Two transitions between isotropic and nematic phases in confined liquid crystals

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The molecular mean-field theory for the nematic-isotropic (N-Iso) phase transition in the vicinity of the surface is derived. We have shown that the nematic order parameter in liquid crystal near the surface is generally different from that in the bulk. It is never equal to zero if the anisotropic interaction with the surface is present. At the same time, transition from the phase with large nematic order parameter at the surface to the phase with small nematic order parameter at the surface is possible on heating. This surface transition always happens at higher temperatures than N-Iso phase transition related to the bulk. The theoretical prediction was well reproduced experimentally.

Because of the fluidic nature of liquid crystals (LCs), their physical properties are critically influenced by surfaces. Many surface-mediated phenomena have been reported (i.e., surface-induced ordering [1–5], surface memory effect [6,7], anchoring transition [8,9], etc.). We may ask whether the phase transition is also influenced by the surface or not. Actually Boamfa *et al.* [10] reported a prewetting transition in a LC system without distinct thermodynamic information. The boundary layer transition has been theoretically predicted as well [11–14]. Ordering of LC molecules at a hard wall in the framework of the Onsager approximation was considered in Ref. [15]. Biaxial N phase induced by the surface was also predicted theoretically [16] and by computer simulation [17]. Landau–de Gennes formalism for the description of anchoring of nematic LCs and N-Iso transition was derived in Refs. [18,19]. Recently, we found two distinct phase transitions between Iso and N phases in a polymer-dispersed LC system based on two experimental results [i.e., (i) a sharp heat anomaly peak above a broad transition peaks and (ii) two successive pretransitional increases of birefringence on cooling from Iso to N] [20]. Here we developed a generalized Maier-Saupe theory [21–23] considering the interactions between molecules as a mechanism for transmission of the order parameter from the surface to the bulk, and succeeded in description of two temperature-induced Iso-N phase transitions at the surface and in the bulk.

Let us first demonstrate one experimental result: highly-sensitive differential scanning calorimetry (HS-DSC) and birefringence measurements. The sample used was a polymer-dispersed LC, a mixture of 4'-n-hepsylcyanobipheny (7CB) and photocurable polymer NOA81 (Norland Optics) (7CB/NOA81 = 69.9/30.1 wt%). Figure 1 reveals the temperature dependence of (a) retardation and (b) heat anomaly. Temperature dependence of retardation demonstrates a two-step change. Namely, the blue dashed line (coinciding with sharp HS-DSC peak) is located at the temperature where retardation starts to show up with even a small jump (see inset), which is attributed to the Iso-N transition at the surface based on our previous measurement using a LC mixture E7

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(Merck) [20]. The second onset of retardation (green dash dot line) indicates the temperature where the bulk nematic order starts to develop.

We consider a simple geometry; LC molecules are located at a flat polymeric surface. The simple illustrations of local molecules are shown in Fig. 2. Since any direct intermolecular interaction is very short range, the surface influences directly only the nearest molecules, but this influence is transmitted through the bulk because of the interactions of the LC molecules with each other. The bulk free energy of LC per unit area, which is parallel to the surface, can be written as a generalized Maier-Saupe theory for inhomogeneous distribution of the nematic order along the z coordinate

$$
\begin{aligned}
F = {} & \rho k_B T \int d^2 \mathbf{a}_1 \int dz_1 f[(\mathbf{a}_1 \cdot \mathbf{n}), z_1] \ln\{ f[(\mathbf{a}_1 \cdot \mathbf{n}), z_1] \} \\
& + \frac{1}{2} \rho^2 \int d^2 \mathbf{a}_1 \int d^2 \mathbf{a}_2 \int dz_1 \int d^3 \mathbf{r}_{12} f[(\mathbf{a}_1 \cdot \mathbf{n}), z_1] \\
& \times f[(\mathbf{a}_2 \cdot \mathbf{n}), z_2] V_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}),
\end{aligned}
\tag{1}
$$

where ρ is the molecular density, z_i is the distance of molecule i from the surface. In Eq. (1) the orientational distribution function for each molecule $f[(\mathbf{a}_i \cdot \mathbf{n}), z_i]$ is assumed to depend on the distance from the surface, $V_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12})$ is the interaction potential between molecules 1 and 2. The first term in Eq. (1) is the orientational entropy and the second term is the internal energy. Since the distribution function $f[(\mathbf{a}_2 \cdot \mathbf{n}), z_2]$ is assumed to be weakly dependent on the distance between molecules r_{12} with respect to that for the intermolecular potential $V_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12})$, then one can estimate the integral over the intermolecular vector $\mathbf{r}_{12}$ in Eq. (1) by the saddle point method [24]. Expanding the distribution function $f[(\mathbf{a}_2 \cdot \mathbf{n}), z_2]$ in Taylor series with respect to coordinate z at point $\mathbf{r}_1$, one obtains

$$
\begin{aligned}
& \rho \int d^3 \mathbf{r}_{12} f[(\mathbf{a}_2 \cdot \mathbf{n}), z_2] V_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}) \\
& = V_0(\mathbf{a}_1, \mathbf{a}_2) f[(\mathbf{a}_2 \cdot \mathbf{n}), z_1] \\
& \quad + \frac{1}{2} V_2(\mathbf{a}_1, \mathbf{a}_2) \frac{\partial^2}{\partial z^2} f[(\mathbf{a}_2 \cdot \mathbf{n}), z_1] + \cdots,
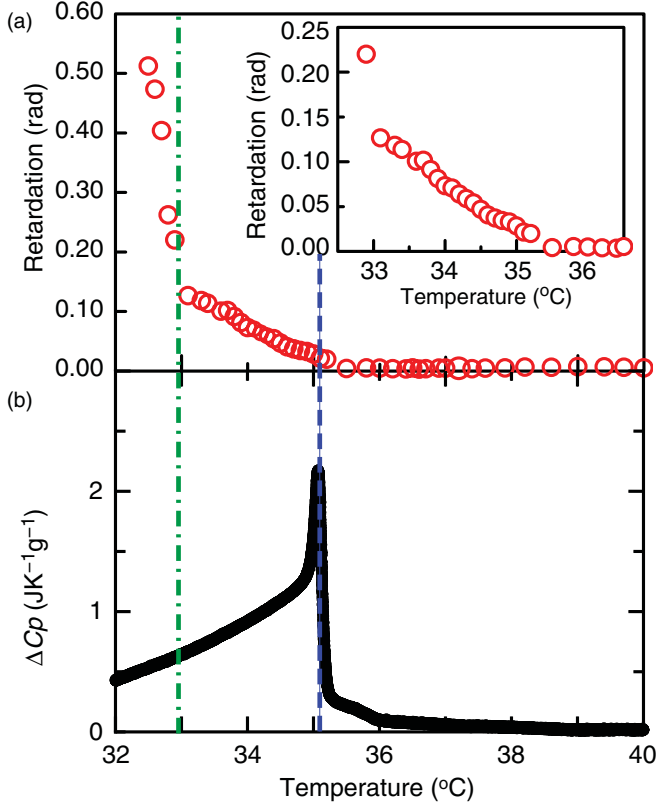\end{aligned}
\tag{2}
$$

FIG. 1. (Color online) Experimental observation of the N-Iso phase transitions in a polymer-dispersed liquid crystal (PDLC) sample of 7CB-NOA81 at the surface and in the bulk: (a) retardation as a function of temperature (the detailed behavior is also shown in an inset); (b) highly-sensitive differential scanning calorimetry data.

where

$$V_i(\mathbf{a}_1, \mathbf{a}_2) \equiv \rho \int d^3 \mathbf{r}_{12} z_{12}^i V_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}). \quad (3)$$

Let us note that in the series in Eq. (2) there are no terms with the odd indices i, because the molecular ordering is nonpolar. Let us approximate values $V_i(\mathbf{a}_1, \mathbf{a}_2)$ by Legendre polynomials

$$-\frac{1}{k_B T} V_i(\mathbf{a}_1, \mathbf{a}_2) = J_i^{(0)} + J_i^{(2)} P_2(\mathbf{a}_1 \cdot \mathbf{a}_2) + \cdots. \quad (4)$$

Minimizing the free energy functional in Eq. (1) with respect to the distribution function $f[(\mathbf{a} \cdot \mathbf{n}), z]$, taking into account the normalizing constraint for the distribution function and approximations in Eqs. (2)–(4), and introducing the local nematic order parameter as

$$S(z) \equiv \int d^2 \mathbf{a} f[(\mathbf{a} \cdot \mathbf{n}), z] P_2(\mathbf{a} \cdot \mathbf{n}), \quad (5)$$

one obtains the following recurrent equations for determination of S(z):

$$S(z) = I_1[S(z)]/I_0[S(z)],$$
$$(6)$$
$$I_k[S(z)] \equiv \int_{-1}^{1} dt\, P_2^k(t) \exp\left\{ \left[J_0^{(2)} S(z) + \frac{1}{2} J_2^{(2)} S''(z) \right] P_2(t) \right\}$$
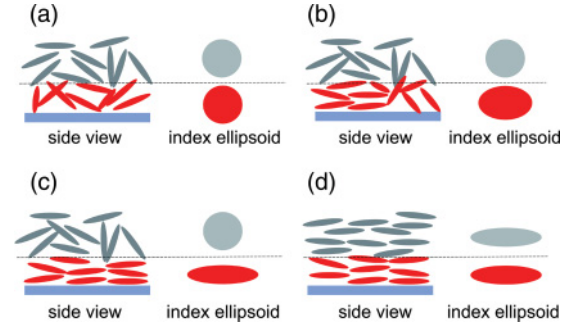

FIG. 2. (Color online) Cartoons showing local molecular orientations in temperature-evolved thermodynamic states. Molecules near surface are highlighted by red thick color: (a) isotropic orientation, (b) pretransitional process toward the surface transition, where N order starts to emerge, (c) just after the surface transition, and (d) developed N order in the bulk as well.

where $t \equiv (\mathbf{a} \cdot \mathbf{n})$ and $P_2^k(t) \equiv (3t^2/2 - 1/2)^k$. The system of differential equations (6) is of the second order with respect to S with surface conditions $S(0) = S_0$ and $S(\infty) = S_\infty$, where S_0 is the nematic order parameter at the polymeric surface, and S_∞ is the nematic order parameter far from the surface.

To find S_0 let us consider very narrow layer $0 < z < z_0$, where direct interactions of LC molecules with the surface are still valuable. Let us also assume that S is almost constant within layer $0 < z < z_0$. The free energy of layer $0 < z < z_0$ per unit area can be written as follows [compare to Eq. (1)]:

$$F_0 = \rho k_B T z_0 \int d^2 \mathbf{a}_1 f_0(\mathbf{a}_1 \cdot \mathbf{n}) \ln[f_0(\mathbf{a}_1 \cdot \mathbf{n})]$$
$$+ \frac{1}{2} \rho^2 z_0 \int d^2 \mathbf{a}_1 \int d^2 \mathbf{a}_2 f_0(\mathbf{a}_1 \cdot \mathbf{n}) f_0(\mathbf{a}_2 \cdot \mathbf{n})$$
$$\times \int d^3 \mathbf{r}_{12} V_{12}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12})$$
$$+ \rho \int d^2 \mathbf{a}_1 f_0(\mathbf{a}_1 \cdot \mathbf{n}) \int_0^{z_0} dz\, V_s(\mathbf{a}_1, z), \quad (7)$$

where the additional third term describes the interaction of molecules with the surface. Similarly to Eq. (4) describing the interactions of the LC molecules with each other, let us
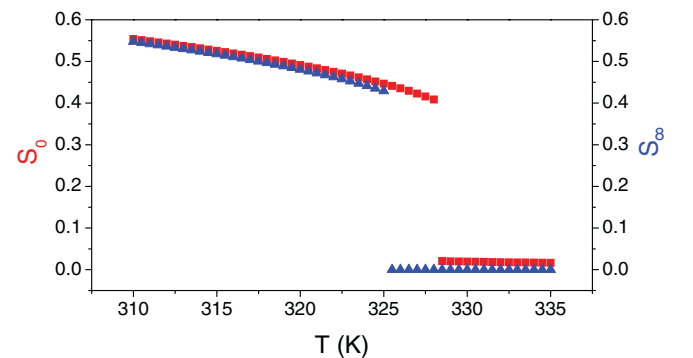

FIG. 3. (Color online) Nematic order parameter in the vicinity of the surface S_0 (red squares) and far from the surface S_∞ (blue triangles). The parameters used are $J_0^{(2)}/k_B = 1476\ K$, $J_s^{(2)}/k_B = 2.95\ K$. Two distinct transitions are related to the surface and to the bulk, as experimentally observed in Fig. 1.

approximate the interactions of LC molecules with the surface $V_s(\mathbf{a}_1, z)$ by Legendre polynomials

$$-\frac{1}{z_0 k_B T} \int_0^{z_0} dz V_s(\mathbf{a}_1, z) = J_s^{(0)} + J_s^{(2)} P_2(\mathbf{a}_1 \cdot \mathbf{k}) + \cdots, \quad (8)$$

where $\mathbf{k}$ is the unit vector perpendicular to the surface. The sign of coefficient $J_s^{(2)}$ is positive (or negative) if the long molecular axes tend to be perpendicular (or parallel) to the surface. Minimizing Eq. (7) with respect to the distribution function $f_0(\mathbf{a} \cdot \mathbf{n})$, and taking into account the normalization of the distribution function and approximations in Eqs. (2)–(4) and (8), one obtains

$$S_0 = I_1^*(S_0)/I_0^*(S_0), \quad (9)$$

$$I_k^*(S_0) \equiv \int_{-1}^1 dt \, P_2^k(t) \exp\left\{\left[J_0^{(2)} S_0 + J_s^{(2)}\right] P_2(t)\right\}.$$

Equation (9) determines the temperature dependence of the order parameter at the surface S_0. The temperature dependence of the order parameter far from the surface S_∞ can be obtained similarly just by solving Eq. (7) within a layer of a thickness z_0 far from the surface after deleting the third term related to the surface (the Maier-Saupe equation for the homogeneous state). Temperature dependencies of S_0 and S_∞ are presented in Fig. 3. One notes that, in contrast to the solution in the infinity, the solution at the surface never corresponds to $S_0 = 0$ if the anisotropic interaction with the surface is present [$J_s^{(2)} \neq 0$]. One also notes from Fig. 3 that the stepwise decrease of nematic order at the surface always happens at higher temperatures than the similar stepwise decrease in the infinity. As we show below, both decreases correspond to separate phase transitions in the whole molecular system. These theoretical predictions are clearly shown in Fig. 1.

Now let us return to the global solution in Eq. (6) determining $S(z)$ distribution at a particular temperature. Taking into account that value $J_2^{(2)} S''(z)$ is small, the exponents in Eq. (6) can be expanded in Taylor series with respect to this value, and one can take into account only the first term in this
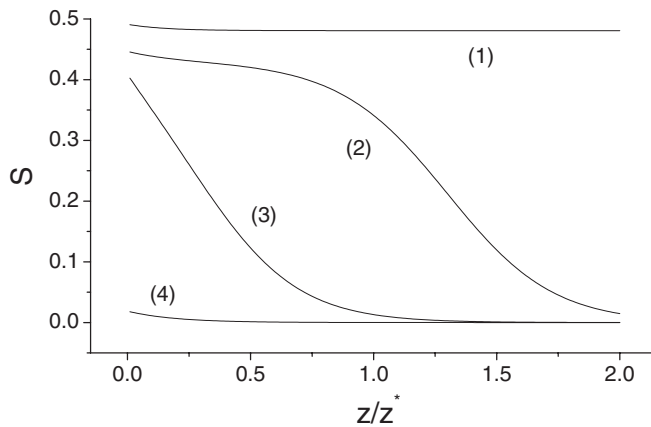
expansion explicitly depending on S''. Then instead of Eq. (6) one can write

$$S'' \approx -\frac{1}{J_2^{(2)}} \frac{S I_0(S) - I_1(S)}{S I_1(S) - I_2(S)}, \quad (10)$$

$$I_k(S) \approx \int_{-1}^1 dt \, P_2^k(t) \exp\left\{J_0^{(2)} S P_2(t)\right\}.$$

The corresponding $S(z/z^*)$ distributions, where z^* is the characteristic dimension of the system, are presented in Fig. 4 at various temperatures. Dependencies $S(z/z^*)$ appear to be independent of z^* if parameter $J_2^{(2)}/z^{*2}$ is fixed. Since the kink points in these curves appear when $S'' = 0$, we find from Eq. (10) that $S = I_1(S)/I_0(S)$ at kink points, which is the conventional Maier-Saupe equation for the homogeneous state. Curves 1 and 3 are the distributions at temperatures with complete loss of stability of Iso and N phases in the bulk, respectively. In these cases the free energy of the homogeneous state should have only one minimum, and the corresponding single kink points at curves 1 and 3 are observed in the infinity. By contrast, in a certain temperature range in between, equation $S = I_1(S)/I_0(S)$ has three solutions at each temperature (i.e., two minima corresponding to Iso and N, and one corresponding to maximum between them). In this condition we obtain curve 2 with large area, where N phase
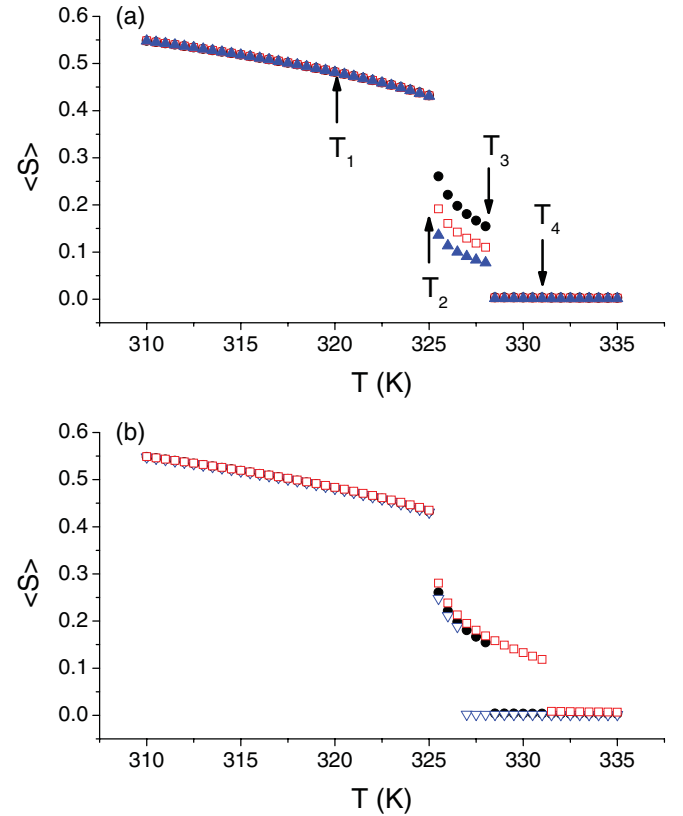

FIG. 5. (Color online) Average nematic order parameter in the bulk of LC at $J_0^{(2)}/k_B = 1476 \, K$. In (a) $J_s^{(2)}/k_B = 2.95 \, K$; $J_2^{(2)}/(k_B z^{*2}) = 6.63 \, K$ (solid circles), 3.32 K (open squares), 1.66 K (solid triangles). In (b) $J_2^{(2)}/(k_B z^{*2}) = 6.63 \, K$; $J_s^{(2)}/k_B = 2.95 \, K$ (solid circles), 1.47 K (open triangles), 5.9 K (open squares). Note the similarity to the experimental retardation data shown in Fig. 1(a).

FIG. 4. Distribution of the nematic order parameter in the bulk of LC. The parameters used are (1) $J_0^{(2)}/k_B = 1476 \, K$, $J_2^{(2)}/(k_B z^{*2}) = 6.63 \, K$, $J_s^{(2)}/k_B = 2.95 \, K$, and $T_1 = 320 \, K$; (2) $T_2 = 325 \, K$; (3) $T_3 = 328 \, K$; and (4) $T_4 = 331 \, K$. Here z^* is the characteristic dimension of the LC system.

(supposed to be metastable in the homogeneous case) becomes stable due to surface effect. Hence curve 2 gives the best conditions for the transmission of S from the surface to the bulk. All curves 1–3 correspond to the temperatures below the phase transition at the surface, while curve 4 corresponds to the temperature above this transition.

Finally, let us estimate the average nematic order parameter in the bulk $\langle S \rangle$. The temperature dependence of $\langle S \rangle$ obtained by integration of the corresponding $S(z)$ dependence is presented in Fig. 5. Solid circles in both Figs. 5(a) and 5(b) correspond to the same set of parameters as in Fig. 4. Temperatures $T_1 - T_4$ correspond to curves 1–4 in Fig. 4, respectively. Totally we have three independent parameters: anisotropy of LC molecules $J_2^{(0)}$ regulating N-Iso transition temperature in the bulk; anisotropy transmission between LC molecules divided by the squared dimension of the system $J_2^{(2)}/z^{*2}$; and anisotropy of orientation of LC molecules at the surface $J_s^{(2)}$. Three curves in Fig. 5(a) correspond to various values of $J_2^{(2)}/z^{*2}$, while three curves in Fig. 5(b) correspond to various values of $J_s^{(2)}$. In particular, from Fig. 5(a) it follows that $\langle S \rangle$

observed between two transitions decreases with the increasing dimension z^*, while the temperature difference between two transitions remains unchanged. On the contrary, from Fig. 5(b) it follows that the temperature difference between two transitions increases with the increasing parameter $J_s^{(2)}$, while $\langle S \rangle$ remains almost unchanged.

Thus, we have shown that confined molecular systems can exhibit the two phase transitions. The lower-temperature one is the N-Iso phase transition related to the bulk. In addition, on further heating, we found a transition from the phase with large S at the surface to the phase with small S at the surface. These two phase transitions result in the two-step change of $\langle S \rangle$ and of the birefringence. This theoretical result coincides with our recent experimental observations [20].

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