Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Calculation of the Elastic Constants of a Nematic Liquid Crystal

Richard G. Priest [a]

[a] Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

To cite this article: Richard G. Priest (1972): A Calculation of the Elastic Constants of a Nematic Liquid Crystal, Molecular Crystals and Liquid Crystals, 17:2, 129-137

To link to this article: http://dx.doi.org/10.1080/15421407208083836

Molecular Crystals and Liquid Crystals. 1972. Vol. 17, pp. 129–137

Printed in Great Britain

A Calculation of the Elastic Constants of a Nematic Liquid Crystal†

RICHARD G. PRIEST

Department of Physics
University of Pennsylvania
Philadelphia, Pennsylvania

Received July 12, 1971

Abstract—A calculation of the Frank elastic constants based on the lattice model of liquid crystals is presented. The calculated temperature dependence of K_{11}, K_{22} and K_{33} is in agreement with experiment. The X-ray structure data for *p*-azoxyanisole is employed to calculate the magnitude of $\frac{1}{2}(K_{11}+K_{22})$ and the result is found to agree with experiment.

In a previous work(1) it was demonstrated that a lattice model can be used to understand the orientational order of the nematic mesophase. This paper is an application of the lattice model to a calculation of the elastic constants. Both qualitative and, in the case of the average of K_{11} and K_{22}, quantitative agreement with experiment are obtained.

1. Macroscopic Theory

The elastic constants are defined, in the macroscopic continuum theory, through the expression for the elastic free energy:(2)

$$F = \tfrac{1}{2}\int d^3r[K_{11}(\nabla\cdot\hat{n})^2 + K_{22}(\hat{n}\cdot\nabla\times\hat{n})^2 + K_{33}(\hat{n}\times\nabla\times\hat{n})^2] \qquad (1)$$

Here $\hat{n}(\mathbf{r})$ is a unit vector, called the director, which lies along the direction of the axis of long range order at the point $\mathbf{r}$. On the molecular scale $n(\mathbf{r})$ is a slowly varying function of $\mathbf{r}$. The three types of distortion corresponding to K_{11}, K_{22}, and K_{33} are respectively: splay, torsion and bending. If the system is uniformly oriented along the z axis the director has the simple form: $\hat{n}(\mathbf{r}) = \hat{z}$. It is useful to write down the form which the director takes when

---

† Supported in part by the Office of Naval Research.

infinitesimal sinusodial distortions of wavevector $\mathbf{q}$ are present.

$$\begin{aligned} \hat{n}(\mathbf{r}) &= \Delta n_s \sin(\mathbf{q}\cdot\mathbf{r})\frac{\mathbf{q}}{|\mathbf{q}|}+\hat{z} \text{ splay} \\ \hat{n}(\mathbf{r}) &= \Delta n_t \sin(\mathbf{q}\cdot\mathbf{r})\frac{\mathbf{q}\times\hat{z}}{|\mathbf{q}|}+\hat{z} \text{ torsion} \\ \hat{n}(\mathbf{r}) &= \Delta n_b \sin(\mathbf{q}\cdot\mathbf{r})\,\hat{\rho}+\hat{z} \text{ bending} \end{aligned} \tag{2}$$

Here Δn is the amplitude of the distortion wave. For splay and torsion: $\mathbf{q}\perp\hat{z}$, for bending: $\mathbf{q}\,||\,\hat{z}$ and $\hat{\rho}$ is any unit vector normal to $\hat{z}$.

From Eq. (1) we obtain the free energies associated with splay, torsion and bending waves. They are $\frac{1}{4}\Omega\,\mathrm{K}_{11}\,q^2(\Delta n_s)^2$, $\frac{1}{4}\Omega\,\mathrm{K}_{22}\,q^2(\Delta n_t)^2$ and $\frac{1}{4}\Omega\,\mathrm{K}_{33}\,q^2(\Delta n_b)^2$ respectively, where Ω is the volume of the system. These free energies will be associated with changes in the free energy, as calculated in the lattice model, introduced by the three types of distortion. In this way the elastic constants will be determined in terms of microscopic parameters.

2. The Lattice Model

The lattice model of liquid crystals assumes an intermolecular interaction:

$V = \sum_{\langle ij\rangle} V_{ij}(\theta_{ij})$, where θ_{ij} is the angle between the long axes of the molecules when they are translated so that the centers of mass of the molecules coincide. The elastic constants are sensitive to the dependence of V_{ij} on $\mathbf{r}_{ij}$. Here $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, with $\mathbf{r}_i$ the coordinate of the ith molecule. The elastic constants also depend on the type of lattice, or more precisely since we are dealing with a liquid, on the two body correlation function for the centers of mass, $g(\mathbf{r})$. This function gives the probability per unit volume of finding the center of mass of a molecule at $\mathbf{r}$ when there is a molecule at the origin.(3) In the interest of simplicity the angular dependence of $V_{ij}(\theta_{ij})$ will be taken to be that of the second Legendre polynomial. The intermolecular interaction is then:

$$V = -\sum_{\langle ij\rangle} A(\mathbf{r}_{ij})\,P_2(\cos\theta_{ij}). \tag{3}$$

The fact that the system is a liquid will be incorporated by replacing the sums over $A(\mathbf{r}_{ij})$ by integrals weighted by $g(\mathbf{r})$. As shown in

Ref. 1 this model may be treated with quite good accuracy by the mean field theory. To obtain such a theory one uses the addition theorem for spherical harmonics to write:

$$P_2(\cos\theta_{ij}) = \frac{4\pi}{5}\sum_m Y_{2m}(\theta_i, \varphi_i)\, Y^*_{2m}(\theta_j, \varphi_j),$$

where $\{\theta, \varphi\}$ are the spherical coordinates of the molecules when the polar axis is the equilibrium orientation direction of the ith molecule. Then the average interaction of the ith molecule with its neighbors can be written as:

$$V_i = -\sum_j A(\mathbf{r}_{ij})\frac{4\pi}{5}\sum_m Y_{2m}(\theta_i, \varphi_i)\,\langle Y^*_{2m}(\theta_j, \varphi_j)\rangle. \tag{4}$$

Here the angle brackets denote a thermodynamic average. In the absence of distortions the z axis is the equilibrium orientation direction of all the molecules. This fact together with the fact that the state is uniaxial implies that $\langle Y^*_{2m}(\theta_j, \varphi_j)\rangle = 0$ unless $m = 0$. Equation (4) becomes:

$$V_i = -[\sum_j A(\mathbf{r}_{ij})\, S]\, P_2(\cos\theta_i), \tag{5}$$

where $S \equiv \langle P_2(\cos\theta_j)\rangle$.

The term in the square brackets is the mean field which is proportional to S. Here S is to be determined self consistently by requiring that $\langle P_2(\cos\theta_i)\rangle$, calculated from the mean field, be equal to S. The free energy in this approximation is⁽⁴⁾:

$$-\beta F = \Omega/v_0 \ln\int_0^1 \exp(C(x))\,\mathrm{d}x, \tag{6}$$

where $C(x) = \beta\sum_i A(\mathbf{r}_{0i})\, S(P_2(x) - \tfrac{1}{2}S)$, v_0 is the volume per molecule, $x = \cos\theta_i$ and $\beta = 1/kT$.

If there is a distortion of the type described in Eq. (2) present, the equilibrium orientation directions of all the molecules are not the same. In fact it is easy to see that $\delta\alpha_{ij}$, the angle between the equilibrium orientation directions of two adjacent molecules i and j, is:

$$\delta\alpha_{ij} = \Delta n(\mathbf{q}\cdot\mathbf{r}_{ij})\cos(\mathbf{q}\cdot\mathbf{r}_i). \tag{7}$$

Such a distortion has two effects. The first is to reduce the value of S. This does not affect the free energy to order q^2 and will therefore be neglected. The second is to reduce the effective coupling between molecules. This does increase the free energy to order q^2.

The reduction in the effective coupling constant may be calculated as follows. In Eq. (4) it is the average $\langle Y^*_{2m}(\theta_j, \varphi_j)\rangle$, with θ_j, φ_j measured in the coordinate system with polar axis parallel to the equilibrium orientation direction of the ith molecule, which is required. A similar average, differing from the above average only in that θ_j, φ_j are measured in the coordinate system with polar axis parallel to the equilibrium orientation direction of the jth molecule, has the value $\sqrt{5/4\pi}\,\delta_{m0}\,S$. It can be seen, by using the transformation properties of the spherical harmonics, that the required average has the value $(\tfrac{3}{2}\cos^2\delta\alpha_{ij} - \tfrac{1}{2})\sqrt{5/4\pi}\,\delta_{m0}\,S$ for the case of $m = 0$. The sum of $\langle Y_{2m\neq 0}(\theta_j, \varphi_j)\rangle$ over all the neighbors of the ith molecule is zero because of the choice of the polar axis of the first coordinate systems. These effects may be interpreted as a reduction in the effective coupling constant by the factor $(\tfrac{3}{2}\cos^2\delta\alpha_{ij} - \tfrac{1}{2})$. The free energy becomes:

$$-\beta F = \Omega/v_0 \ln \int_0^1 \exp\left[C(x)(\tfrac{3}{2}\cos^2\delta\alpha_{ij} - \tfrac{1}{2})\right] \mathrm{d}x. \qquad (8)$$

Using Eq. (7) and keeping only the terms in q^2 the increase in the free energy is:

$$\Delta F = \tfrac{3}{4}\Omega/v_0\, S^2 \sum_i A(\mathbf{r}_{0i})(\Delta n)^2 (\mathbf{q}\cdot\mathbf{r}_{0i})^2 \cos^2(\mathbf{q}\cdot\mathbf{r}_i). \qquad (9)$$

After the average over $\cos^2(\mathbf{q}\cdot\mathbf{r}_i)$ is taken the elastic constants are obtained by comparison with the macroscopic elastic free energy. They are:

$$\mathrm{K}_{11} = \mathrm{K}_{22} = \tfrac{3}{4}S^2\, 1/v_0 \sum_i A(\mathbf{r}_{0i})\, \rho_{0i}^2$$

$$\mathrm{K}_{33} = \tfrac{3}{2}S^2\, 1/v_0 \sum_i A(\mathbf{r}_{0i})\, z_{0i}^2 \qquad (10)$$

It has been assumed that $A(\mathbf{r}_{0i})$ is cylindrically symmetric about the z axis. $\boldsymbol{\rho}_{0i}$ is the component of $\mathbf{r}_{0i} \perp \hat{z}$ and z_{0i} is the z component of $\mathbf{r}_{0i}$.

The fact that $\mathrm{K}_{11} = \mathrm{K}_{22}$ in this theory is a consequence of assuming that the spatial dependence of $V_{ij}(\theta_{ij})$ can be separated from the rotational dependence as in Eq. (3). This assumption is clearly incorrect to the extent that hard core repulsion of molecules is important. For example Eq. (3) assigns equal interaction energies to the configurations of Fig. 1. On the other hand the fact that $K_{11} \neq K_{33}$ is a consequence of the anisotropy in $g(\mathbf{r})$.

Equation (10) predicts temperature dependence of the elastic constants through S^2. As pointed out by Saupe⁽⁵⁾ it is necessary to include an additional temperature dependent factor, namely $[v(T=T_c)/v(T)]^{7/3}$. $v(T)$ is the molar volume at temperature T, and T_c is the transition temperature. This is necessary because the elastic constants have dimensions of (energy/length) and the coupling constants vary approximately as $(\text{length})^{-6}$. When this factor is included all the other parameters assume their transition temperature values.

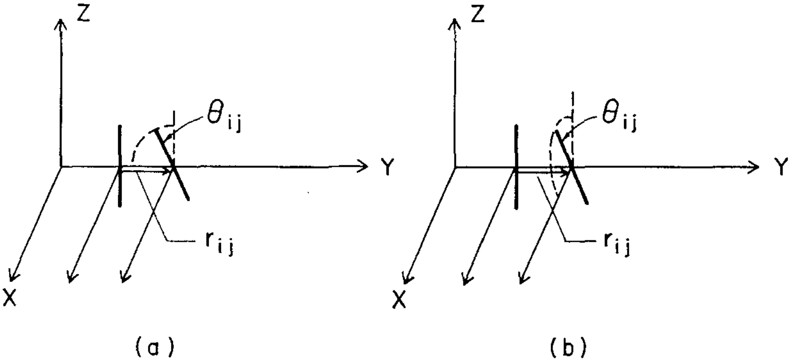

Figure 1. The intermolecular interaction $V_{ij} = -A\ P_2(\cos\theta_{ij})$ is the same for the configurations shown in (a) and (b).

From the fact⁽⁶⁾ that the mean field theory predicts that $\sum_i A(\mathbf{r}_{oi}) = 4.56\ kT_c$ the results of Eq. (10) can be written in the form:

$$\frac{\sum_i A(\mathbf{r}_{oi})\rho_{oi}^2}{\sum_i A(\mathbf{r}_{oi})} = \frac{\frac{1}{2}(K_{11}+K_{22})\frac{4}{3}v_0(v(T=T_c)/v(T))^{7/3}}{S^2\,4.56\,kT_c} \equiv B_\rho \qquad (11)$$

$$\frac{\sum_i A(\mathbf{r}_{oi})\,z_{oi}^2}{\sum_i A(\mathbf{r}_{oi})} = \frac{K_{33}\,\frac{2}{3}v_0(v(T=T_c)/v(T))^{7/3}}{S^2\,4.56\,kT_c} \equiv B_z,$$

where an average of K_{11} and K_{22} has been used.

3. Application to P-azoxyanisole (PAA)

The quantities B_ρ and B_z are theoretically temperature independent. Table 1 presents the values of B_ρ and B_z calculated from Zwetkov's⁽⁷⁾ measurements of the elastic constants of *p*-azoxyanisole. Saupe's results⁽⁶⁾ for the molar volumes were used. The experimental values⁽⁸⁾ of S were used to avoid some of the error involved in the mean field theory. As can be seen from the Table, B_ρ and B_z are remarkably constant over a range of temperatures. The average taken does not include the data point at 134 °C. Zwetkov reported $T_c = 134.5$ °C instead of the accepted value of 135.5 °C. The sample used in his experiment may not have been pure enough to give reliable results so near T_c, thus accounting for the anomolous behaviour of the elastic constants at 134 °C.

TABLE 1

T (°C)	K_{11} (dyne)	K_{22} (dyne)	K_{33} (dyne)	B_ρ (Å²)	B_z (Å²)
120	5.1 10^{-7}	3.3 10^{-7}	11.3 10^{-7}	21.0	28.3
125	4.6	2.9	9.4	22.3	27.8
129	3.9	2.4	7.6	21.9	26.4
133	2.9	1.7	5.6	21.3	25.8
134	2.4	—	4.3	—	27.6
Average				21.6	27.1

The temperature dependence of the three elastic constants and the related quantities B_ρ and B_z.

In order to calculate B_ρ and B_z from the left hand side of Eq. (11) the sums are replaced by weighted integrals.

$$B_\rho = \frac{\int d^3r\, A(\mathbf{r})\, g(\mathbf{r})\, \rho^2}{\int d^3r\, A(\mathbf{r})\, g(\mathbf{r})}$$

$$B_z = \frac{\int d^3r\, A(\mathbf{r})\, g(\mathbf{r})\, z^2}{\int d^3r\, A(\mathbf{r})\, g(\mathbf{r})} \qquad (12)$$

To evaluate the integrals of Eq. (12) it is necessary to use the X-ray data to determine the appropriate form of $g(\mathbf{r})$. Also some reasonable assumptions about the form of $A(\mathbf{r})$ must be made. To facilitate the discussion I will employ cylindrical coordinates with origin at the central molecule and z axis parallel to the equilibrium orientation direction of the central molecule.

The first observation that can be made is that $A(\rho, z)$ must fall off rapidly as z approaches a length L, where L is the thickness of a layer of molecules normal to the z axis. (The appendix shows how L may be calculated from the X-ray data and the molar volume.) This is equivalent to saying that only nearest neighbor molecules interact. However, to retain a three dimensional character $A(\rho, z)$ must be appreciable as long as $z \lesssim L/2$. Therefore I assume that $A(\rho, z) = A(\rho)$ for $-z_c < z < z_c$ and $A(\rho, z) = 0$ otherwise. The experimental value of B_z may be used to calculate z_c thereby giving a check on the validity of the assumption made here. Specifically we should find $L/2 \lesssim z_c \lesssim L$. Since, as will be shown below, this is indeed the case, it is possible to take $g(\rho, z)$ independent of z. This is because for small z it surely is independent of z (reflecting the molecular shape), and for large z it does not matter because $A(\rho, z)$ is zero for large z.

The quantity obtained from the X-ray study of Vainshtein *et al.*⁽⁹⁾ is

$$Z(\rho) = \int_{-L/2}^{L/2} g(\rho, z)\,\mathrm{d}z.$$

Since $g(\rho, z)$ is independent of z we have:

$$g(\rho) = Z(\rho)/L. \tag{13}$$

Using the method of the appendix we find: $L \cong 14$ Å for PAA. The function $Z(\rho)$ shows a well defined first shell of neighbors out to about 5.5 Å. It is natural to assume that $A(\rho)$ is constant inside this shell and zero outside of it. To summarize, the product $A(\mathbf{r})g(\mathbf{r})$ has the form: $A(\rho, z)g(\rho, z) = AZ(\rho)/L$ for: $0 < \rho < 5.5$ Å and $-z_c < z < z_c$; $A(\rho, z)g(\rho, z) = 0$ otherwise. It is now possible to evaluate B_ρ:

$$B_\rho = \frac{\int_0^{5.5} Z(\rho)\rho^3\,\mathrm{d}\rho}{\int_0^{5.5} Z(\rho)\rho\,\mathrm{d}\rho}. \tag{14}$$

This integral was done by crude numerical integration using the experimental values of $Z(\rho)$ for PAA in a magnetic field.⁽⁹⁾ The result is 19.1 $(\text{Å})^2$ in good agreement with Table 1. Note that with the above assumptions this result does not depend on either of the two parameters A and z_c. The expressions for B_z is also very easy to evaluate, the result being: $B_z = \frac{1}{3}z_c{}^2$. To obtain agreement with Table 1, z_c must be approximately 9 Å. This value does fall between $L/2$ and L indicating that the assumptions made about $A(\mathbf{r})$ and $g(\mathbf{r})$ are not unreasonable.

Conclusions

The most important result of this calculation is the surprisingly good agreement between theory and experiment on the value of B_ρ. The theory itself is an improvement over that of Saupe⁽⁵⁾ in three respects. First it shows, in effect, that an assumption made implicitly by Saupe is correct within the mean field theory. Saupe's calculation assumes that the partial derivative of the orientational part of the entropy with respect to q^2, at constant order parameter S, is zero. Since, to the level of approximation of this calculation, this is the case, the temperature dependence of the elastic constants obtained here is the same as that obtained by Saupe. Second, it predicts a positive value for K_{11} rather than a negative one. Third it takes better account of the structure of the liquid than does Saupe's calculation.

The chief defect of the lattice model, in its simple form, is that it predicts that $K_{11} = K_{22}$. Fortunately this does not affect its application to the order parameter calculation because that problem is sensitive only to quantities analogous to the average of K_{11} and K_{22}.

Acknowledgement

I would like to thank Dr. A. B. Harris for many helpful suggestions.

Appendix

There is no real layer structure in nematic liquid crystals. It is, however, possible to construct a series of mathematical layers, perpendicular to the z axis, with the thickness L such that the average number of layer boundaries intersected by a molecule is one. By definition $Z(\rho)$ is the number of molecules intersecting unit area of a plane normal to the z axis at the point ρ from a central molecule. In a nematic $Z(\rho = \infty)$ is the average number of molecules intersecting unit area normal to the z axis. The number of molecules contained in a cylinder (parallel to the z axis) of height D and base area A can be seen to be: $AZ(\rho = \infty) D/L$. Therefore $L = vZ(\rho = \infty)/N_0$ where v is the molar volume and N_0 the Avogadro number.

REFERENCES

1. Priest, R. G., *Phys. Rev. Letters*, **26**, 423 (1971).
2. Groupe D'Etude des Cristaux Liquides (Orsay), *J. Chem. Phys.* **51**, 816 (1969).
3. In the notation of Terrell L. Hill: *Statistical Mechanics*. McGraw-Hill, New York 1956, 182, this is $\rho^{(2)}(r_{12})/\rho$.
4. The Term $-\frac{1}{2}S$, which appears in the expression for $C(x)$, is essentially a correction for double counting. For further details of the approximation see B. Strieb, H. B. Callen, and G. Horwitz, *Phys. Rev.* **145**, 288 (1966).
5. Saupe, Alfred, *Z. Naturforschg.* **15a**, 810 (1960).
6. Maier, Wilhelm and Saupe, Alfred, *Z. Naturforschg.* **15a**, 287 (1960).
7. Swetkoff, V., *Acta Physicochim. URSS.* **6**, 865 (1937); corrected for the magnetic anisotropy values according to Swetkoff, V., *Acta Physiocochim. URSS.* **18**, 358 (1943).
8. Lippmann, H., *Ann. Physik* (7) **2**, 287 (1958).
9. Vainshtein, B. K., Chistyakov, I. G., Kosterin, E. A. and Chaikovskii, V. M., *Mol. Cryst. and Liq. Cryst.* **8**, 457 (1969).