Normal modes of director fluctuations in a nematic droplet

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(Received 3 October 1996)

Director fluctuations in nematic liquid crystals are readily analyzed in terms of the normal modes of the director field. In this paper, we examine the dynamics of fluctuations in the radial director field of a spherical nematic droplet in terms of its normal modes. We find independent twist-bend and splay-bend modes and consider thermal excitations. The results may be useful for understanding light scattering by polymer dispersed liquid crystals. [S1063-651X(97)06204-1]

PACS number(s): 61.30.Cz

I. INTRODUCTION

The scattering of light by condensed matter is due to spatial variations of the dielectric permittivity. In nematic liquid crystals, this is caused primarily by spatial variations of the order parameter. These inhomogeneities may be caused by external fields (such as surface interactions) and by thermal fluctuations. Since director fluctuations are Goldstone modes, long-wavelength fluctuations with large amplitudes are excited even at modest temperatures, and these are responsible for the strong scattering and turbid appearance of bulk nematic liquid crystals. Light scattering by bulk nematics has been studied extensively [1,2,4–6]. The spectrum of director fluctuations in a planar geometry has been examined [4], with good agreement between theory and experiment. More recently, director fluctuations have been analyzed in the case of a nematic liquid crystal confined to a cylindrical capillary [5].

Polymer dispersed liquid crystal (PDLC) materials consist of micrometer-sized nematic droplets dispersed in a polymer matrix. In the droplets, the director field is spatially nonuniform, and light scattering by these materials is due both to the mismatch between the refractive indices of the polymer and the liquid crystal and to the spatial inhomogeneities of the director field. Thermally excited director fluctuations are particularly important; these contribute significantly to dynamic light scattering [6]. In order to describe dynamic light scattering by PDLCs, it is essential to understand the dynamics of director fluctuations. In this paper we discuss director dynamics in a spherical nematic droplet, with strong normal anchoring at the surface, that is, with the director radially aligned everywhere in the ground state. Although other ground-state configurations are possible [7], the radial configuration is realized frequently and it is amenable to simple analysis. We ignore spatial variations in the degree of orientational order and describe the nematic liquid crystal in terms of the director rather than the order parameter tensor. We also ignore the effects of flow and work in the one elastic constant approximation. We identify the normal modes in such a radial nematic droplet and calculate their thermal amplitudes and relaxation times. This allows the description of dynamic light scattering by a nematic liquid crystal droplet in PDLC materials.

II. DIRECTOR DYNAMICS IN A NONPLANAR GEOMETRY

In the Oseen-Frank formalism [8], the free energy $\mathcal{F}$ of a nematic liquid crystal depends on distortions of the director field $\hat{\mathbf{n}}(\mathbf{r})$. Explicitly,

$$\mathcal{F}=\int F(\hat{\mathbf{n}})d^3\mathbf{r}, \tag{1}$$

where the bulk free-energy density F has the form

$$F(\hat{\mathbf{n}})=\frac{1}{2}K_1(\boldsymbol{\nabla}\cdot\hat{\mathbf{n}})^2+\frac{1}{2}K_2(\hat{\mathbf{n}}\cdot\boldsymbol{\nabla}\times\hat{\mathbf{n}})^2+\frac{1}{2}K_3(\hat{\mathbf{n}}\times\boldsymbol{\nabla}\times\hat{\mathbf{n}})^2 \tag{2}$$

corresponding to the canonical deformations of splay, twist, and bend; $\hat{\mathbf{n}}$ is a unit vector. To obtain the equations of motion, it is necessary to describe the generalized thermodynamic force acting on the director. To this end, we write the free energy in terms of the unnormalized field $\mathbf{n}=n\hat{\mathbf{n}}$ and consider variations $\boldsymbol{\epsilon}$ of the unnormalized field $\mathbf{n}(\mathbf{r})$ such that $\boldsymbol{\epsilon}$ vanishes on the sample boundaries. Then $\hat{\mathbf{n}}=\hat{\mathbf{n}}_0+(\mathbf{I}-\hat{\mathbf{n}}_0\hat{\mathbf{n}}_0)\boldsymbol{\epsilon}$, where $\hat{\mathbf{n}}_0$ is an arbitrary director field about which variations are considered, $\mathbf{I}$ is the unit tensor of rank 2, and $\hat{\mathbf{n}}_0\hat{\mathbf{n}}_0$ is a dyad. Substitution into Eq. (1) gives

$$\mathcal{F}=\mathcal{F}_0-\int \tilde{\mathbf{h}}(\hat{\mathbf{n}}_0)\cdot\boldsymbol{\epsilon}\, d^3\mathbf{r}, \tag{3}$$

where $\tilde{\mathbf{h}}=-(\delta F/\delta\hat{\mathbf{n}})(\mathbf{I}-\hat{\mathbf{n}}\hat{\mathbf{n}})$. Since $\boldsymbol{\epsilon}$ is an unconstrained variation, we regard $\tilde{\mathbf{h}}$ as the thermodynamic force acting on the director. We note that the functional derivative $\delta F/\delta\hat{\mathbf{n}}=-\mathbf{h}$, where $\mathbf{h}$ is the molecular field introduced by de Gennes [2] and $\tilde{\mathbf{h}}=\mathbf{h}-(\mathbf{h}\cdot\hat{\mathbf{n}})\hat{\mathbf{n}}$. The quantity $\mathbf{h}\cdot\hat{\mathbf{n}}$ may be interpreted as the Lagrange multiplier associated with the constraint that $n^2=1$. The condition for equilibrium is that $\tilde{\mathbf{h}}=\mathbf{0}$ or $\mathbf{h}=(\mathbf{h}\cdot\hat{\mathbf{n}})\hat{\mathbf{n}}$ [2].

Away from equilibrium, in the absence of flow, the thermodynamic force is balanced by a viscous force and the dynamics is described by

$$\gamma\frac{\partial\hat{\mathbf{n}}}{\partial t}=\tilde{\mathbf{h}}, \tag{4}$$

1063-651X/97/55(4)/4378(4)/$10.00

where γ is a viscosity coefficient. This is our starting point, and we note that it differs [3] from Ref. [2].

The free-energy density in the one-elastic-constant approximation $K_1=K_2=K_3=K$ is

$$F=\frac{1}{2}K\{(\nabla\cdot\hat{\mathbf{n}})^2+(\nabla\times\hat{\mathbf{n}})^2\} \tag{5}$$

and $\mathbf{h}=K\nabla^2\hat{\mathbf{n}}$. This gives the equation of motion for the director

$$\frac{\gamma}{K}\frac{\partial\hat{\mathbf{n}}}{\partial t}=\nabla^2\hat{\mathbf{n}}-(\hat{\mathbf{n}}\cdot\nabla^2\hat{\mathbf{n}})\hat{\mathbf{n}} \tag{6}$$

in the one-constant approximation.

III. NORMAL MODES OF A SPHERICAL DROPLET WITH RADIAL CONFIGURATION

A. Equations of motion

We consider a spherical nematic droplet of radius r_0, with a radial static equilibrium configuration $\hat{\mathbf{n}}_0=\hat{\mathbf{r}}$. Fluctuations about the equilibrium configuration are described by the field $\boldsymbol{\delta}(\mathbf{r})$ such that $\hat{\mathbf{n}}=\hat{\mathbf{n}}_0+\boldsymbol{\delta}$. Rigid homeotropic anchoring is assumed both at the surface and at the origin, that is, $\boldsymbol{\delta}(r_0)=\boldsymbol{\delta}(0)=0$. Substitution into Eq. (6) gives the equation of motion for the decay of the fluctuations,

$$\frac{\gamma}{K}\frac{\partial\boldsymbol{\delta}}{\partial t}=(\nabla^2\boldsymbol{\delta})(\mathbf{I}-\hat{\mathbf{n}}_0\hat{\mathbf{n}}_0)-(\hat{\mathbf{n}}_0\cdot\nabla^2\hat{\mathbf{n}}_0)\boldsymbol{\delta}. \tag{7}$$

Since for a normal mode in a dissipative system $\partial\boldsymbol{\delta}/\partial t=-\boldsymbol{\delta}/\tau$ to lowest order, this becomes

$$-k^2\boldsymbol{\delta}=(\boldsymbol{\nabla}^2\boldsymbol{\delta})(\mathbf{I}-\hat{\mathbf{r}}\hat{\mathbf{r}})+\frac{2}{r^2}\boldsymbol{\delta}, \tag{8}$$

where $k^2=\gamma/\tau K$. The normal modes are the eigenfunctions of Eq. (8). We note that $\boldsymbol{\delta}\cdot\hat{\mathbf{r}}=0$ and we look for solutions of the form $\boldsymbol{\delta}=R(r)\boldsymbol{\Gamma}$, where $\boldsymbol{\Gamma}$ is a linear combination of vector spherical harmonics [9] such that its radial component is zero. We find the solutions

$$\boldsymbol{\Gamma}_{lm}^{(1)}=\mathbf{X}_{lm}(\theta,\phi)=\frac{1}{\sqrt{l(l+1)}}\left[\frac{-mY_l^m}{\sin\theta}\hat{\boldsymbol{\theta}}-\frac{i\partial Y_l^m}{\partial\theta}\hat{\boldsymbol{\phi}}\right] \tag{9}$$

and

$$\boldsymbol{\Gamma}_{lm}^{(2)}=\mathbf{Z}_{lm}(\theta,\phi)=\frac{1}{\sqrt{l(l+1)}}\left[\frac{i\partial Y_l^m}{\partial\theta}\hat{\boldsymbol{\theta}}-\frac{mY_l^m}{\sin\theta}\hat{\boldsymbol{\phi}}\right], \tag{10}$$

where $\mathbf{X}_{lm}$ and $\mathbf{Z}_{lm}$ are orthonormal, and $R(r)$ must satisfy

$$\frac{\partial^2R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left(k^2-\frac{l(l+1)-2}{r^2}\right)R=0. \tag{11}$$

The solution for $R(r)$ is the spherical Bessel function of order $\nu=\sqrt{l(l+1)-7/4}$, that is,

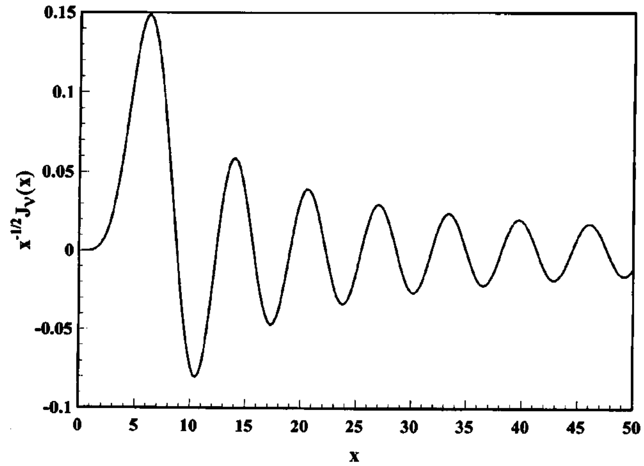

FIG. 1. Function $R_{nl}(r)\sim x^{-1/2}J_\nu(x)$, where $x=k_{nl}r$, as a function of x. Here $l=5$.

$$R_{nl}(r)=\left(\frac{r}{r_0}\right)^{-1/2}J_\nu(k_{nl}r), \tag{12}$$

where the eigenvalue k_{nl} is determined from the requirement that $J_\nu(k_{nl}r_0)=0$ is the nth zero of the Bessel function. The elementary normal modes are therefore

$$\delta_{nlm}^{(1)}=R_{nl}(r)\mathbf{X}_{lm}(\theta,\phi) \tag{13}$$

and

$$\delta_{nlm}^{(2)}=R_{nl}(r)\mathbf{Z}_{lm}(\theta,\phi), \tag{14}$$

with relaxation times $\tau_{nl}=\gamma/Kk_{nl}^2$. Since the relaxation time is independent of m, the general normal modes are

$$\boldsymbol{\delta}_{nl}=R_{nl}(r)\sum_m[A_{nlm}\mathbf{X}_{lm}(\theta,\phi)+B_{nlm}\mathbf{Z}_{lm}(\theta,\phi)], \tag{15}$$

where A_{nlm} and B_{nlm} are arbitrary constants subject to the requirement that $\boldsymbol{\delta}_{nl}$ is real.

B. Normal mode distortions

It is convenient to separate the elementary normal modes into the scalar part $R_{nl}(r)$ and the vector fields $\mathbf{X}_{lm}(\theta,\phi)$ and $\mathbf{Z}_{lm}(\theta,\phi)$. The function $R_{nl}(r)$ is shown in Fig. 1.

The real contributions from the vector fields are

$$\mathbf{X}_{lm}^r(\theta,\phi)=c\left[-\frac{m\cos m\phi}{\sin\theta}P_l^m(\cos\theta)\hat{\boldsymbol{\theta}}+\sin m\phi\frac{\partial P_l^m(\cos\theta)}{\partial\theta}\hat{\boldsymbol{\phi}}\right] \tag{16}$$

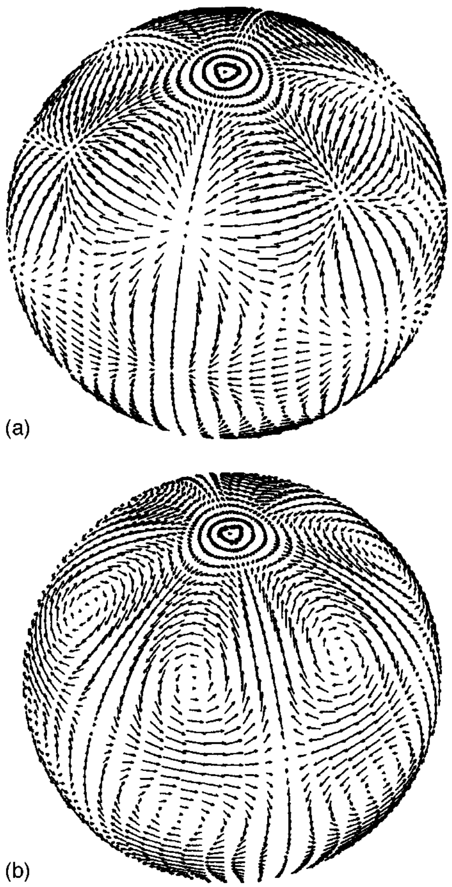

FIG. 2. (a) Splay-bend mode $\mathbf{Z}_{lm}(\theta,\phi)$ for $l=5$ and $m=3$. (b) Twist-bend mode $\mathbf{X}_{lm}(\theta,\phi)$ for $l=5$ and $m=3$.

and

$$\mathbf{Z}^{r}_{lm}(\theta,\phi)=c\left[-\sin m\phi\frac{\partial P_l^m(\cos\theta)}{\partial\theta}\hat{\boldsymbol{\theta}} -\frac{m\cos m\phi}{\sin\theta}P_l^m(\cos\theta)\hat{\boldsymbol{\phi}}\right], \tag{17}$$

where the normalization constant

$$c=\sqrt{\frac{2l+1}{\pi l(l+1)}\frac{(l-m)!}{(l+m)!}}.$$

The vector fields $\mathbf{X}^{r}_{nlm}(\theta,\phi)$ and $\mathbf{Z}^{r}_{nlm}(\theta,\phi)$ are shown in Figs. 2(a) and 2(b).

One can write Eq. (7) as

$$-k_{nl}^2\boldsymbol{\delta}_{nl}=\tilde{\mathcal{L}}\boldsymbol{\delta}_{nl}, \tag{18}$$

where $\tilde{\mathcal{L}}\boldsymbol{\delta}=(\nabla^2\boldsymbol{\delta})(\mathbf{I}-\hat{\mathbf{n}}_0\hat{\mathbf{n}}_0)-(\hat{\mathbf{n}}_0\cdot\nabla^2\hat{\mathbf{n}}_0)\boldsymbol{\delta}$. Since $\tilde{\mathcal{L}}$ is a Sturm-Liouville operator, the elementary normal modes $\boldsymbol{\delta}_{lm}$ form a complete orthogonal set. It is interesting to note that $\boldsymbol{\nabla}\cdot[R(r)\mathbf{X}_{lm}]=0$; hence the $\mathbf{X}_{lm}$ mode does not contribute to the splay energy $\frac{1}{2}K_1(\boldsymbol{\nabla}\cdot\hat{\mathbf{n}})^2$. Similarly, $\hat{\mathbf{n}}_0\cdot\boldsymbol{\nabla}\times[R(r)\mathbf{Z}_{lm}]=0$; hence the $\mathbf{Z}_{lm}$ mode does not contribute to the twist energy $\frac{1}{2}K_2(\hat{\mathbf{n}}\cdot\boldsymbol{\nabla}\times\hat{\mathbf{n}})^2$. Thus there are two types of modes, a twist-bend mode ($\mathbf{X}_{lm}$) and a splay-bend mode ($\mathbf{Z}_{lm}$), as in the case of the planar geometry [4].

C. Normal mode amplitudes

Amplitudes of the normal modes may be determined from the equipartition theorem. For a given distortion field $\boldsymbol{\delta}$, the free energy $\mathcal{F}$ is given by Eq. (3).

$$\mathcal{F}=\mathcal{F}_0-\int\tilde{\mathbf{h}}(\hat{\mathbf{n}}_0)\cdot\boldsymbol{\delta}d^3\mathbf{r}. \tag{19}$$

If the distortion is from an equilibrium state $\hat{\mathbf{n}}_0$, then $\tilde{\mathbf{h}}(\hat{\mathbf{n}}_0)=0$, but the free energy $\mathcal{F}$ energy may be written as

$$\mathcal{F}=\mathcal{F}_0-\int\tilde{\mathbf{h}}\left(\hat{\mathbf{n}}_0+\frac{\boldsymbol{\delta}}{2}\right)\cdot\boldsymbol{\delta}d^3\mathbf{r}. \tag{20}$$

To first order, $\tilde{\mathbf{h}}(\hat{\mathbf{n}}_0+\boldsymbol{\delta}/2)=\frac{1}{2}K\tilde{\mathcal{L}}\boldsymbol{\delta}$, and the free energy becomes

$$\mathcal{F}=\mathcal{F}_0-\frac{1}{2}K\int(\tilde{\mathcal{L}}\boldsymbol{\delta})\cdot\boldsymbol{\delta}d^3\mathbf{r}. \tag{21}$$

Since the normal modes form a complete orthogonal set, an arbitrary distortion $\boldsymbol{\delta}$ may be expressed in terms of these as

$$\boldsymbol{\delta}=\sum_{n,l,m}R_{nl}(r)[A_{nlm}\mathbf{X}_{lm}(\theta,\phi)+B_{nlm}\mathbf{Z}_{lm}(\theta,\phi)]. \tag{22}$$

Since $\tilde{\mathcal{L}}\boldsymbol{\delta}_{nl}=-k_{nl}^2\boldsymbol{\delta}_{nl}$ [cf. Eq. (18)], we obtain at once for such a deformation

$$\mathcal{F}=\mathcal{F}_0+\frac{K}{4}\sum_{n,l,m}k_{nl}^2\{|A_{nlm}|^2+|B_{nlm}|^2\}r_0^3J_{\nu+1}^2(k_{nl}r_0). \tag{23}$$

The equipartition theorem gives then the amplitudes

$$|A_{nlm}|^2=|B_{nlm}|^2=\frac{2kT}{Kr_0^3k_{nl}^2J_{\nu+1}^2(k_{nl}r_0)}. \tag{24}$$

For an arbitrary deformation, we note from Eq. (22) that

$$\langle\delta^2\rangle=\frac{3kT}{4\pi Kr_o}\sum_{n,l,m}[1/(r_0k_{nl})^2].$$

We write this as

$$\langle\delta^2\rangle=\frac{3kT}{4\pi Kr_0}\sum_{n,l,m}\frac{1}{x_{nl}^2}, \tag{25}$$

where x_{nl} is the nth zero of $J_\nu(x)$, where $\nu=\sqrt{l(l+1)-7/4}$. Although we do not have a closed-form expression for the sum in Eq. (25), we conjecture that $\Sigma_{n,l,m}1/x_{nl}^2=c(r_0/l_{\mathrm{mol}})$, where l_{mol} is a molecular length and c is a dimensionless constant of order unity. This is analogous to the case of normal modes of a gas-filled rigid sphere, where the sum equals $q_{\max}=2\pi/l_{\mathrm{mol}}$ and $q_{\max}$ is the cutoff in q space. This gives $\langle\delta^2\rangle=c(3kT/4\pi Kl_{\mathrm{mol}})$, that is, the mean-squared amplitude of the fluctuations in real space is independent of the droplet size.

IV. SUMMARY

We have shown that in a spherical nematic droplet, with a radial ground-state configuration, there exist two normal modes: a twist-bend mode ($\mathbf{X}_{lm}$) and a splay-bend mode ($\mathbf{Z}_{lm}$). These may be expressed simply in terms of vector spherical harmonics; the relaxation time for both modes is a function of the mode order. The amplitudes of thermally excited modes are given explicitly; we conjecture that the mean-squared amplitude of director fluctuations is independent of droplet size. Since the director dynamics is known, the structure factor for light scattering can be calculated. This will be presented elsewhere.

The formalism presented here constrains the radial defect to be located at the center of the droplet. A more realistic model, not subject to this constraint, would describe the free energy in terms of the dyad $\hat{\mathbf{n}}\hat{\mathbf{n}}$. A yet more realistic model would use the full order parameter tensor description. A study of the tractability of these models is currently under way.

ACKNOWLEDGMENTS

We are grateful to E. C. Gartland and R. Petschek for useful discussions. This work was supported by the National Science Foundation under ALCOM Grant No. DMR89-20147.

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