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Soft-mode dynamics in nematic liquid crystals

R. Blinc, S. Lugomer, and B. Žekš
Institute "Jožef Stefan", University of Ljubljana, Ljubljana, Yugoslavia

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The dynamic properties of the molecular model proposed by Maier-Saupe (MS) for nematic liquid crystals are investigated. It is shown that the model predicts diffusive optic soft modes, describing nematic-order-parameter fluctuations which condense at the isotropic-nematic stability limit. Since the MS Hamiltonian in its usual form does not exhibit the full symmetry of the high-temperature phase, no symmetry-recovering Goldstone mode is predicted. A rotationally invariant form of the Maier-Saupe Hamiltonian, on the other hand, predicts the existence of two different diffusive optic soft modes in the nematic phase, in addition to a doubly degenerate "magnon" mode which is the Goldstone mode of the isotropic-nematic transition.

I. INTRODUCTION

Maier and Saupe[1] have proposed a simple microscopic model for nematic liquid crystals. Whereas the static properties of this model were studied in great detail, the dynamic properties do not seem to have been investigated at all. It is the purpose of this paper to elucidate the dynamics of the Maier-Saupe (MS) model with particular emphasis on the existence of soft modes, the condensation of which should result in an isotropic-nematic phase transition. The stability of the various phases against homogeneous and inhomogeneous fluctuations and the susceptibilities of the system will be investigated as well. The problem of the existence of symmetry-recovering Goldstone modes, the frequency of which should vanish in the long-wavelength limit in the low-symmetry phase, will be discussed. It will be shown that these modes, which are a necessary consequence of the breaking of a continuous symmetry group at the isotropic-nematic phase transition, are not predicted by the usual form of the MS Hamiltonian as this does not contain the full symmetry of the high-temperature phase. A rotationally invariant form of the MS Hamiltonian, on the other hand, does predict the existence of the Goldstone modes.

The present work is thus complementary to the macroscopic approach to liquid-crystal dynamics,[2-4] as well as to the approach[5] which is the extension of the microscopic theory of collective modes in classical liquids.

II. THE HAMILTONIAN

Taking into account dispersion forces between anisotropic molecules and averaging over their center-of-mass positions, Maier and Saupe[1] derived the following Hamiltonian:

$$\mathcal{H} = -\sum_{i,j} A_{ij}\left(\tfrac{3}{2}\cos^2\vartheta_{ij} - \tfrac{1}{2}\right), \tag{1}$$

where ϑ_{ij} is the angle between the long axes of the molecules i and j. A_{ij} is a constant which measures the strength of the interaction.

To minimize the free energy associated with the above orientational interaction, the molecules prefer—below a certain temperature—a parallel orientation of the long axes of the molecules. It is this orientational long-range ordering which characterizes the onset of the nematic phase.

The above Hamiltonian (1) is usually replaced by a separable interaction

$$\mathcal{H}_{\mathrm{MS}} = -\sum_{i,j} A_{ij}\left(\tfrac{3}{2}\cos^2\vartheta_i - \tfrac{1}{2}\right)\left(\tfrac{3}{2}\cos^2\vartheta_j - \tfrac{1}{2}\right) = -\sum_{i,j} A_{ij}\eta_i\eta_j , \tag{2}$$

where ϑ_i is the angle between the long axis of the ith molecule and the preferred direction in space, i.e., the nematic axis, and where

$$\eta_i = \left(\tfrac{3}{2}\cos^2\vartheta_i - \tfrac{1}{2}\right) = \left(\tfrac{3}{2}n_{z,i}^2 - \tfrac{1}{2}\right). \tag{3}$$

Here, we specified the orientation of a given molecule in space by the unit vector $\vec{n}_i$:

$$\vec{n}_i = (\sin\vartheta_i\,\cos\varphi_i\,,\ \sin\vartheta_i\,\sin\varphi_i\,,\ \cos\vartheta_i). \tag{4}$$

In the molecular-field approximation, Eq. (2) is replaced by

$$\mathcal{H}_{\mathrm{MS},i}^{\mathrm{MFA}} = -2\sum_j A_{ij}\langle\eta_j\rangle\eta_i . \tag{5}$$

Here,

$$\langle\eta_j\rangle = \langle\eta\rangle + \delta\langle\eta_j\rangle , \tag{6}$$

where the thermodynamic average $\langle\eta\rangle$ is the nematic order parameter and $\delta\langle\eta_j\rangle$ represents small deviations from the homogeneous state.

In a quasilattice type model, Eq. (5) now becomes

$$\mathcal{H}^{\mathrm{MFA}}_{\mathrm{MS},i} = (V_0\langle\eta\rangle + V_{\vec{q}}\,\delta\langle\eta_i\rangle)\eta_i\ , \tag{7}$$

where

$$V_0 = 2\sum_{j\neq i} A_{ij} \tag{8}$$

and $V_{\vec{q}}$ is the corresponding Fourier transform

$$V_{\vec{q}} = 2\sum_{j} A_{ij}e^{i\vec{q}(\vec{R}_j-\vec{R}_i)}\ . \tag{9}$$

In a "continuum" model analogous expressions are obtained. The only difference is that V_0 and V_q are now given by

$$V_0 = 2\frac{N}{V}\int A_{ij}\rho_1(\vec{r}_i,\vec{r}_j)\,d^3r_j \tag{10}$$

and

$$V_{\vec{q}} = 2\frac{N}{V}\int A_{ij}\rho_1(\vec{R}_i,\vec{R}_j)\exp[i\vec{q}(\vec{R}_i-\vec{R}_j)]\,d^3r_j\ , \tag{11}$$

where N/V is the density and ρ_1 is the conditional probability density to find the jth molecule in the place $\vec{R}_j$ if we know that the ith is in the place $\vec{R}_i$.

It should be noted that the Hamiltonian (2) does not contain the full symmetry of the isotropic phase. With the help of the unit vectors $\vec{n}_i$ and $\vec{n}_j$, which specify the orientations of the two molecules, Eq. (1) can be rewritten as

$$\mathcal{H} = -\tfrac{3}{2}\sum_{ij} A_{ij}(\vec{n}_i\vec{n}_j)^2 + \tfrac{1}{2}\sum_{ij} A_{ij}\ , \tag{12}$$

which can be contrasted with the usually used form of the Maier-Saupe Hamiltonian as given by Eq. (2)

$$\mathcal{H}_{\mathrm{MS}} = -\sum_{ij} A_{ij}(\tfrac{3}{2}n^2_{z,i}-\tfrac{1}{2})(\tfrac{3}{2}n^2_{z,j}-\tfrac{1}{2})\ . \tag{13}$$

Whereas the difference between these two forms is not significant in the static case, it is important when dynamic properties are investigated.

Since we are not taking into account the relative motion of the centers of gravity of the molecules, the second term in Eq. (12) is a constant and can be left out. In the MFA approximation we can rewrite Eq. (12) as

$$\begin{aligned}\mathcal{H}^{\mathrm{MFA}}_i = -\tfrac{3}{2}\times 2\sum_j A_{ij}(&\langle n^2_{jx}\rangle n^2_{ix} + \langle n^2_{jy}\rangle n^2_{iy} + \langle n^2_{jz}\rangle n^2_{iz}\\ &+ 2\langle n_{jx}n_{jy}\rangle n_{ix}n_{iy} + 2\langle n_{jx}n_{jz}\rangle n_{ix}n_{iz}\\ &+ 2\langle n_{jy}n_{jz}\rangle n_{iy}n_{iz})\ .\end{aligned} \tag{14}$$

III. STATIC PROPERTIES

A. Rotationally noninvariant MS Hamiltonian, homogeneous case $\vec{q}=0$

Let us first discuss the static properties of the Hamiltonian (2) in the homogeneous case $\langle\eta_j\rangle = \langle\eta\rangle$ using the molecular-field approximation

$$\mathcal{H}_{\mathrm{MS}} = -V_0\langle\eta\rangle\eta\ . \tag{15}$$

The nematic order parameter $\langle\eta\rangle$ is determined as a solution of the self-consistent equation

$$\langle\eta\rangle = \frac{\int_0^1 dx\,(\frac{3}{2}x^2-\frac{1}{2})\exp[\beta V_0\langle\eta\rangle\,(\frac{3}{2}x^2-\frac{1}{2})]}{\int_0^1 dx\exp[\beta V_0(\frac{3}{2}x^2-\frac{1}{2})]}\ , \qquad \beta = 1/kT. \tag{16}$$

One solution of this system—which corresponds to the isotropic phase—exists at all temperatures

$$\langle\eta\rangle = 0\ , \tag{17a}$$

whereas another—which corresponds to the nematic phase—

$$\langle\eta\rangle \neq 0\ , \tag{17b}$$

exists only below a certain temperature T_c.

To see which of these two solutions represents a stable state, we have to investigate the free energy of the system

$$F = \langle\mathcal{H}\rangle - TS\ , \tag{18}$$

where

$$\langle\mathcal{H}\rangle = -\tfrac{1}{2}NV_0\langle\eta\rangle^2 \tag{19a}$$

and

$$\begin{aligned}S &= -Nk\langle\ln\rho\rangle\\ &= -Nk\left\langle \ln\frac{\exp(\beta V_0\langle\eta\rangle\eta)}{4\pi\int_0^1 dx\exp[\beta V_0\langle\eta\rangle(\frac{3}{2}x^2-\frac{1}{2})]}\right\rangle.\end{aligned} \tag{19b}$$

The stability conditions are

$$\left(\frac{\partial F}{\partial\langle\eta\rangle}\right)_{\langle\eta\rangle_0} = 0 \tag{20a}$$

and

$$\left(\frac{\partial^2 F}{\partial\langle\eta^2\rangle}\right)_{\langle\eta\rangle_0} > 0\ . \tag{20b}$$

Equation (20a) is equivalent to Eq. (16). The condition for the stability of the solution $\langle\eta\rangle_0$ can thus be expressed as the requirement that the inverse susceptibility of the system is a positive quantity

$$\begin{aligned}\chi^{-1} &= \frac{1}{NV_0}\left(\frac{\partial^2 F}{\partial\langle\eta\rangle^2}\right)_{\langle\eta\rangle_0}\\ &= 1 - \beta V_0(\langle\eta^2\rangle_0 - \langle\eta\rangle_0^2) > 0\ .\end{aligned} \tag{21}$$

In the isotropic phase

$$\langle\eta\rangle_0 = 0, \quad \langle\eta^2\rangle_0 = 1/5\,, \tag{22a}$$

so that

$$\chi^{-1} = 1 - \beta V_0/5 = 1 - T_0/T, \quad T > T_c\,. \tag{22b}$$

The stability limit of the isotropic phase T_0 is given by

$$T_0 = V_0/5k\,. \tag{23a}$$

In the nematic phase, $\langle\eta\rangle_0$ and $\langle\eta^2\rangle_0$ are both different from zero. The stability limit of the nematic phase T_0^- will be always larger than T_0. Since the stability limits of the two phases do not coincide, the phase transition will be of first order. The transition will take place at a temperature T_c, where the free energies of the two phases become equal. Evidently one has

$$T_0 < T_c < T_0^-\,. \tag{23b}$$

B. Rotationally noninvariant MS Hamiltonian, fluctuations with $\vec{q}=0$

Let us now allow for small deviations from the homogeneous state

$$\langle\eta_j\rangle = \langle\eta\rangle + \delta\langle\eta_j\rangle\,, \tag{24a}$$

$$\delta\langle\eta_j\rangle = \delta\langle\eta_i\rangle e^{i\vec{q}(\vec{R}_j - \vec{R}_i)} \tag{24b}$$

and investigate the stability of the system against fluctuations with a finite wave vector $\vec{q}$. The MFA Hamiltonian is now

$$\mathcal{H}_i^{\mathrm{MFA}} = -\,(V_0\langle\eta\rangle + V_{\vec{q}}\,\delta\langle\eta_i\rangle)\eta_i\,.$$

Using the same procedure as in case (i), we obtain the wave-vector-dependent susceptibility $\chi(\vec{q})$ of the system as

$$\chi^{-1}(\vec{q}) = \frac{V_{\vec{q}}}{V_0} - \frac{(V_{\vec{q}})^2}{V_0 kT}(\langle\eta^2\rangle_0 - \langle\eta\rangle_0^2)\,. \tag{25}$$

Equation (25) coincides with (21) for $\vec{q}=0$. It should be mentioned that $\chi(\vec{q})$ can be determined by measuring the dynamic structure factor for coherent neutron scattering integrated over all frequencies.

The isotropic phase is stable against inhomogeneous order fluctuations as long as

$$\chi^{-1}(\vec{q}) = (V_{\vec{q}}/V_0)(1 - \beta V_{\vec{q}}/5) > 0, \quad T > T_c\,. \tag{26}$$

The system becomes unstable, $\chi^{-1}(\vec{q}) = 0$, as soon as with lowering temperature the condition

$$kT = V_{\vec{q}}/5$$

is fulfilled.

The value of $\vec{q}$, for which $V_{\vec{q}}$ is a maximum, thus determines the nature of the instability. If $V_{\vec{q}}$ has a maximum for $\vec{q}=0$, the system will make a transition to a homogeneously ordered nematic state. If, however, $V_{\vec{q}}$ has a maximum for a finite $\vec{q} = \vec{q}_0 \neq 0$, the system will become unstable against inhomogeneous fluctuations of wave vector $\vec{q}_0$, resulting in a cholesteric state. It should be noted that this can happen only if the intermolecular forces are not completely short range so that second-nearest-neighbor interactions are important.

C. Rotationally invariant Maier-Saupe Hamiltonian

In the homogenous case, where $\langle n_{jx}^2\rangle = \langle n_x^2\rangle$ etc., we can rewrite the MFA Hamiltonian [Eq. (14)] as

$$\begin{aligned}\mathcal{H}^{\mathrm{MFA}} = -\tfrac{3}{2}V_0(&\langle n_x^2\rangle n_x^2 + \langle n_y^2\rangle n_y^2 + \langle n_z^2\rangle n_z^2 \\ &+ 2\langle n_x n_y\rangle n_x n_y + 2\langle n_x n_z\rangle n_x n_z \\ &+ 2\langle n_y n_z\rangle n_y n_z)\,.\end{aligned} \tag{27}$$

The self-consistent equations are now

$$\langle n_\alpha n_\beta\rangle = \frac{\int e^{-\beta\mathcal{H}^{\mathrm{MFA}}} n_\alpha n_\beta\, d\Omega}{\int e^{-\beta\mathcal{H}^{\mathrm{MFA}}}\, d\Omega}, \quad \alpha, \beta = x, y, z\,. \tag{28}$$

The integration goes over the whole solid angle and is performed with the help of Eq. (4).

In the high-temperature isotropic phase we find

$$\langle n_x^2\rangle = \langle n_y^2\rangle = \langle n_z^2\rangle = \tfrac{1}{3}\,, \tag{29}$$

$$\langle n_x n_y\rangle = \langle n_x n_z\rangle = \langle n_y n_z\rangle = 0\,. \tag{30}$$

This solution, which exists at all temperatures, corresponds to $\langle\eta\rangle = 0$.

In order to investigate the low-temperature solution, let us assume that the molecules order along the z axis, and that there is no preferential ordering in the xy plane. In such a case we have

$$\langle n_x n_y\rangle = \langle n_x n_z\rangle = \langle n_y n_z\rangle = 0, \tag{31}$$

$$\langle n_x^2\rangle = \langle n_y^2\rangle = \tfrac{1}{2}(1 - \langle n_z^2\rangle)\,. \tag{32}$$

It should be noted that this assumption breaks the symmetry of the high-temperature phase. From Eqs. (3) and (4) we see that

$$\langle n_z^2\rangle = \tfrac{1}{3}(2\langle\eta\rangle + 1)\,, \tag{33}$$

$$\langle n_x^2\rangle = \langle n_y^2\rangle = \tfrac{1}{3}(1 - \langle\eta\rangle)\,. \tag{34}$$

When we insert Eqs. (31)–(34) into Eq. (27), it reduces to

$$\mathcal{H}^{\mathrm{MFA}} = -\,V_0\langle\eta\rangle\eta\,, \tag{35}$$

thus demonstrating that in the homogeneous static case there is no difference between the usual and the rotationally invariant form of the MS Hamiltonian.

IV. DYNAMIC PROPERTIES

We shall assume that the collective normal modes in liquid crystals are so strongly overdamped that the real part of the mode frequency may be neglected in comparison with the imaginary one and the system can be treated in a relaxational approximation.

A. The rotationally noninvariant MS Hamiltonian

The relaxational equations of motion for the deviations from the MFA solutions are

$$\frac{d\langle\eta\rangle_t}{dt} = -\frac{1}{T_1}(\langle\eta\rangle_t - \langle\langle\eta\rangle_t\rangle)\,, \tag{36}$$

where T_1 is a constant and, where

$$\langle\eta\rangle_t = \langle\eta\rangle + \delta\langle\eta\rangle e^{-t/\tau}\,, \tag{37}$$

$$\langle\langle\eta\rangle_t\rangle = \langle\eta\rangle + \delta\langle\langle\eta\rangle\rangle e^{-t/\tau}\,. \tag{38}$$

The system is assumed to relax towards the time dependent equilibrium value $\langle\langle\eta\rangle_t\rangle$, which is determined by the instantaneous molecular field

$$\langle\langle\eta\rangle_t\rangle = \frac{\int \exp(-\beta\mathcal{H}_i^{\mathrm{MFA}})\eta\, d\Omega}{\int \exp(-\beta\mathcal{H}_i^{\mathrm{MFA}})\, d\Omega}\,, \tag{39}$$

where $\mathcal{H}_i^{\mathrm{MFA}}$ is given by Eq. (7) so that inhomogeneous fluctuations are accounted for. Equation (36) can be rewritten as

$$\frac{d\langle\eta\rangle_t}{dt} = -\frac{1}{T_1}(\delta\langle\eta\rangle\chi_{\eta\eta}^{-1})\,. \tag{40}$$

The relaxation time governing the approach to equilibrium is obtained with the help of Eqs. (37) and (38) as

$$1/\tau = (1/T_1)\chi_{\eta\eta}^{-1}; \tag{41}$$

$1/\tau$ thus represents the relaxation time for the nematic order parameter fluctuations. Equation (41) predicts—together with Eqs. (25) and (26)—a critical slowing down of this diffusive "soft" mode at the corresponding stability limits. The temperature dependence of the relaxation time τ is shown in Fig. 1 for the special case $\vec{q} = 0$. The nematic mode represents a fluctuation in the magnitude of the orientation of the molecules and can be observed, for example, by NMR relaxation or scattering techniques.

It should be noted that the above soft mode represents a diffusive "optic" mode. There is no mode in the low-temperature phase, the frequency of which goes to zero, or the relaxation time to infinity, as $\vec{q} \to 0$. These Goldstone-like[3] acoustic branches have been lost in replacing the rotationally invariant Hamiltonian, which contains the full symmetry of the isotropic phase by an anisotropic one.

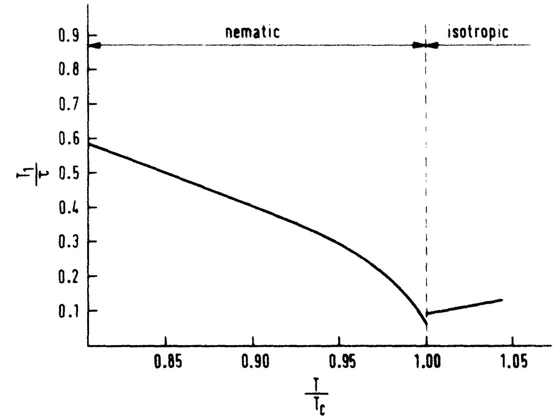

FIG. 1. Temperature dependence of the nematic (T_1/τ) relaxational soft mode as obtained from the rotationally noninvariant form of the Maier-Saupe Hamiltonian.

B. Rotationally invariant form of the Maier-Saupe Hamiltonian

Let us now investigate the dynamic properties of the Hamiltonian

$$\mathcal{H} = -\tfrac{3}{2}\sum_{i,j} A_{ij}(\vec{n}_i\vec{n}_j)^2\,. \tag{42}$$

The relaxational equations of motion for the deviations from the MFA solutions are

$$\frac{d}{dt}\langle n_{i\alpha}n_{i\beta}\rangle_t = -\frac{1}{T_1}(\langle n_{i\alpha}n_{i\beta}\rangle_t - \langle\langle n_{i\alpha}n_{i\beta}\rangle_t\rangle)\,, \tag{43}$$

where $\alpha, \beta = x, y, z$ and

$$\langle\langle n_{i\alpha}n_{i\beta}\rangle\rangle_t = \frac{\int e^{-\beta\mathcal{H}_i^{\mathrm{MFA}}} n_{i\alpha}n_{i\beta}\, d\Omega}{\int e^{-\beta\mathcal{H}_i^{\mathrm{MFA}}}\, d\Omega}\,. \tag{44}$$

$\mathcal{H}_i^{\mathrm{MFA}}$ is given by Eq. (14), and $\langle\langle n_{i\alpha}n_{i\beta}\rangle\rangle_t$ by

$$\langle\langle n_{i\alpha}n_{i\beta}\rangle\rangle_t = \langle n_{i\alpha}n_{i\beta}\rangle + \delta\langle\langle n_{i\alpha}n_{i\beta}\rangle\rangle e^{-t/\tau}\,. \tag{45}$$

Introducing collective coordinates by the Fourier transform

$$\delta\langle n_\alpha n_\beta\rangle_{\vec{q}} = \sum_i \delta\langle n_{i\alpha}n_{i\beta}\rangle e^{i\vec{q}\vec{R}_i} \tag{46}$$

and using Eq. (45), we find

$$\begin{aligned} T_1/\tau\,\delta\langle n_\alpha n_\beta\rangle_{\vec{q}} = {}& \delta\langle n_\alpha n_\beta\rangle_{\vec{q}} - \tfrac{3}{2}\beta V_{\vec{q}}(\langle n_\alpha n_\beta n_x^2\rangle\delta\langle n_x^2\rangle_{\vec{q}} + \langle n_\alpha n_\beta n_y^2\rangle\delta\langle n_y^2\rangle_{\vec{q}} + \langle n_\alpha n_\beta n_z^2\rangle\delta\langle n_z^2\rangle_{\vec{q}} + 2\langle n_\alpha n_\beta n_x n_y\rangle\delta\langle n_x n_y\rangle_{\vec{q}} \\ & + 2\langle n_\alpha n_\beta n_x n_z\rangle\delta\langle n_x n_z\rangle_{\vec{q}} + 2\langle n_\alpha n_\beta n_y n_z\rangle\delta\langle n_y n_z\rangle_{\vec{q}}) + \tfrac{3}{2}\beta V_{\vec{q}}\langle n_\alpha n_\beta\rangle(\langle n_x^2\rangle\delta\langle n_x^2\rangle_{\vec{q}} + \langle n_y^2\rangle\delta\langle n_y^2\rangle_{\vec{q}} + \langle n_z^2\rangle\delta\langle n_z^2\rangle_{\vec{q}})\,, \end{aligned} \tag{47}$$

where $V_{\vec{q}}$ is given by Eq. (9).

We thus have a system of six linear equations for the fluctuation eigenvectors $\delta\langle n_\alpha n_\beta\rangle_{\vec{q}}$ ($\alpha, \beta = x, y, z$). The eigenvectors must satisfy the relation

$$\delta\langle n_x^2\rangle + \delta\langle n_y^2\rangle + \delta\langle n_z^2\rangle = 0\,, \tag{48}$$

so that only five of these equations are independent. This corresponds to the fact that the nematic order parameter is—as pointed out by de Gennes[6]—a symmetric second-rank tensor of zero trace which has five independent components.

The nature of the solution for τ depends on the averages

$$\begin{aligned}\langle n_x^4\rangle = \langle n_y^4\rangle &= \tfrac{3}{8}\langle \sin^4\vartheta\rangle \\ &= \tfrac{3}{8} - \tfrac{3}{4}\langle\cos^2\vartheta\rangle + \tfrac{3}{8}\langle\cos^4\vartheta\rangle\ ,\end{aligned} \tag{49a}$$

$$\langle n_z^4\rangle = \langle\cos^4\vartheta\rangle\ , \tag{49b}$$

$$\begin{aligned}\langle n_x^2 n_z^2\rangle = \langle n_y^2 n_z^2\rangle &= \tfrac{1}{2}\langle\sin^2\vartheta\cos^2\vartheta\rangle \\ &= \tfrac{1}{2}\langle\cos^2\vartheta\rangle - \tfrac{1}{2}\langle\cos^4\vartheta\rangle\,,\end{aligned} \tag{49c}$$

$$\langle n_x^2 n_y^2\rangle = \tfrac{1}{8}\langle\sin^4\vartheta\rangle = \tfrac{1}{8} - \tfrac{1}{4}\langle\cos^2\vartheta\rangle + \tfrac{1}{8}\langle\cos^4\vartheta\rangle\,. \tag{49d}$$

In the isotropic phase $T > T_c$, one easily finds that

$$\langle n_x^4\rangle = \langle n_y^4\rangle = \langle n_z^4\rangle = \tfrac{1}{5}\ , \tag{50a}$$

$$\langle n_x^2 n_z^2\rangle = \langle n_y^2 n_z^2\rangle = \langle n_x^2 n_y^2\rangle = \tfrac{1}{15} \tag{50b}$$

and all five possible fluctuations relax with the same wave-vector-dependent relaxation time

$$T_1/\tau(\vec{q}) = (1 - \beta V_{\vec{q}}/5) = \chi^{-1}(\vec{q})\,, \tag{51}$$

where $\chi^{-1}(\vec{q})$ is given by Eq. (26).

This result is easy to understand. The ellipsoid, which can be ascribed to the equilibrium value of the order-parameter tensor, reduces to a sphere for $T > T_c$. Above T_c all orientations of the order parameter tensor are thus equivalent, and therefore all possible deformations relax with the same relaxation time. Equation (51) predicts a critical slowing down of $\tau(\vec{q})$ as $\beta V_{\vec{q}}/5 \to 1$. Depending on the value of $\vec{q}$ for which $V_{\vec{q}}$ is a maximum, we find—after the diffusive soft mode has condensed out—a homogeneous nematic ($\vec{q} = 0$) or a spiral cholesteric ($\vec{q} \neq 0$) low temperature phase.

In the following we shall be concerned with the nematic solution.

If one assumes that $V_{\vec{q}}$ is isotropic

$$V_{\vec{q}} \approx V_0 - aq^2 \tag{52}$$

we see that

$$T_1/\tau(\vec{q}) = 1 - T_0/T + \beta a q^2/5, \quad \beta = 1/kT\,. \tag{53a}$$

The above diffusive soft mode has thus an optic character ($1/\tau \neq 0$ for $\vec{q} = 0$), except at the stability limit T_0, where

$$T_1/\tau(\vec{q}) = \beta a q^2/5\,. \tag{53b}$$

The degeneracy of the soft mode is lifted in the nematic phase. We find two different diffusive optic soft modes:

$$\text{(i)}\ \ T_1/\tau(\vec{q}) = 1 - 3\beta V_{\vec{q}}\langle n_x^2 n_y^2\rangle\,, \tag{54a}$$

with the eigenvectors

$$\delta\langle n_x n_y\rangle_{\vec{q}} \neq 0 \text{ or } \delta\langle n_y^2\rangle_{\vec{q}} - \delta\langle n_x^2\rangle_{\vec{q}} \neq 0\,, \tag{54b}$$

and

$$\text{(ii)}\ \ T_1/\tau(\vec{q}) = 1 + \tfrac{9}{2}\beta V_{\vec{q}}(\langle n_x^2 n_z^2\rangle - \langle n_x^2\rangle\langle n_z^2\rangle) \tag{55a}$$

with the eigenvectors

$$\delta\langle n_x^2\rangle_{\vec{q}} + \delta\langle n_y^2\rangle_{\vec{q}} = -\,\delta\langle n_z^2\rangle_{\vec{q}}, \tag{55b}$$

in addition to a doubly degenerate diffusive "acoustic" magnon mode

$$\begin{aligned}\text{(iii)}\ \ T_1/\tau(\vec{q}) &= 1 - 3\beta V(\vec{q})\langle n_x^2 n_z^2\rangle \\ &= (V_0 - V_{\vec{q}})/V_0\end{aligned} \tag{56a}$$

with the eigenvectors

$$\delta\langle n_x n_z\rangle_{\vec{q}} \neq 0, \quad \langle n_y n_z\rangle_{\vec{q}} \neq 0\,. \tag{56b}$$

The fifth mode, which would represent a rotation of the nematic-order-parameter ellipsoid around the z axis, is not a real normal mode of the system in view of our assumption of the isotropy in the xy plane. If, however, our order-parameter tensor would be biaxial, i.e., a general ellipsoid and not an axially symmetric one, the fifth mode would be present too.

The nature of the four nematic-order-fluctuation modes is illustrated in Fig. 2. The first (i) mode represents a change in the magnitude of the two smaller principal axes of the order-parameter ellipsoid with the largest (z) axis remaining constant. The increase in the magnitude of the x axis is compensated by a decrease in the magnitude of the y axis and vice versa. It can be called a "biaxial" nematic soft mode, since it tends to destroy the "uniaxial" nematic symmetry. The second (ii) mode represents a decrease in the magnitude of the z axis which is compensated by an increase in the x and y principal axes and vice versa. It is an uniaxial nematic soft mode. Whereas the above two modes thus represent a change in the magnitude of the local anisotropy, the doubly degenerate third (iii) mode represents a rotation of the local anisotropy out of the z direction. The rotational ellipsoid rotates in the xy or the yz plane. It is this last mode which is the Goldstone mode[7] of the isotropic-nematic transition.

In the transition from the isotropic liquid to the nematic phase, the continuous rotational symmetry

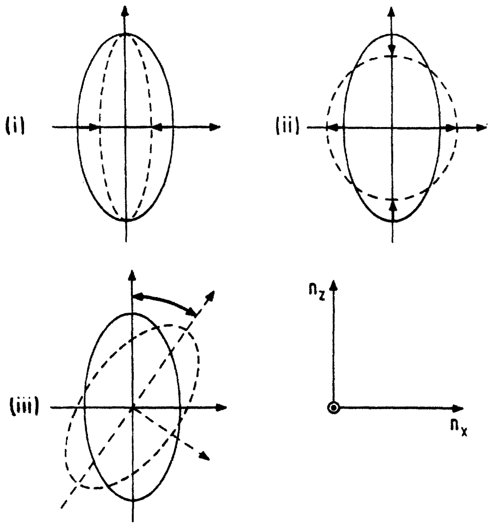

FIG. 2. Illustration of the normal mode motion for the four nematic order parameter modes as obtained from the rotationally invariant form of the Maier-Saupe Hamiltonian. The doubly degenerate second sound mode (iii) is the Goldstone mode of the transition.

decreases[8] from O_3 to $D^z_{2\infty}$:

$$T_3\times O_3 \text{ (isotropic liquid)} \rightarrow T_3\times D^z_{2\infty} \text{ (nematic phase)},$$

$$O_3 = D^z_{2\infty}\times D^y_{2\infty}\times D^x_{2\infty}\ . \qquad (57)$$

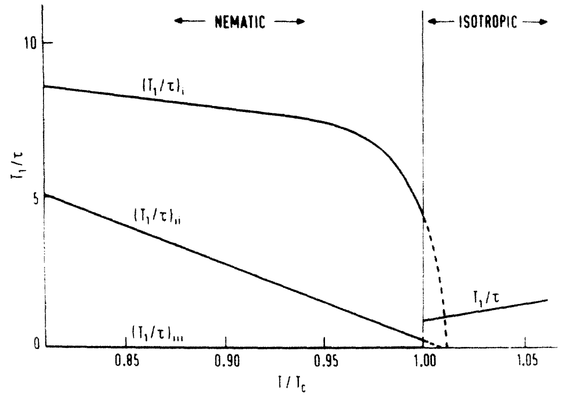

FIG. 3. Temperature dependence of the four nematic order parameter fluctuation modes for $\vec{q}=0$.

The Goldstone mode tries to recover the symmetry which is broken in the low-temperature phase. Its frequency vanishes in the long-wavelength limit ($1/\tau\rightarrow 0$, $\vec{q}\rightarrow 0$) and the motion corresponds to the continuous group $D^x_{2\infty}\times D^y_{2\infty}$, which is broken at T_c.

The temperature dependence of the relaxation times τ^{-1} of these three modes is shown in Fig. 3 for $\vec{q}=0$. The frequencies $1/\tau$ of the modes (i) and (ii) vanish at the stability limit of the nematic phase.

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