 - \sqrt{\frac{2S-1}{2S}}\,. \tag{4b}$$

This leads for large S to the result $\varepsilon = 1/4S$ just like in the Holstein-Primakoff[18] representation.

3. *Elementary excitations*

With the aid of transformations (3) and (4), the hamiltonian (2) takes the following form:

$$H = H_1 + H_2 + H_3 + H_4, \tag{5}$$

where

$$H_1 = -\frac{\sqrt{2S}}{2}\cos\varphi\,\{(\Omega_1 + 2S\,\Omega_2 \sin\varphi)\sum_i A_j - S\sin\varphi \sum_{i,k} J_{jk}(A_j + A_k)\}, \tag{6}$$

$$H_2 = (\Omega_1 \sin\varphi + 2S\,\Omega_2 \sin^2\varphi)\sum n_j - \frac{S\,\Omega_2}{2}\cos^2\varphi \sum A_j^2 + S\cos^2\varphi \sum J_{jk}(n_j + n_k) - \frac{S}{2}\sin^2\varphi \sum J_{jk} A_j A_k, \tag{7}$$

$$H_3 = \varepsilon\frac{\sqrt{2S}}{2}\cos\varphi\,[\Omega_1 + 2S\,\Omega_2\cos\varphi]\sum(n_j b_j + b_j^+ n_j) + \frac{\sqrt{2S}}{2}\Omega_2 \sin\varphi\cos\varphi \sum(n_j A_j + A_j n_j) - \frac{\varepsilon S}{2}\sqrt{2S}\sin\varphi\cos\varphi \cdot \sum J_{jk}(n_k b_k + b_k^+ n_k + n_j b_j + b_j^+ n_j) - \frac{\sqrt{2S}}{2}\sin\varphi\cos\varphi \sum J_{jk}(n_j A_k + A_j n_k), \tag{8}$$

$$H_4 = -\frac{\varepsilon S}{2}\cos^2\varphi\,\Omega_2 \sum [A_j(n_j b_j + b_j^+ n_j) + (n_j b_j + b_j^+ n_j) A_j] - \Omega_2 \sin^2\varphi \sum n_j^2 - \cos^2\varphi \sum J_{jk} n_j n_k + \frac{\varepsilon S}{2}\sin^2\varphi \sum J_{jk}[A_j(n_k b_k + b_k^+ n_k) + (n_j b_j + b_j^+ n_j) A_k], \tag{9}$$

with

$$A_j = b_j^+ + b_j,$$

$$n_j = b_j^+ b_j.$$

Now the condition for the system to achieve a ground state is given by $H_1 = 0$ leading to

$$\Omega_1 = 2S(J - \Omega_2)\sin\varphi. \tag{10}$$

where $J = \Sigma J_{jk}$. Thus if $\Omega_2 = 0$ then

$$\Omega_1 = 2SJ\sin\varphi. \tag{11}$$

The hamiltonian H_2 would yield elementary excitations for the system while the effect of anharmonic terms are discussed in the last Chapter. We take the Fourier transform for H_2, by letting

$$\begin{aligned} b_{\vec{q}} &= \frac{1}{\sqrt{N}} \sum_j e^{\vec{j}\cdot\vec{rj}}\, b\,, \\ b^+_{\vec{q}} &= \frac{1}{\sqrt{N}} \sum_j e^{-\vec{iq}\cdot\vec{rj}}\, b^+, \end{aligned} \tag{12}$$

so H_2 becomes,

$$H_2 = \sum_{\vec{q}} \left[2W n_{\vec{q}} + W(\vec{q}) \left(2n_{\vec{q}} + b^+_{\vec{q}}\, b^+_{\vec{q}} + b_{\vec{q}}\, b_{\vec{-q}} \right) \right], \tag{13}$$

where

$$W = \frac{\Omega_1}{2}\sin\varphi + S\Omega_2 \sin^2\varphi + SJ(0)\cos^2\varphi, \tag{14}$$

$$W(\vec{q}) = -\frac{S}{2}(\Omega_2\cos^2\varphi + J(\vec{q})\sin^2\varphi). \tag{15}$$

Writing

$$H_2 = \sum_{\vec{q}} \left[W(n_{\vec{q}} + n_{\vec{-q}}) + W(\vec{q})(n_{\vec{q}} + n_{\vec{-q}} + b^+_{\vec{-q}}\, b^+_{\vec{q}} + b_{\vec{q}}\, b_{\vec{-q}}) \right], \tag{16}$$

and letting

$$\begin{aligned} b_{\vec{q}} &= u(\vec{q})\, B_{\vec{q}} + v(\vec{p})\, B^+_{\vec{-q}}, \\ b^+_{\vec{q}} &= u(\vec{q})\, B^+_{\vec{q}} + v(\vec{p})\, B_{\vec{-q}}, \\ u^*(\vec{q}) &= u(\vec{q}) = u(\vec{-q}), \\ v^*(\vec{q}) &= v(\vec{q}) = v(\vec{-q}), \\ u^2(\vec{q}) - v^2(\vec{q}) &= 1, \end{aligned} \tag{17}$$

H_2 is transformed into

$$H_2 = \sum_{\vec{q}} \omega(\vec{q})\, B^{+}_{\vec{q}} B_{\vec{q}}, \tag{18}$$

$$\omega^2(\vec{q}) = X^2(\vec{q}) - W^2(q), \tag{19}$$

where

$$X(\vec{q}) = W + W(\vec{q}). \tag{20}$$

Furthermore, we assume an expansion for $J(\vec{q})$ as

$$J(\vec{q}) = J(0)(1 - \alpha_1 q^2),\ q \sim 0, \tag{21}$$

$$J(\vec{q}) = J(q_0)[1 - \alpha_2 (q - q_0)^2],\ q \sim q_0, \tag{22}$$

and inserting these expansions along with

$$\begin{aligned} \cos^2\varphi &= \lambda (T - T_c), \\ \sin^2\varphi &= 1 - \lambda (T - T_c), \end{aligned} \tag{23}$$

the frequency takes the following form:

$$\omega^2(\vec{q}) = P_1 (T - T_c) + Q_1 q^2,\ q \sim 0, \tag{24}$$

$$\omega^2(\vec{q}) - \Omega^2 + P_2 (T - T_c) + Q_2 (q - q_0)^2,\ q \sim q_0, \tag{25}$$

where

$$\begin{aligned} P_1 &= S^2 J(0)[J(0) - Q_2]\lambda, \\ Q_1 &= S^2 J^2(0)\alpha_1, \\ \Omega^2 &= S^2 J(0)[J(0) - J(q_0)], \\ P_2 &= S^2 J(0)[J(q_0) - \Omega_2]\lambda, \\ Q_2 &= S^2 J(0) J(q_0)\alpha_2. \end{aligned} \tag{26}$$

A remark should be made regarding the relation (23) which we have assumed in analogy with ferroelectric case. Here T_c indicates the transition temperature at which a nematic-isotropic liquid phase occurs; λ is a constant with the dimension T^{-1}. A rough plot of above frequencies indicates that there exists for large q a rotonic contribution analogous to that in liquid helium (see Fig. 1).

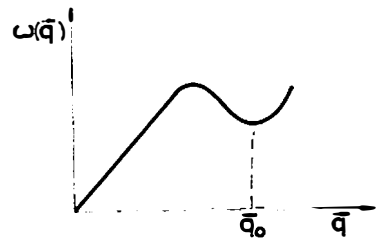

Fig. 1. A dispersion law for a nematic liquid crystal. The region $\vec{q} = \vec{q}_0$ indicates a rotonic part of the spectrum.

Further we observe that for small values of q, $\omega^2(q) \sim q^2$. Thus, this gives rise to the existence of a zero-sound[19]. Therefore, the zero-sound velocity c and the rotonic mass M^* are given by

$$c = \frac{\sqrt{Q_1}}{\hbar}, \qquad M^* = \frac{\hbar \Omega_2}{Q_2}. \tag{27}$$

To estimate these quantities we have to evaluate Q_1, Q_2, and Ω occuring in Equ. (26). To do this we specify,

$$J(\vec{q}) = \frac{V(\vec{q})}{S^2 N}, \tag{28}$$

where N is a normalization factor obtained by normalizing $J(\vec{q})$ to the condition (see Ref.[20])

$$S^2 J(\vec{q}_m) = -kT_c,$$

where k is the Boltzmann constant and q_m is the first minimum in $V(\vec{q})$ as a function of $\vec{q}$ (see Fig. 2). Needless to say, it is not reasonably known as to what intermolecular potential function $V_{ij}(|\vec{r}_i - \vec{r}_j|)$ should be assumed. A

hard core of the Lennard-Jones type potential for fluids is generally assumed. Also, other potential functions might well be used. Then we take a Fourier transform for such a potential to obtain

$$V(q) = -\frac{A}{2\pi^2}\left[\int_{r_0}^{\infty} \frac{\sin q r}{q r^5}\,\mathrm{d}r - \left(\frac{1}{2}\,3.7\cdot 10^{-6}\,\mathrm{cm}\right)^6 \int_{r_0}^{\infty} \frac{\sin q r}{q r^{11}}\,\mathrm{d}r\right], \quad (29)$$

where the parameters A and r_0 are due to Ref.[14]

$$A = 13\cdot 10^{-9}\ \mathrm{erg\ cm^6},$$

$$r_0 = 6\sigma = 3.427\cdot 0.164\ \text{Å} \cong 0.6\ \text{Å}.$$

The above numerical values are chosen for para-azoxyanisole as a typical nematic crystal. Since r_0 should not be taken too seriously, we estimated

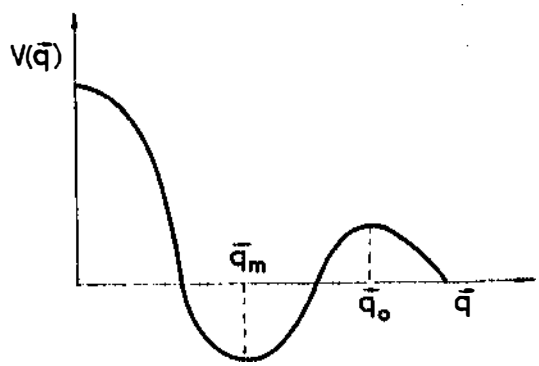

Fig. 2. A Fourier transform for the two-particle potential energy for a nematic liquid crystal; the region $\vec{q} = \vec{q}_m$ indicates a thermal motion such that $S^2 J(\vec{q}_m) = -kTc$, Tc being a liquid crystal — isotropic liquid transition temperature.

$V(\vec{q})$ for $r_0 = 0.5$ Å using a CDC computer at Vinča. The obtained curve is given in Fig. 2. The results for $S = 1$ are as follows

$$q_m = 8.60\ \text{Å}^{-1},\quad V(q_m) = 8.98\cdot 10^{13}\ \mathrm{erg\ cm^3},$$

$$q_0 = 14.1\ \text{Å}^{-1},\quad V(q_0) = 4.71\cdot 10^{13}\ \mathrm{erg\ cm^3}, \quad (30)$$

$$V(0) = 4.8\cdot 10^{18}\ \mathrm{erg\ cm^3}.$$

These yield,

$$N = 2 \cdot 10^{32}$$

$$\alpha_1 = 2.1 \cdot 10^{-17} \text{ cm}^2 \tag{31}$$

$$\alpha_2 = 3.2 \cdot 10^{-17} \text{ cm}^2.$$

With the help of these numerical values the velocity of sound c and the rotonic mass M^* are estimated as $c = 10^6$ cm/sec and $M^* = 1.2 \cdot 10^{-24}$ g. It is safe to remark that these estimations may not be unique as they depend on our choice of the potential function.

4. *Conclusion*

We have presented a new approach to liquid crystals especially of nematic type by exploring the pseudo-spins in order to describe the spontaneous orientations of rod-like molecules. Then the hamiltonian of such a system has been conveniently expressed in terms of pseudo-spins in analogy with the hamiltonian of hydrogen-bonded ferroelectrics. Assuming that the intermolecular potential has a Lennard-Jones form, we obtain an expression for the collective excitation frequency. Such a frequency was analyzed in two important regions, one being around the first maximum in $V(\vec{q})$, i. e. $\vec{q}_0$, and the other around the origin $\vec{q} \sim 0$. The latter yields an expression for a zero-sound velocity while the former gives an estimation for the rotonic mass. The existence of a zero-sound is undersandable as such a property is possible even in classical liquids[19, 21]. However, the rotonic part of the spectrum is rather striking in so much as a phenomenon typical for a quantum liquid like a liquid helium. We have estimated the values of sound velocity and rotonic mass which open a possibility of an experimental verification of the present model. Furthermore, the anharmonic terms in the hamiltonian may give a contribution to the frequency width and shift to the unperturbed collective frequency. Such a study is possible by following the work of Maradudin and Fein[22] concerning the scattering of neutrons by an anharmonic crystal lattice. Also, the change in specific heat at a nematic-isotropic liquid transition has been reported by Kreutzer et al.[23]. It is interesting to test our model by obtaining a comparable estimation for the same quantity. This work is in progress.

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KVANTNA TEORIJA TEČNIH KRISTALA

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Sadržaj

Tečni kristal je fluid sa takvom molekularnom strukturom koja prouzrokuje jedan istaknuti smer u svakoj tački materijala. Prema Friedelu tečni kristali mogu biti nematski, smektički i kolesterični. U smektičkim tečnim

kristalima velike izdužene molekule leže u paralelnim slojevima tako da duže ose stoje okomito na ravan slojeva dok fluidnost nastaje tako što slojevi klize jedan povrh drugog. Međutim, u nematskim i kolesteričnim tečnim kristalima molekule nisu ograničene pomoću slojeva već mogu proizvoljno da se orijentišu na taj način da dozvole orijentacije manje-više kontinualno u prostoru tečnog kristala. Opšte osobine ovih kristala proučene su u Ref.[1-8].

U ovom radu pažnja je koncentrisana na nematske kristale da bismo proučili onovna pobudenja u blizini temperature prelaza iz faze nematkog kristala u fazu izotropne tečnosti.

Uređenje molekula opisano je pomoću z-komponente pseudo-spina odnosno fiktivnog spina, dok je hamiltonijan sistema napisan pomoću skupa operatora komponenata pseudo-spina. Zatim je prelaskom na bozonske operatore kreiranja i anihiliranja razdvojen harmonijski komad hamiltonijana od neharmonijskog. Sopstvene vibracije sistema dobijene su metodom dijagonalizacije harmonijskog komada hamiltonijana.

Ukazano je na postojanje dveju interesantnih oblasti spektra pobuđenja. Jedna oblast je oko vrednosti $\vec{q} = 0$, gde $\vec{q}$ označava vektor recipročne rešetke dok je druga oblast oko vrednosti $\vec{q} = \vec{q}_0$, gde $\vec{q}_0$ označava drugi maksimum u Fourier-ovoj transformaciji intermolekularnog potencijala. Prva oblast predstavlja tzv. linearni deo spektra dok druga oblast predstavlja tzv. rotonski deo spektra.

Da bi se dobijeni rezultati proverili merenjem eksplicitno su izračunate dve značajne veličine a to su brzina nultog zvuka koja karakteriše linearni deo spektra kao i masu rotona koja karakteriše rotonski deo spektra. Taj drugi deo spektra predstavlja vrlo značajno otkriće jer ukazuje na sličnost između dinamike tečnih kristala i dinamike kvantnih tečnosti kao što je tečni helijum iako sa gledišta kinematike ova dva sistema prividno nemaju sličnosti.