Phase Transitions in Liquid Crystals Under Negative Pressures

V. Manjuladevi, R. Pratibha, and N. V. Madhusudana

Raman Research Institute, C. V. Raman Avenue, Bangalore- 560080, India

We report the first measurements of orientational order parameters and phase transition temperatures in nematic and smectic *A* liquid crystals under negative pressures generated by an isochoric cooling of small droplets embedded in a glass former. Comparison of isobaric and isochoric measurements allows us to estimate the coefficients coupling the order parameter and density of an extended Landau–de Gennes model of the nematic phase.

A liquid under negative pressure is in a metastable state [1]. Several natural phenomena crucially depend on such a state: for example, sap ascent in tall trees [2] and the initial inflationary phase in the expansion of the universe [3]. The latter is analogous to the cavitation phenomena which occurs in a liquid under tension, usually due to thermal fluctuations. Recently [4], quantum fluctuations have been shown to induce cavitation in the superfluid phase of helium-4. Ice (*I*) has a lower density than water, and the phase transition between them has been studied under negative pressures [5]. Liquid crystals (LCs) exhibit several phase transitions involving changes in appropriate symmetries [6,7] and are ideally suited for investigating such transitions between phases in *both* of which the medium is under tension. The uniaxial nematic (*N*) phase exhibited by compounds made of rodlike organic molecules breaks the rotational symmetry of the isotropic phase [7]. The long axes of the molecules are on the average oriented about the director $\hat{n}$, which is a dimensionless unit vector that is apolar in nature. The spontaneously oriented liquid crystal exhibits a variety of electro-optic effects which are exploited in the flat panel display industry. The orientational order parameter S ($= \langle 3\cos^2\theta - 1\rangle/2$, where θ is the angle between $\hat{\zeta}$, the long axis, and $\hat{n}$) is the $S_{nn}^{\zeta\zeta}$ component of a second rank tensor. The smectic *A* (Sm*A*) liquid crystal breaks the translational symmetry along $\hat{n}$, and exhibits a quasi-long-range one-dimensional periodicity [7].

The Landau–de Gennes (LdG) theory describes the nematic-isotropic (*NI*) transition quite well. The free energy density is given by [7]

$$F_{\text{LdG}} = \frac{a}{2}(T - T^*)S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4, \quad (1)$$

where the third order term with the coefficient B is nonzero in view of the second rank tensor nature of S. This term leads to a first order *NI* transition in which S jumps to ~ 0.3 at T_{NI} and T^* is a hypothetical second order transition point which is slightly below T_{NI}. Experiments show that the density also jumps by $\sim 0.2\%$ at T_{NI}, clearly indicating that the order parameter is coupled to density. The LdG model has been extended to incorporate such a

coupling, by assuming that the relevant term is $S^2\delta\rho^2$ in which $\delta\rho$ ($= \rho_N - \rho_I$) is the difference in density between nematic and isotropic phases [8]. This term would not discriminate between positive and negative signs of $\delta\rho$, which is inappropriate. We write the density dependent terms of the free energy as

$$F_\rho = -\frac{M}{2}\delta\rho S^2 + \frac{\Lambda}{2}\delta\rho^2 \quad (2)$$

in which the first term ensures that the density increases with the order parameter, which has a positive sign for rodlike molecules for better packing. The second term is the energy cost of changing the density from its equilibrium value in the isotropic liquid. At a fixed pressure, $\delta\rho$ adjusts itself to minimize F_ρ yielding $\delta\rho = MS^2/2\Lambda$. Substituting this value in the total free energy $F = F_{\text{LdG}} + F_\rho$, the form in Eq. (1) is recovered with a renormalized quartic term $C' = C - M^2/2\Lambda$. Experimentally $T_{NI} - T^*$ is about 1 to 2°, while the molecular mean field theory of Maier and Saupe would give a much larger value [7]. Indeed, it has been shown that inclusion of a density dependent intermolecular interaction can reduce this discrepancy [9]. Measurements of both the order parameter and the density as functions of pressure above 1 bar have been used to compare the relative importance of density and temperature in a couple of cases [10]. Experiments under constant volume (i.e., isochoric) conditions are ideally suited for such an investigation. As the temperature is lowered, such a medium will have a density which is lower than in equilibrium, and hence it will be in a metastable state. The medium experiences a tensile stress, i.e., negative pressure, which increases in magnitude as the temperature is lowered. The medium can go over to the stable state by cavitation [1], i.e., by developing a vapor bubble, which grows to the required size if at nucleation it has a radius beyond a critical value r^*. A vapor embryo of radius r has an energy $E_r = -\frac{4}{3}\pi r^3 P + 4\pi r^2\sigma$ where P is the magnitude of the negative pressure and σ the surface tension. E_r has a maximum with a potential barrier height of $16\pi\sigma^3/3P^2$. The barrier height is lowered at larger negative pressures. Extraneous influences like surface nonuniformities can lower the barrier considerably and lead to heterogeneous nucleation of

bubbles. A technique for creating very large negative pressures (~1 kbar) by isochoric cooling of small water drops embedded in quartz crystals was developed some years ago and used to approach the homogeneous nucleation limit for cavitation [11], which corresponds to a first order transition from the (low density) metastable to the (normal density) stable state of the medium. It would be of obvious interest to carry out such studies on liquid crystals and other soft materials to explore their properties under tensile stress which relatively enhances the effect of attractive interactions. Organic compounds cannot withstand high temperatures used to encapsulate water droplets. Several techniques have been developed during the past couple of decades for embedding relatively small (~ a few μm) spherical LC droplets in polymer matrices [12]. The polymer dispersed liquid crystals (PDLCs) exhibit very interesting electro-optic responses and have been used in commercial display devices which do not require polarizers. The liquid crystal partially dissolves in the polymer matrix. In view of the viscoelasticity of the latter and the small size of N drops, cavitation phenomena have not been noticed in PDLCs.

Our strategy to overcome the above problems is to embed the LC drops in a matrix made of a glass-forming material. The glass transition point T_g has to be moderately high, but not above 200 °C to prevent thermal decomposition of the LC molecules. Another requirement is that the LC compounds should not dissolve in the glass former. After testing a few different materials, we have found that sucrose which is readily available is well suited for the purpose. It has a T_g of about 78 °C [13], and as it is a carbohydrate, it does not dissolve in most of the mesogenic compounds whose molecules have phenyl rings. Spherical drops are not suited for measurements of optical anisotropy of the liquid crystal. In order to be able to apply an electric field to the sample, we prepare it between two indium tin oxide (ITO) coated glass plates. The plates are coated with a thin layer of a polyimide, cured, and subsequently unidirectionally rubbed using a soft tissue. This ensures that the nematic director aligns along the rubbing direction. A small quantity of sucrose mixed with some spacer beads of 10 μm diameter is placed on one of the plates which is heated on an aluminum block to 185 °C, when the sugar melts and starts to flow. The mesogenic compound which is in the form of a powder is then sprinkled on the melt and the second ITO plate is placed on the sample such that the rubbing directions of the two plates are parallel. The top plate is pressed against the bottom one, and the sandwich is rapidly cooled to room temperature. Care is taken to ensure that the sandwiched sample is present only in the center of the cell leaving an air gap all around which is used to measure the thickness d of the cell using an interferometric technique. Observation under a polarizing microscope (Leitz, model Ortholux) shows that the mesogenic material forms drops of different sizes with the lateral dimensions varying

between a few μm to a few 100 μm surrounded by sucrose, which forms a continuous background (Fig. 1). The drop which is in the optically anisotropic nematic phase appears bright, and the surrounding optically isotropic glass looks dark. The somewhat irregular boundary between the two media is caused by the high viscosity of sucrose even in its molten state. The LC medium is aligned with the director along the rubbing direction, indicating that it is in direct contact with the two glass plates. Typically, at room temperature, all the drops have cavities which is a clear signature of complete isolation of the drops from the outside atmosphere. In this Letter, we report results on two mesogenic systems, viz., (i) p-cyanophenyl trans-4-butyl cyclohexane carboxylate (CBCC) with the phase sequence: crystal 54.8 °C N 68.3 °C I, and (ii) a mixture (MCB) of 30 wt% of 4-octyl-4′-cyanobiphenyl (8CB) with 4-octyloxy 4′-cyanobiphenyl (8OCB) with the phase sequence: SmA 57.8 °C N 70 °C I. All the compounds were obtained from Messrs Roche.

The sample is mounted in a hot stage (INSTEC) to maintain and measure its temperature to an accuracy of about 5 mK. Both the SmA and N phases are uniaxial media characterized by two principal refractive indices μ_e and μ_o for a light beam polarized parallel and perpendicular to the director (i.e., the optic axis), respectively. The optical path difference $\Delta l = d\Delta\mu$, where $\Delta\mu$ is the birefringence, is measured for the wavelength $\lambda = 5893$ Å using a quarter wave plate compensator. A large LC drop with a diameter of a few 100 μm and having a good orientation of the sample in the LC phases (see Fig. 1) is chosen for measurements. Δl is measured modulo λ, and to get the absolute value, a large voltage (3.5 V) at 2.1 kHz is applied between the two ITO plates which reorients the director along the field reducing the apparent Δl to zero. As the voltage is gradually reduced, the director rotates back increasing Δl, and its absolute value at $V = 0$ can hence be measured. The measurements are made near the center of the chosen drop to avoid edge effects. The cavity disappears at 74 °C in CBCC and at 76 °C in MCB. The isochoric measurements are made on cooling the sample from the I phase. In CBCC the nematic phase supercools below
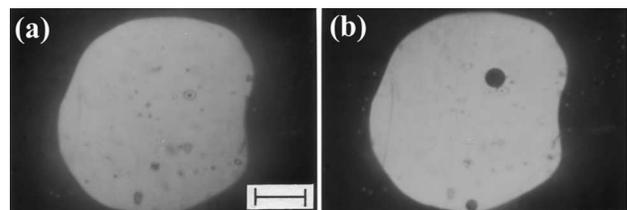
FIG. 1. Photomicrographs of a large drop of CBCC embedded in a glass matrix of sucrose, between crossed polarizers set at 45° to the orientation direction of $\hat{n}$, which is horizontal. The scale bar corresponds to 160 μm. (a) The appearance of the drop before the formation of cavity and (b) after cavitation.

the melting point and cavitation occurs around 35 °C, while in MCB cavitation occurs in the SmA phase around 40 °C, suddenly increasing Δl in both the cases. The measurements of Δl are continued down to room temperature. The measurements are then made in the heating mode, right up to the I phase. $\Delta \mu$ is calculated using the measured values of Δl and d and are presented as functions of temperature in Fig. 2. $\Delta \mu$ values are accurate to $\pm 0.5\%$. At any temperature, $\Delta \mu$ is lower for the drop without a cavity, i.e., in the metastable N and SmA LCs under negative pressure, compared to that for the drop with the cavity, in which the density is higher. Independent Δl measurements were also made on both the systems under constant pressure using samples taken between two ITO coated glass plates, without the sucrose matrix. These values compare well with the data obtained for the drops with cavities. Further the data on CBCC agree with those available in the literature [14]. To a good approximation $S \simeq \Delta \mu / \Delta \mu_o$, where $\Delta \mu_o$ is the value in the fully aligned state. The isochoric order parameter is significantly smaller than the isobaric value, the difference between the two increasing at lower temperatures (Fig. 2). CBCC which has a cyclohexane ring has a smaller value of $\Delta \mu$ compared to that of MCB. In CBCC for the drops without cavity T_{NI} is 0.9 °C lower than in the presence of cavity, while in MCB, T_{NI} and T_{AN} are lower by 0.6 °C and 1.8 °C, respectively. We have conducted high pressure (P) measurements of both the systems [15] and get $(dT_{NI}/dP) = 41°/\text{kbar}$ for CBCC and $(dT_{NI}/dP) = 27°/\text{kbar}$ and $(dT_{AN}/dP) = 14°/\text{kbar}$ for MCB. Using these values, the negative pressures for the drops without cavity are estimated to be 22 bars at T_{NI} for CBCC, and 25 bars at T_{NI} and 129 bars at T_{AN} for MCB. In the latter case, the cavitation occurs at negative pressure ~ 230 bars. The smallness of this value is related with the low surface tension which is ~ 25 dynes/cm for 8CB [16] (compared to ~ 80 dynes/cm for water).

When the sample in which cavitation has occurred is heated, the cavity reduces in size and finally disappears at a temperature T_o in the isotropic phase. In the isochoric case, ρ is fixed and $\delta \rho$ in Eq. (2) is given by $\rho_o - \rho_{is}(T)$ where ρ_o is the density at T_o and $\rho_{is}(T) = \rho_o[1 + \alpha(T_o - T)]$, α being the coefficient of thermal expansion. Using this value of $\delta \rho$, the total free energy $F = F_{\text{LdG}} + F_{\rho}$ is now minimized with respect to S. On the other hand, as mentioned earlier in the isobaric case Eq. (1) with C replaced by the renormalized C' is valid. Using the density data available in the literature [14], $\Delta \mu$ values within about 1 °C of T_{NI} in both isobaric and isochoric samples have been least squares fitted to the appropriate equations and are shown in Fig. 3 for both the systems studied. For the purpose of illustration, we list the parameters (in cgs units) only for CBCC: $T_{NI} = 339.5$ K, $T^* = 338$ K, $a/(\Delta \mu_o)^2 = 3.2 \times 10^7$, $B/(\Delta \mu_o)^3 = 1.08 \times 10^{10}$, $C/(\Delta \mu_o)^4 = 1.49 \times 10^{11}$, $M/(\Delta \mu_o)^2 = 3.8 \times 10^{10}$, $\Lambda = 6.1 \times 10^{10}$, $\alpha = 8.5 \times 10^{-4}$, $\delta \rho_{NI} = (M/2\Lambda)S_{NI}^2 = 7.3 \times 10^{-4}$ g/cm^3. The measured density available in the literature [14] is not accurate near T_{NI}. As $(\bar{\mu}^2 - 1)/(\bar{\mu}^2 + 2)$ is $\propto \rho$, where $\bar{\mu}^2 = (\mu_e^2 + 2\mu_o^2)/3$, μ_e and μ_o [14] were used to calculate ρ. The estimated value of $\delta \rho_{NI}$ is close to the theoretical value given above. In MCB $\Lambda = 4 \times 10^{10}$ cgs units and $\delta \rho_{NI} = 5.1 \times 10^{-4}$ g/cm^3. Note in both cases Λ is of the order of inverse compressibility for typical mesogens [6].

The apolar nature of $\hat{n}$ also has the consequence that an external electric field couples to the medium through its dielectric anisotropy $\Delta \varepsilon$. The orientational part of the energy density F_{diel} is given by $-\varepsilon_0 \Delta \varepsilon (\hat{n} \cdot \vec{E})^2/2$, where ε_o is the vacuum dielectric constant. If the director is strongly anchored at the two plates (which is the usual case), $\hat{n}$ reorients in the center of the cell at a threshold voltage (independent of the thickness d) $V_{th} = \pi[K_{11}/(\varepsilon_0 \Delta \varepsilon)]^{1/2}$ where K_{11} is the splay elastic constant, relevant to the initial distortion of the director [7]. In the highly polar

FIG. 2. Temperature dependence of the birefringence $\Delta \mu$, measured in the LC phases of embedded drops in (a) CBCC and (b) MCB. In (b) the thick arrow indicates SmA-N transition. A jump in $\Delta \mu$ can be noted in both cases after the formation of cavity in the cooling mode.
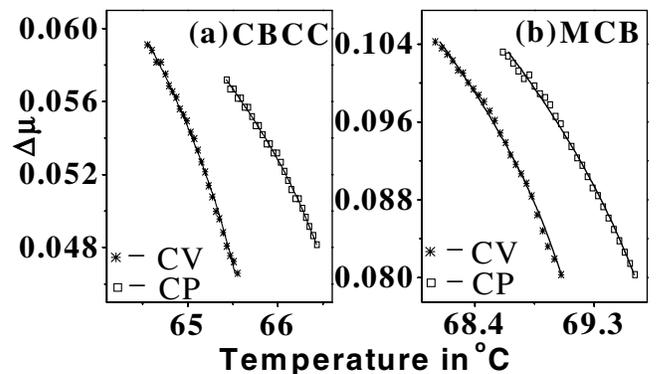
FIG. 3. The birefringence data within about $\sim 1°$ of T_{NI} in both constant pressure and constant volume conditions fitted to the phenomenological model described in the text for (a) CBCC and (b) MCB.
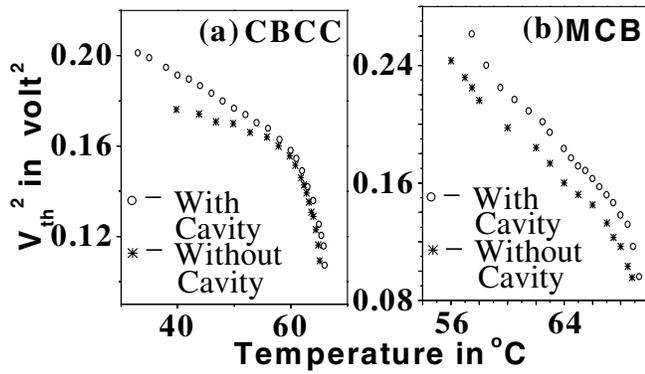
FIG. 4. Temperature variations of the square of the threshold voltage for splay distortion in the nematic phase of (a) CBCC and (b) MCB.

compounds $\Delta\varepsilon$ mainly depends on the dipolar contribution, and is $\propto S/T$ [6] and in the mean field approximation [7], K_{11} is $\propto S^2$. As such, $V_{th}^2/T \propto S$. Indeed, as shown in Fig. 4, for both the systems the value of V_{th}^2 is higher for the drop with the cavity compared to that without a cavity. Again, V_{th}^2 values measured in ordinary cells at atmospheric pressure for both the systems compare well with the values obtained for the drops with cavities. In CBCC which exhibits only the N phase $V_{th}^2/T \propto \Delta\mu$, the proportionality constant being $\simeq 0.0063$ (to within $\pm 1.5\%$) for the drops both with and without cavity. In MCB, smecticlike short range order grows as T_{AN} is approached. As such the mean field theory is no longer valid and $V_{th}^2/T\Delta\mu$ varies from 0.003 to 0.0055 for the drop both with and without cavity as the temperature is lowered.

The measurements of S in isochoric conditions should be compared with predictions of molecular theories which take into account both the hard-rod and attractive intermolecular interactions. For this purpose, it would be better to choose compounds without flexible end chains or the highly polar cyano groups in which dipolar interactions lead to strong short range order effects. Such materials will have $T_{NI} \sim 100$ °C, and it would be very useful if suitable glass-forming materials with a $T_g \sim 200$ °C are identified. Indeed, the technique developed in this work is suitable for other studies. We are setting up experiments to measure the rotational viscosity for the two types of drops.

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