Normal-Distortion-Mode Approach to Liquid-Crystal Elastic Energy

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It is shown that Frank's "saddle" distortion contribution to the nematic liquid-crystal distortional elastic energy is required, in addition to the splay, twist, and bend energies retained in more recent treatments. "Normal distortion modes" for these four distortions are described. Measurement methods and their interpretations are discussed for the corresponding four elastic constants k_{11} (splay), k_{22} (twist), k_{33} (bend), and k_{44} (saddle). Previously reported values for k_{11} and k_{22} are actually for $k_{11}+k_{44}$ and $k_{22}+k_{44}$, respectively. The Nehring-Saupe molecular approach yields $k_{44}=\frac{1}{2}(k_{11}+k_{22})$.

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The standard expression[1-3] for the elastic energy density g associated with distortion of the director field $\hat{\mathbf{n}}$ for a nematic liquid crystal in the absence of chiral or polar effects consists of the terms

$$g_{11}=\tfrac{1}{2}k_{11}(\nabla\cdot\hat{\mathbf{n}})^2 \text{ (splay energy)}, \quad (1)$$

$$g_{22}=\tfrac{1}{2}k_{22}(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 \text{ (twist energy)}, \quad (2)$$

and

$$g_{33}=\tfrac{1}{2}k_{33}(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2 \text{ (bend energy)}. \quad (3)$$

A fourth energy term, originally discussed by Frank,[4] is required because (a) the above terms do not involve all of the distortional degrees of freedom, (b) the energy associated with the leftover degrees of freedom should have the same order of magnitude as the terms given above, yet (c) the standard expression predicts zero energy for these leftover distortions.

Our analysis begins with the six nonzero first derivatives of the director vector field $\hat{\mathbf{n}}$, evaluated at the origin in a system in which $\hat{\mathbf{n}}=\hat{\mathbf{k}}$ (along z) at the origin. These derivatives are[2]

$$\partial n_x/\partial x\equiv a_{11},\quad \partial n_y/\partial y\equiv a_{22},\quad \partial n_y/\partial x\equiv a_{12},$$
$$\partial n_x/\partial y\equiv a_{21},\quad \partial n_x/\partial z\equiv a_{31},\quad \partial n_y/\partial z\equiv a_{32}, \quad (4)$$

The first derivatives of n_z vanish at the origin because $\hat{\mathbf{n}}$ is a unit vector.

The director vector field in the neighborhood of the origin, to first order in x, y, and z except for higher-order terms needed for normalization and for evaluating Eq. (19), is then

$$\hat{\mathbf{n}}=(a_{11}x+a_{21}y+a_{31}z)\hat{\mathbf{i}}+(a_{12}x+a_{22}y+a_{32}z)\hat{\mathbf{j}}+[1-(a_{11}x+a_{21}y+a_{31}z)^2-(a_{12}x+a_{22}y+a_{32}z)^2]^{1/2}\hat{\mathbf{k}}. \quad (5)$$

We now evaluate (at the origin) and analyze in turn the three elastic energy terms of Eqs. (1)-(3). For the splay energy density we have

$$g_{11}=\tfrac{1}{2}k_{11}(\nabla\cdot\hat{\mathbf{n}})^2=\tfrac{1}{2}k_{11}(a_{11}+a_{22})^2. \quad (6)$$

Choosing the appropriate terms from Eq. (5) and rearranging them as

$$a_{11}x\hat{\mathbf{i}}+a_{22}y\hat{\mathbf{j}}=\tfrac{1}{2}(a_{11}+a_{22})(x\hat{\mathbf{i}}+y\hat{\mathbf{j}})+\tfrac{1}{2}(a_{11}-a_{22})(x\hat{\mathbf{i}}-y\hat{\mathbf{j}}), \quad (7)$$

we note that the second term contributes nothing to the splay energy. Because of the cross term $k_{11}a_{11}a_{22}$ in Eq. (6), we cannot choose $a_{11}x\hat{\mathbf{i}}$ and $a_{22}y\hat{\mathbf{j}}$ as independent splay "normal distortion modes." Instead, we are led to choose (*splay normal mode*)

$$\tfrac{1}{2}(a_{11}+a_{22})(x\hat{\mathbf{i}}+y\hat{\mathbf{j}}) \quad (8)$$

as the *single* splay normal distortion mode.

Using similar reasoning, we can write the twist energy as

$$g_{22}=\tfrac{1}{2}k_{22}(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2=\tfrac{1}{2}k_{22}(a_{12}-a_{21})^2. \quad (9)$$

The appropriate terms from Eq. (5) yield

$$a_{12}x\hat{\mathbf{j}}+a_{21}y\hat{\mathbf{i}}=\tfrac{1}{2}(a_{12}-a_{21})(x\hat{\mathbf{j}}-y\hat{\mathbf{i}})+\tfrac{1}{2}(a_{12}+a_{21})(x\hat{\mathbf{j}}+y\hat{\mathbf{i}}). \quad (10)$$

The second term contributes nothing to the twist energy, so we define a *twist normal mode*:

$$\tfrac{1}{2}(a_{12}-a_{21})(x\hat{\mathbf{j}}-y\hat{\mathbf{i}}). \quad (11)$$

Here again, only a *single* twist normal distortion vector field is needed to describe this mode.

The bend energy density, written as

$$g_{33}=\tfrac{1}{2}k_{33}(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2=\tfrac{1}{2}k_{33}(a_{31}^2+a_{32}^2), \quad (12)$$

shows that there are two bend distortion modes (*bend normal modes*):

$$a_{31}z\hat{\mathbf{i}} \text{ and } a_{32}z\hat{\mathbf{j}}. \quad (13)$$

These modes are degenerate in the sense that either mode can be eliminated by suitable rotation of the x and y axes, so there is really one mode described by two parameters.

We see that the standard distortion terms in Eqs. (1)–(3) account for only four of the six degrees of freedom required by the six derivatives in Eq. (4). The remaining two normal distortion modes, consisting of the leftover terms from Eqs. (7) and (10), are (*saddle normal modes*)

$$\tfrac{1}{2}(a_{11}-a_{22})(x\hat{\mathbf{i}}-y\hat{\mathbf{j}}) \text{ and } \tfrac{1}{2}(a_{12}+a_{21})(x\hat{\mathbf{j}}+y\hat{\mathbf{i}}). \quad (14)$$

The mode vectors transform to each other upon 45° rotation of the coordinate system about z. Accordingly, the modes in Eq. (14) are degenerate, and suitable axis rotations about z can eliminate either mode.

This distortion is called a saddle normal distortion mode because the director vectors are perpendicular to a saddle-shaped surface. (Frank[4] used the designation "saddle splay.") This distortion field and those for other modes are shown in Fig. 1.

To obtain the energy associated with this saddle distortion, we define a saddle-energy coefficient k_{44} such that the corresponding energy contribution g_{44} is half k_{44} multiplied by the sum of the squares of the mode amplitudes. So (*saddle*)

$$g_{44}=\tfrac{1}{2}k_{44}\{(a_{11}-a_{22})^2+(a_{12}+a_{21})^2\}, \quad (15)$$

in analogy with the forms of the other three terms: splay,

$$g_{11}=\tfrac{1}{2}k_{11}(a_{11}+a_{22})^2=\tfrac{1}{2}k_{11}(\nabla\cdot\hat{\mathbf{n}})^2, \quad (16)$$

twist,

$$g_{22}=\tfrac{1}{2}k_{22}(a_{12}-a_{21})^2=\tfrac{1}{2}k_{22}(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2, \quad (17)$$

bend,

$$g_{33}=\tfrac{1}{2}k_{33}(a_{31}^2+a_{32}^2)=\tfrac{1}{2}k_{33}(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2. \quad (18)$$

We can write Eq. (15) in vector form to be consistent with the vector forms for the other terms:

$$g_{44}=\tfrac{1}{2}k_{44}\{-2\hat{\mathbf{n}}\cdot\nabla^2\hat{\mathbf{n}}-(\nabla\cdot\hat{\mathbf{n}})^2 -(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2-2(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2\}. \quad (19)$$

The total elastic energy density is given by

$$g=g_{11}+g_{22}+g_{33}+g_{44}. \quad (20)$$

From Fig. 1 and the discussion of Eq. (14) we see that the saddle mode involves both splaylike and twistlike average alignment deviations of neighboring molecules to an equal extent. One could accordingly suggest that $k_{44}\approx\frac{1}{2}(k_{11}+k_{22})$, but certainly not that $k_{44}=0$. In fact, we will see that the "molecular approach" of Nehring and Saupe[5] leads to $k_{44}=\frac{1}{2}(k_{11}+k_{22})$.

Notice also that if $k_{11}=k_{22}=k_{44}=k$ and $k_{33}=2k$, the form of the free-energy density is proportional to $\sum_{ij}\nabla_i n_j\nabla_i n_j$. This form is the one that is produced by simple models of the nematic state such as those with pairwise intermolecular interactions depending only on the angle between the long molecular axes. It is also the simplest term appearing in field-theoretic models. It is easy to see that, with $k_{44}=0$, there is no set of ratios k_{11}/k_{33}, k_{22}/k_{33} which can produce $\sum_{ij}\nabla_i n_j\nabla_i n_j$. This is a convincing argument that the k_{44} term is needed. It is also worth noting that in the case $k_{11}=k_{22}=k_{44}=k_{33}/2$, we have from Eq. (24): $k'_{11}=k'_{22}=k'_{33}$. This is the conventional result following from the simple models.

It is appropriate to review the assumptions leading to our elastic-energy expression. From the simplest point of view, we accept the standard splay, twist, and bend energy terms as being correct for the corresponding distortions, and add a fourth term to describe the energy of the remaining "saddle" distortion. From a more general point of view, we assume that in analogy to normal vibrational modes there exist for this problem "normal distortion modes" whose description requires independent parameters equal in number to the number of distortional degrees of freedom. We require that the mode energies be quadratic in the distortion amplitudes. These

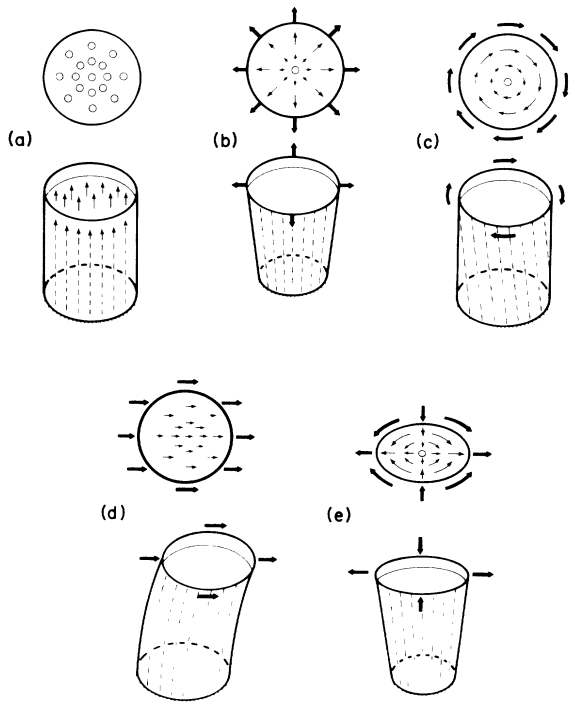

FIG. 1. Normal distortion modes for nematic liquid crystal with no chiral or dipolar effects. (a) The undistorted material in a right-circular cylindrical cup with vertical grooves on the inside wall (shown as dashed lines) to align the director field $\hat{\mathbf{n}}$ vertically along the wall, and hence vertically elsewhere, as indicated by the circled dots in the top view. (b) The splay mode, achieved by expanding the top rim of the cup outward with forces indicated by thick arrows; the top view also shows projections of the directors as thin arrows. (c) The twist mode. (d) The bend mode. (e) The saddle mode, achieved by pushing in on two opposite sides and pulling out on the other two sides of the rim. Note that in each mode the distortion field has the same form throughout the cup—there is nothing unique about the distortion on the cup axis.

normal modes are chosen so that no cross terms occur in the elastic-energy expression. These assumptions lead to the same results, namely splay and twist modes described by one parameter each, and bend and saddle modes described by two parameters each.

Because the g_{44} term is frequently ignored,[1-3,6] it is necessary to outline its history. According to Nehring and Saupe,[5] Oseen introduced a related term but dropped it because it did not enter the Euler-Lagrange equations for the equilibrium structures. Frank[4] reintroduced the term, and accurately described the form of the "pure saddle-splay curvature." Ericksen[7] argued that its evaluation requires knowledge of surface forces whose experimental interpretation is uncertain, but did not claim that this term vanishes. However, his work induced others[1,2,6] to drop this term. Nehring and Saupe[5] noted that elastic constants which do not enter the Euler-Lagrange equations may still be important for the equilibrium structure, and gave examples. They included Frank's "saddle-splay" term, and reintroduced second-derivative terms first derived by Oseen which do not concern us because we consider only first-derivative distortions.

Frank's term also appears in a fairly recent work by Meiboom, Sammon, and Brinkman.[8] Their expression (ignoring their spontaneous twist q_0) is

$$g=\tfrac{1}{2}k'_{11}(\nabla\cdot\hat{\mathbf{n}})^2+\tfrac{1}{2}k'_{22}(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2+\tfrac{1}{2}k'_{33}(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2 + \tfrac{1}{2}(k'_{22}+k'_{24})\nabla\cdot[(\hat{\mathbf{n}}\cdot\nabla)\hat{\mathbf{n}}-(\nabla\cdot\hat{\mathbf{n}})\hat{\mathbf{n}}]. \quad (21)$$

The k'_{ij} above are primed because the energy densities in the first, second, and fourth terms do not correspond in general to our g_{11}, g_{22}, and g_{44} energy densities, respectively. They do correspond if only one normal distortion mode is present. For comparison, our free-energy density expressed in a form as close as possible to that of Meiboom, Sammon, and Brinkman[8] is

$$g=\tfrac{1}{2}k_{11}(\nabla\cdot\hat{\mathbf{n}})^2+\tfrac{1}{2}k_{22}(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2+\tfrac{1}{2}k_{33}(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2+\tfrac{1}{2}k_{44}\{2\nabla\cdot[(\hat{\mathbf{n}}\cdot\nabla)\hat{\mathbf{n}}-(\nabla\cdot\hat{\mathbf{n}})\hat{\mathbf{n}}]+(\nabla\cdot\hat{\mathbf{n}})^2+(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2\}. \quad (22)$$

The first three terms correspond to g_{11}, g_{22}, and g_{33} in Eqs. (16)-(18), respectively. The last (g_{44}) term has a different form than g_{44} in Eq. (19), but they are identical mathematically. We thus have two different coordinate-system-free ways of expressing the free-energy density, that of Eqs. (16)-(20) and of Eq. (22).

If only the saddle mode is present, the last terms of Eqs. (21) and (22) (and corresponding terms of Frank[4] and of Nehring and Saupe[5]) are equivalent because $\nabla\cdot\hat{\mathbf{n}}=\nabla\times\hat{\mathbf{n}}=0$, and all other terms vanish. Thus the saddle-mode free-energy density contains a divergence, whose volume integral can be converted to a surface integral. One might think this energy scales as surface area rather than volume. *However,* if we consider, for example, a distorted volume as in Fig. 1(e), of radius R and height h, with $a_{11}=a$, $a_{22}=-a$, and other $a_{ij}=0$ in Eq. (5), we find that the scalar product of the vector in square brackets with a lateral-surface-area vector is proportional to R. The lateral surface area is $2\pi Rh$, so the integral over the lateral surface scales as the *volume,* πR^2h. (The top and bottom contribute nothing to the integral.) This illustrates that the saddle mode contributes to volume elastic energy.

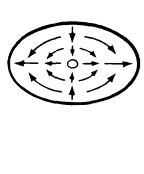

FIG. 2. Proposed arrangement for magnetically inducing the saddle distortion in a nematic liquid crystal. Arrows indicate the magnetic field, and also the director projections for one of the two possible distortion modes. The cylindrical container distortion for that mode is also shown.

Nehring and Saupe[5] find from a "molecular approach" that

$$k'_{24}=\tfrac{1}{2}(k'_{11}-k'_{22}). \quad (23)$$

We find that Eqs. (15)-(20) and (22) agree with Eqs. (21) and (23) if we make the correspondences below [expressions in square brackets apply only if Eq. (23) is valid]:

$$\begin{aligned}
k'_{11}&=k_{11}+k_{44}\ \ [=\tfrac{3}{2}k_{11}+\tfrac{1}{2}k_{22}],\\
k'_{22}&=k_{22}+k_{44}\ \ [=\tfrac{3}{2}k_{22}+\tfrac{1}{2}k_{11}],\\
k'_{33}&=k_{33}\ \ [=k_{33}],\\
k'_{24}&=k_{44}-k_{22}\ \ [=\tfrac{1}{2}(k_{11}-k_{22})],\\
k_{11}&=k'_{11}-\tfrac{1}{2}(k'_{22}+k'_{24})\ \ [=\tfrac{3}{4}k'_{11}-\tfrac{1}{4}k'_{22}],\\
k_{22}&=\tfrac{1}{2}(k'_{22}-k'_{24})\ \ [=\tfrac{3}{4}k'_{22}-\tfrac{1}{4}k'_{11}],\\
k_{44}&=\tfrac{1}{2}(k'_{22}+k'_{24})\ \ [=\tfrac{1}{4}(k'_{11}+k'_{22})=\tfrac{1}{2}(k_{11}+k_{22})].
\end{aligned} \quad (24)$$

We see that to prevent a splay (k_{11}) or twist (k_{22}) instability, previously reported ratios of k'_{11}/k'_{22} based on the Fréedericksz effect as discussed below must fall within the range $\frac{1}{3}<k'_{11}/k'_{22}<3$. The ratios tabulated by de Gennes[1] fall within this range. Other ratios, for polymeric nematic liquid crystals ($k_{11}/k_{22}=11.4$, for example[9]), based on an analysis[6] of light scattering from low-frequency thermally generated *dynamic* distortion modes, fall far outside the $\frac{1}{3}$ to 3 range. We conjecture that such measurements are not of k'_{11}/k'_{22} but may be of k_{11}/k_{22} as defined in this work.

How must previous measurements and uses of the k_{ii}

be reinterpreted because of the reintroduction of the saddle elastic-energy term? Concerning the measurements, we examine the four examples of the Fréedericksz effect collected and illustrated by Chandrasekhar.[2] These involve two parallel plates of mean separation d, with the boundary conditions that the directors at the plates are parallel (or in one case perpendicular) to the plates. For the twisted nematic cell, the directors on the two surfaces are perpendicular to each other. A uniform magnetic field H is applied in the appropriate direction, and above a critical field H_c the direction field between the plates deforms. For H perpendicular to the plates, the critical-field expression becomes

$$H_c=(\pi/d)[k_{11}+k_{44})/\chi_a]^{1/2}, \quad (25)$$

so k_{11} in the original expression goes to $k_{11}+k_{44}$. The deformation above H_c was formerly called a splay distortion, but it is really a combined splay and saddle distortion whose vector field projection is the sum of the vectors in Figs. 1(b) and 1(e). Similarly, for H parallel to the plates but perpendicular to the directors at the walls,

$$H_c=(\pi/d)[(k_{22}+k_{44})/\chi_a]^{1/2}. \quad (26)$$

Above H_c the so-called twist distortion is really a combined twist and saddle distortion, whose vector field projection is the sum of the vectors in Figs. 1(c) and 1(e). For the same H but with directors perpendicular at the walls, the expression is unchanged and is

$$H_c=(\pi/d)(k_{33}/\chi_a)^{1/2}. \quad (27)$$

The expression for the twisted nematic cell is more complex, and requires replacement of both k_{11} and k_{22} by $k_{11}+k_{44}$ and $k_{22}+k_{44}$, respectively. In these formulas, χ_a is the parallel magnetic susceptibility less the perpendicular susceptibility.

It is evident that k_{44} cannot be obtained from the above expressions which only give the combinations $k_{11}+k_{44}$ and $k_{22}+k_{44}$, previously interpreted as k_{11} and k_{22}, respectively. To find k_{11}, k_{22}, and k_{44} separately, one needs to measure the energy density for a pure splay, pure twist, or pure saddle distortion as illustrated in Figs. 1(b), 1(c), and 1(e), respectively. If the pure "normal" distortions cannot be obtained, arrangements which will give better than the 1:1 splay:saddle and twist:saddle ratios achieved previously would, in conjunction with previous results from 1:1 arrangements, provide numerical values for k_{11}, k_{22}, and k_{44} separately. Two such possible arrangements are a radial electric field to determine k_{11} or a circumferential magnetic field to determine k_{22}, acting on an initially axially oriented liquid crystal. The saddle distortion necessary for determining k_{44} could be induced magnetically by the arrangement shown in Fig. 2.

A more complex Fréedericksz ordering pattern was discovered recently by Lonberg and Meyer[10] and discussed further by several authors.[11-16] It occurs for large k_{11}/k_{22} ratios as found in polymer liquid crystals. Analysis of this effect may provide a way of determining the k_{ii} separately for these materials.

In conclusion, our analysis indicates that the fourth, saddle, contribution to the nematic-liquid-crystal elastic energy density introduced by Frank[4] must be retained. Its coefficient k_{44} should be measured, to see whether the Nehring-Saupe[5] relation $k_{44}=\frac{1}{2}(k_{11}+k_{22})$ derived from a molecular approach is accurate. Many previous reports of measurement or use of the splay and twist coefficients k_{11} and k_{22} must be reinterpreted as dealing with $k_{11}+k_{44}$ and $k_{22}+k_{44}$, respectively.

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[1]P. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, London, 1974).

[2]S. Chandrasekhar, *Liquid Crystals* (Cambridge Univ. Press, London, 1977).

[3]H. J. Deuling, in *Liquid Crystals,* edited by L. Liebert, Solid State Physics Supplement 14 (Academic, New York, 1978).

[4]F. C. Frank, Disc. Faraday Soc. **25**, 19 (1958).

[5]J. Nehring and A. Saupe, J. Chem. Phys. **54**, 337 (1971).

[6]Orsay Liquid Crystal Group, J. Chem. Phys. **51**, 816 (1969).

[7]J. L. Ericksen, Arch. Ration. Mech. Anal. **10**, 189 (1962).

[8]S. Meiboom, M. Sammon, and W. F. Brinkman, Phys. Rev. A **27**, 438 (1983).

[9]V. G. Taratuta, A. J. Hurd, and R. B. Meyer, Phys. Rev. Lett. **55**, 246 (1985).

[10]F. Lonberg and R. B. Meyer, Phys. Rev. Lett. **55**, 718 (1985).

[11]C. Oldano, Phys. Rev. Lett. **56**, 1098 (1986).

[12]W. Zimmermann and L. Kramer, Phys. Rev. Lett. **56**, 2655 (1986).

[13]E. Miraldi, C. Oldano, and A. Strigazzi, Phys. Rev. A **34**, 4348 (1986).

[14]U. D. Kini, J. Phys. (Paris) **47**, 693 (1986).

[15]U. D. Kini, J. Phys. (Paris) **47**, 1829 (1986).

[16]H. M. Zenginoglou, J. Phys. (Paris) **48**, 1599 (1987).