Blue phase of liquid crystals: light scattering and elastic moduli

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The Landau theory is used to calculate the elastic moduli of the blue phase of liquid crystals. The possibility of determining these moduli by measuring the light scattering by fluctuations of the order parameter is discussed.

Phase transitions from an isotropic liquid to the blue phase and then to the cholesteric phase provide a unique case of a crystallization process which can be interpreted quantitatively in Landau's theory.[1–3] Landau's theory predicts several phases with an order parameter periodic in three dimensions [the order parameter is usually chosen to be the traceless part of the dielectric tensor $\hat{\epsilon}(\mathbf{r})$]. Interest has previously been focused on the "microscopic" characteristics of the blue phases, such as the structure of the order parameter inside the unit cell. In the present letter we calculate some macroscopic quantities: the elastic moduli. This problem is also of interest because the elastic properties of crystals are determined by the fourth-rank tensor λ_{iklm}, and this tensor has been suggested for use as an order parameter for a phenomenological description of the crystallization process.[4–6]

We begin by considering the scattering light by long-wave fluctuations of the order parameter as a method for measuring elastic moduli. In many regards, this scattering is analogous to the diffuse thermal scattering of x rays.[7] It is concentrated near Bragg reflections, so that the wave vector of the scattered wave is $\mathbf{k}_1 = \mathbf{k}_0 + \vec{\tau} + \mathbf{q}$, where $\mathbf{k}_0$ is the wave vector of the incident wave, $\vec{\tau}$ is the reciprocal-lattice vector corresponding to the reflection under consideration, and $\mathbf{q}$ is the wave vector of the fluctuation. In the case of long-wave ($|\mathbf{q}| \ll |\vec{\tau}|$) acoustic fluctuations, one can use the equations of the theory of elasticity of a homogeneous medium. The change in the dielectric constant caused by these fluctuations, $\delta\hat{\epsilon}$, may be considered as simply the consequence of small lattice displacements[7] $\mathbf{u}(\mathbf{r})$:

$$\delta\hat{\epsilon}(\mathbf{r}) = \hat{\epsilon}(\mathbf{r}-\mathbf{u}) - \hat{\epsilon}(\mathbf{r}) \approx -(\mathbf{u}\vec{\nabla})\hat{\epsilon}(\mathbf{r}) = -i\sum_{\vec{\tau}}(\mathbf{u}\vec{\tau})\hat{\epsilon}_{\vec{\tau}}e^{i\vec{\tau}\mathbf{r}}, \tag{1}$$

where $\hat{\epsilon}_{\vec{\tau}}$ is the unperturbed value of the Fourier harmonic of the dielectric constant of the blue phase. The principal assumption embodied in (1) is that the change in $\hat{\epsilon}_{\vec{\tau}}$ is negligible (the change caused, for example, by rotations due to the strain). Only the fluctuations of $\hat{\epsilon}$ due to the rapidly oscillating factors $\exp(i\vec{\tau}\mathbf{r})$ are taken into account. Repeating the familiar arguments,[7] we find the following cross section for diffuse scattering of light near the reflection $\vec{\tau}$:

$$\frac{d\sigma}{do_1} = \frac{\mathbf{k}_0^4}{16\pi^2}|\mathbf{e}_1^*\hat{\epsilon}_{\vec{\tau}}\mathbf{e}_0|^2 k_B T V \tau_i \tau_k (\lambda_{ilkm} q_l q_m)^{-1}, \tag{2}$$

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where T is the temperature, and V the volume of the crystal. The only difference between (2) and the expression in Ref. 7 is in the polarization-structure factor $|\mathbf{e}_1^* \hat{\epsilon}_{\vec{\tau}} \mathbf{e}_0|^2$. The polarization properties of the diffuse scattering determined by this factor turn out to be the same as for Bragg scattering in the kinematic approximation.[3,8] By measuring the intensity distribution in the diffuse spot near the Bragg reflection (i.e., by measuring the dependence of $d\sigma/do_1$ on $\mathbf{q}$), we can thus determine all the elastic moduli of the blue phase. The scattering intensifies markedly (in proportion to $|\mathbf{q}|^{-2}$) with decreasing $\mathbf{q}$, and it is the same in order of magnitude (corresponding estimates will be given below) as in nematic and cholesteric liquid crystals (at comparable values of $\mathbf{q}$). The interference between the diffuse and Bragg scattering, which is theoretically possible, was ignored in the derivation of (2).

We turn now to the calculation of the elastic-modulus tensor λ_{iklm}. Here we need to calculate the free energy as a function of the small strain $(\hat{u})_{ik}$; the coefficient of the term quadratic in the strain gives us λ_{iklm}. These calculations can be carried out directly from the total free-energy functional only for the bulk modulus (in which case the crystal retains its cubic symmetry, simplifying the calculations). In order to calculate all the elastic moduli (of which there are three in cubic crystals), we make a further assumption: The magnitude and tensor form of all the Fourier harmonics of the order parameter remain unchanged in spite of the strain, and the entire increment in elastic energy is due to a change in spacing between planes, i.e., a change in the lengths of the wave vectors of the individual harmonics of $|\vec{\tau}|$ from their equilibrium waves. Under these assumptions, the entire free energy F_{el} is equal to the difference between the gradient terms in the total free energy before and after the deformation and is given by

$$F_{el} = \frac{c_1}{2} \sum_{\vec{\tau}} |\epsilon(\vec{\tau}, 2)|^2 [(\tau' - 2q_0)^2 - (\tau - 2q_0)^2], \tag{3}$$

where c_1 is the coefficient of the gradient term in the free energy,[1-3] τ and τ' are the moduli of the reciprocal-lattice vectors before and after the deformation, $q_0 = 2\pi/p$, p is the pitch of the cholesteric spiral, and $|\epsilon(\vec{\tau},2)|^2$ is the square modulus of one of the components of the tensor Fourier harmonic $\hat{\epsilon}_{\vec{\tau}}$. Both experimental and theoretical results show that this component (the "plane mode") is much larger than the other components, so that only it is retained in (3).

We assume that the crystal is deformed in a uniform manner, so that we have $\mathbf{r}' = \mathbf{r} + \mathbf{u} = \mathbf{r} + \tilde{u}\mathbf{r}$, and the tensor $\tilde{u}_{ik} = \partial u_i / \partial x_k$ is constant throughout the volume of the crystal. It is not difficult to show, the within terms of second order in $\tilde{u}_{ik}$, we have

$$\tau' \approx \tau - \frac{(\vec{\tau}\,\hat{u}\,\vec{\tau})}{\tau} - \frac{(\vec{\tau}\,\hat{u}\,\vec{\tau})^2}{\tau^3} + \frac{2(\vec{\tau}\,\hat{u}^2\,\vec{\tau})}{\tau} - \frac{(\vec{\tau}\,\tilde{u}^{\mathrm{tr}}\,\tilde{u}\,\vec{\tau})}{2\tau}, \tag{4}$$

where $(\hat{u})_{ik} = (1/2)(\tilde{u}_{ik} + \tilde{u}_{ki})$. Substituting (4) into (3), and using the relation $\Sigma_{\vec{\tau}} \tau_i \tau_k = \delta_{ik} \Sigma_{\vec{\tau}} \tau^2/3$ (which is obvious for cubic crystals) and also a sum rule which follows from the condition for a minimum of the free energy,[9] $\Sigma_{\vec{\tau}} \tau(\tau - 2q_0)|\epsilon(\vec{\tau},2)|^2 = 0$, we find $F_{el} = (1/2)\lambda_{iklm} \times (\hat{u})_{ik} (\hat{u})_{lm}$, where λ_{iklm} is the elastic-modulus tensor which we are seeking:

$$\lambda_{iklm} = 2c_1 q_0 \sum_{\vec{\tau}} |\epsilon(\vec{\tau}, 2)|^2 \tau_i \tau_k \tau_l \tau_m / \tau^3 . \quad (5)$$

The expression derived here for λ_{iklm} satisfies the Cauchy condition $\lambda_{iklm} = \lambda_{ilkm}$, so that two elastic moduli turn out to be equal in the blue phases in our approximation: $\lambda_{xxyy} = \lambda_{xyxy}$.

The quantities $|\epsilon(\vec{\tau},2)|^2$ in (5) have been calculated from Landau's theory[2,3] and also measured.[8,10] A surprising property of the blue phases BPI and BPII is that the ratios $|\epsilon(\vec{\tau},2)|$ for different $\vec{\tau}$ are nearly independent of the temperature and of q_0. Consequently, $\epsilon(\vec{\tau},2)$ can be written approxmately as $\epsilon(\vec{\tau},2) = A_{\vec{\tau}}\epsilon$, where ϵ is a scalar order parameter which depends on T and q_0 (in both meaning and magnitude, ϵ is similar to the anisotropy of the dielectric constant ϵ_a in nematic and cholesteric liquid crystals).[8] Using the experimental ratios[10] $|\epsilon(\vec{\tau},2)|$, we find $\lambda_{xxxx} = 0.28K_2q_0^2$ and $\lambda_{xxyy} = 0.07K_2q_0^2$, for BPI from (5), while for BPII we find $\lambda_{xxxx} = 0.36K_2q_0^2$ and $\lambda_{xxyy} = 0.032K_2q_0^2$ (here $K_2 = 2c_1\epsilon^2$ is one of the Frank moduli). The bulk modulus K turns out to be identical in the two phases: $K = \lambda_{xxxx} + 2\lambda_{xxyy} = 0.42K_2q_0^2$. A numerical calculation of K from the total free energy yields a value a few percent smaller (the details of these numerical calculations will be published separately). The parameter η, which characterizes the elastic anisotropy of cubic crystals, depends on only the ratios of the harmonics of $|\epsilon(\vec{\tau},2)|$: $\eta = (\lambda_{xxxx} - \lambda_{xxyy})/(2\lambda_{xyxy}) \approx 1.5$ for BPI and $\eta \approx 5.1$ for BPII.

Since λ_{iklm} is known, we can calculate the diffuse scattering cross section in (2). In order of magnitude we find $(d\sigma/do_1) \sim k_B T k_0^4 V/(c_i q^2)$, i.e., the same results as for nematic and cholesteric liquid crystals, but for certain scattering configurations the cross section can increase dramatically, especially in BPII, because of the relation $\lambda_{xxyy} \ll \lambda_{xxxx}$. In the approximation which we are using here, the quantity ϵ does appear in (2), and the diffuse scattering of the light is nearly independent of the temperature, while the Bragg scattering increases rapidly with decreasing[8] T.

In deriving (5) we considered only a single mechanism for the appearance of an elasticity of the blue phases: a change in the distance between planes. Two factors have been left out of this discussion: the relaxation of $\hat{\epsilon}_{\vec{\tau}}$ during deformations and the changes in the angles between the vectors $\vec{\tau}$ during shear deformations. Incorporating the first of these factors leads to a decrease in λ_{iklm}, while incorporating the second leads to an increase in the shear moduli; however, a quantitative analysis of the effect of these two factors requires laborious numerical calculations. Interestingly, expression (5) also yields the correct expression for the elastic moduli of a cholesteric liquid crystal ($\lambda_{zzzz} = K_2q_0^2$, and otherwise $\lambda_{iklm} = 0$).

We note in conclusion that the diffuse scattering of light in the blue phases which we have discussed here was apparently observed experimentally in Ref. 11. An explanation of the oscillations in time of the diffuse-scattering intensity in Ref. 11 requires incorporating the viscosity of the blue phases. The experimental results on the temperature dependence of the shear modulus (see Ref. 12 and the other references cited here) agree qualitatively with (5), but a quantitative comparison is difficult since the measurements were carried out with polycrystalline samples.

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