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Local self-consistent approach to the phase transition at the nematic liquid-crystal-wall interface

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The nematic-isotropic transition for a semi-infinite sample is analyzed by means of the Maier-Saupe theory. The effect of a delocalized surface field acting on the nematic molecules, and of the incomplete interaction between the nematic molecules, are taken into account in the van der Waals approximation. We show that the existence of a surface transition is governed by the strength of the surface potential. The spatial profile of the order parameter and the degree of extra order near the walls are determined for different temperatures. The surface tension of nematic origin is calculated near the bulk transition temperature. It is estimated to be one order of magnitude smaller than the total surface tension experimentally detected with standard techniques.

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The critical surface behavior of ordered media is a problem of broad interest, which appears in an enormous variety of physical systems [1–4]. We limit ourselves to considering the influence of a surface on the nematic-isotropic phase transitions. In the bulk, these systems undergo first-order phase transition. However, near the substrate, a boundary layer can appear in which the ordering is very different from the bulk one. Theoretically, the existence of this boundary layer in a nematic sample was predicted by Sheng [5], using a Landau-de Gennes theory. In Ref. [5] the nematic order at the surface was assumed perfect and temperature independent. In this framework, it has been shown that there is a critical thickness of the sample below which the transition from the nematic phase to the isotropic phase becomes continuous. Subsequently, experimental works have verified the dependence of the nematic-isotropic phase transition on the thickness of the sample [6,7]. To take into account the influence of the surface treatment on the nematic-isotropic phase transition [8], Sheng extended his model to consider also the surface energy [9]. It was assumed to describe the direct interaction between the liquid crystal with the substrate. According to this more general model, the surface order parameter was found temperature dependent. A detailed study of the nematic wall interface was carried out through a molecular model of the nematic free energy [10].

The very simplest approach to the molecular theory of liquid crystals is based on the Maier-Saupe mean field theory [11]. It has been used to investigate the behavior of a nematic liquid crystal in the presence of an external field [12] and near the wall in the presence of a surface ordering field [13,14]. The basic mechanisms involved in these phenomena were discussed in these works. The analyses were perfomed by assuming that the substrate was treated in such a manner to induce homeotropic orientation to the nematic liquid crystal. In this case, the biaxiality due to the presence of the surface can be neglected. Furthermore, the surface potential describing the interaction between the substrate and the liquid crystal was supposed to be short range in nature and represented in the form $-G\delta(z)S$, where z is the coordinate normal to the surface, S is the scalar order parameter, and G is a constant denoting the strength of the potential.

In this paper, we reanalyze the problem of a semi-infinite sample in the framework of the Maier-Saupe mean field theory by considering a more realistic form for the potential, which takes into account the van der Waals nature of the surface field, and the incomplete interaction between the nematic molecules due to the presence of a surface. This fact leads to significant modifications in the critical surface behavior of a liquid-crystalline system: while it does not change the qualitative aspects of the phase diagram, the quantitative description is more rigorous. In particular, the determination of the temperature dependence of the surface tension near the nematic-isotropic phase transition can be easily done, and the general trends agree with the experimental data [15]. It is shown that, according to the strength of the surface field, the surface tension presents a minimum just before the transition, followed by a strong variation at the transition.

Let us consider a sample of nematic liquid crystal (NLC) bounded on one side by a substrate in such a way that the solid-NLC interface is defined in $z=0$, and the sample is assumed to be uniform in the x and y directions. As in Refs. [12–14], it is supposed that the easy axis of the interface is normal to it, and that the nematic liquid crystal can be considered a uniaxial medium also at the surface. If θ denotes the angle between the long axis of a molecule with the z axis, the van der Waals interaction with the surface can be expressed by

$$V_S(z)=-H(z)P_2(\theta)=-\frac{h}{z^3}P_2(\theta), \tag{1}$$

where $P_2(\theta)$ denotes the Legendre polynomial and h is a constant coupling. The interaction of a nematic molecule with the substrate is minimum for $\theta=0$, i.e., for a homeotropic alignment at the surface, as assumed above. $V_S(z)$ has the functional form similar to the interaction of a nematic liquid crystal with an external field of amplitude $H(z)$ and anisotropy equal to one.

The bulk potential, taking into account the incomplete interaction between the nematic molecules, can be put in the form

$$V_N(\theta,z)=-v\left[1-\left(\frac{r_0}{2z}\right)^3\right]P_2(\theta)S(z), \qquad (2)$$

where $S(z)$ is the z-dependent scalar order parameter and v is the Maier-Saupe molecular parameter [11]. r_0 is a typical molecular dimension that is defined as the lower molecular cut off of the van der Waals interaction. Equations (1) and (2) hold in the r^{-6} van der Waals approximation for the molecular interactions. In this manner, the effective total potential is given by

$$V(\theta,\zeta)=V_S+V_N=-v\left[\left(1-\frac{1}{\zeta^3}\right)S(\zeta)+\frac{\mu}{\zeta^3}\right]P_2(\theta), \qquad (3)$$

where we have introduced the reduced quantities

$$\zeta=2\frac{z}{r_0}, \quad 2\leqslant\zeta<\infty, \qquad (4)$$

and

$$\mu=\frac{8h}{vr_0^3}, \qquad (5)$$

which denotes the strength of the surface field measured in units of the strength of the bulk field. The total macroscopic potential, obtained by statistical average, is then given by

$$V=\langle V(\theta,\zeta)\rangle=-v\left[\left(1-\frac{1}{\zeta^3}\right)S^2(\zeta)+\frac{\mu}{\zeta^3}S(\zeta)\right]. \qquad (6)$$

This kind of ordering potential favors perpendicular alignment at the wall, and we do not consider competing potentials.

Notice that in this approach the z dependence of the macroscopic potential comes from two sources: (1) the van der Waals surface field and (2) the incomplete interaction among the NLC molecules. As it follows from Eq. (6), it is impossible to compensate the incomplete nematic-nematic interaction by means of a surface interaction. In fact, the first contribution depends on S^2, whereas the second one is linear in this quantity. In particular, to $\mu=0$ does not correspond the usual bulk nematic molecular potential. These are not only new ingredients in the theory, but represent the physical nature of the interaction in a better manner.

To explore the thermodynamic effects of this kind of potential, in the framework of the Maier-Saupe model, we determine the temperature dependence of the scalar order parameter S through the local self-consistency relation

$$S(\zeta)=\frac{1}{Z}\int_{-1}^{1}P_2(\cos\theta)e^{-\beta V(\theta,\zeta)}d(\cos\theta), \qquad (7)$$

where $\beta=1/k_BT$, with k_B being the Boltzmann constant and T the absolute temperature. Furthermore, in Eq. (7), Z is the single molecule orientational partition function, defined as

$$Z(\zeta)=\int_{-1}^{1}e^{-\beta V(\theta,\zeta)}d(\cos\theta). \qquad (8)$$

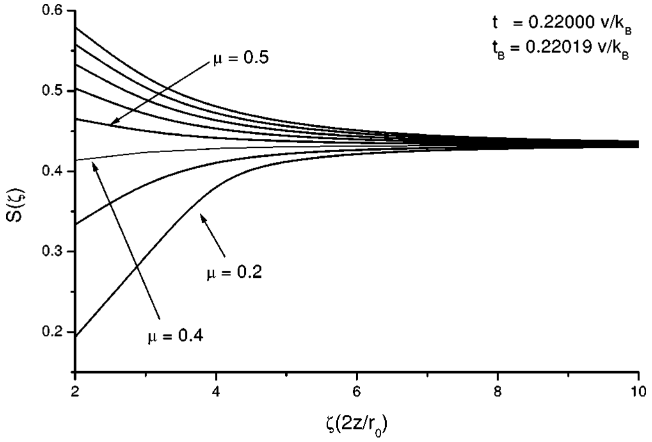

FIG. 1. The spatial dependence of the order parameter for a temperature close to the bulk nematic-isotropic transition.

The equilibrium value of the scalar order parameter is determined by choosing the solution that minimizes the free energy. The free energy for unit area is written as

$$\begin{aligned} f=\frac{F}{A}&=\int_{r_0}^{\infty}f_V(z)dz \\ &=\frac{r_0}{2}\int_2^{\infty}\rho\left[-\frac{1}{\beta}\ln Z(\zeta)+\frac{1}{2}v\left(1-\frac{1}{\zeta^2}\right)S(\zeta)^3\right]d\zeta, \end{aligned} \qquad (9)$$

where ρ is the particle density of the fluid. It will be assumed, in a first approximation, as position and temperature independent. The surface tension connected to the nematic order can be easily obtained through the relation

$$\gamma(T)=\int_{r_0}^{\infty}[f_V(z)-f_b]dz, \qquad (10)$$

where $f_b=f_V(z\rightarrow\infty)$ refers to the bulk value of $f_V(z)$. The total surface tension of an NLC is $\gamma_t(T)=\gamma_i(T)+\gamma(T)$, where $\gamma_i(T)$ is the isotropic part. As in normal liquid it is a decreasing function of T, and does not present critical behavior close to the nematic-isotropic phase transition temperature (T_{NI}). On the contrary, $\gamma(T)$ is connected with the spatial variation of the scalar order parameter $S=S(z)$. This contribution to $\gamma_t(T)$ is expected to exhibit a critical behavior at T_{NI}. To complete the analysis we also introduce an adsorption parameter as is done in Ref. [13], defined as

$$\Gamma(T)=\int_{r_0}^{\infty}[S(z)-S_b]dz, \qquad (11)$$

where S_b is the bulk value of the scalar order parameter. The function Γ is a measure of the extra order near the wall.

The trends of $S(z)$ vs z are exhibited in Fig. 1 for a temperature slightly below the bulk transition temperature for illustrative values of the parameter μ. $S(z)$ changes drasti-

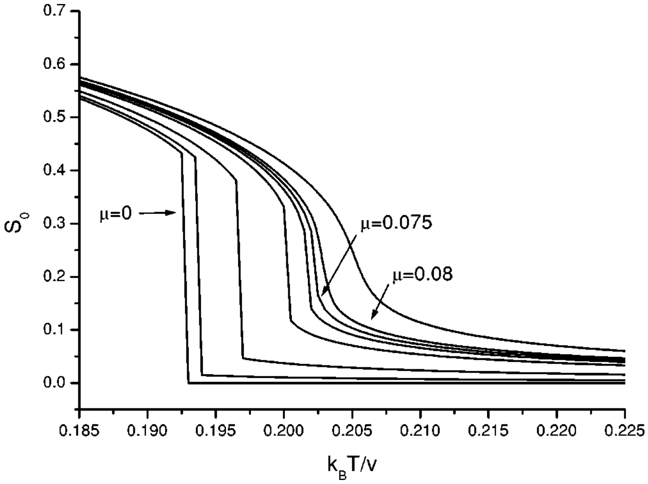

FIG. 2. Surface order parameter $S_0 = S(z=0,T)$ versus reduced temperature $t = k_BT/v$ for different values of the surface field strength μ.

cally in a surface layer whose thickness is of the order of several molecular dimensions, and tends to the bulk value for large z. Notice, however, that the order parameter has a positive slope for $\mu < \mu_0$ and a negative one for $\mu > \mu_0$. The existence of μ_0 is easily understood because $dS(z)/dz = 0$ at least in two circumstances: when $z \rightarrow \infty$, i.e., in the bulk, where the order parameter has a constant value, or in the case in which its z dependence is absent. This is possible when $\mu_0 = S_0(T)$. Therefore, for the case depicted in Fig. 1, the value of μ corresponding to the inversion of the slope of order parameter is $\mu = 0.432\,74$, which coincides with the value of the order parameter in the entire sample because the z dependence is completely lost at this value. Notice, however, that once the value of μ is fixed, there is only one temperature for which the effect of the incomplete interactions is compensated by the effect of the van der Waals field. This value of the surface field strength indicates the regions for which the interface is more or less ordered than the bulk, for a given temperature below the critical temperature.

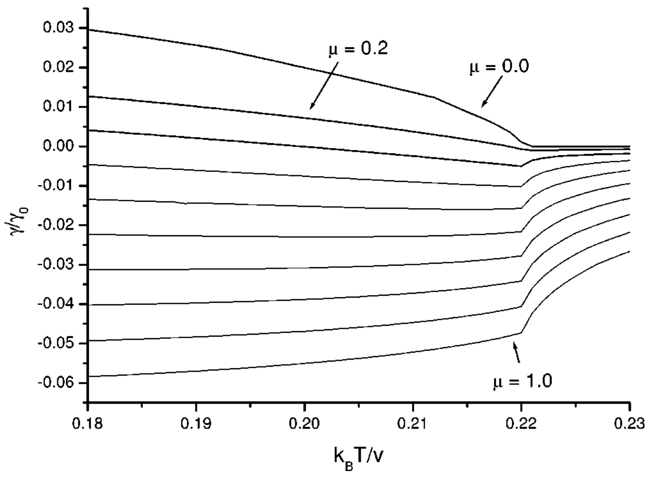

FIG. 3. Surface tension γ/γ_0 versus the reduced temperature $t = k_BT/v$ for different values of the surface field strength μ, where $\gamma_0 = \rho v r_0/2 \approx 65$ erg/cm^2.

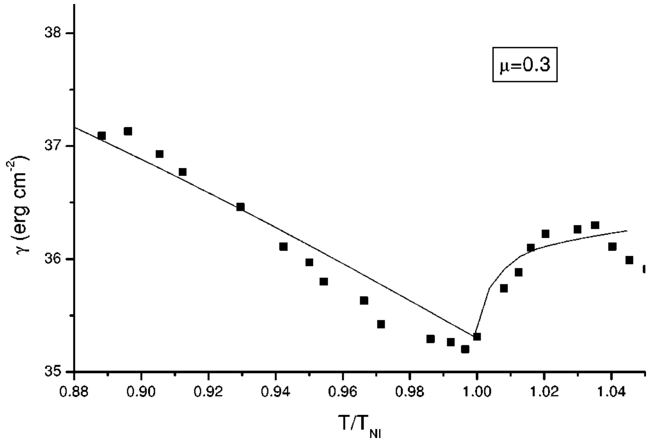

FIG. 4. Surface tension γ versus T/T_{NI}, where T_{NI} is the bulk nematic-isotropic phase transition. Squares are the experimental data of Ref. [15] for PAA; solid lines are the results of the presented model.

The surface order parameter $S_0(T) = S(z=0,T)$ as a function of the reduced temperature $(t = k_BT/v)$ is reported in Fig. 2, for a few values of the surface field μ defined in Eq. (5). An evident feature in the behavior of $S_0(T)$ is that it is discontinuous at the surface transition temperature until $\mu = \mu^* \approx 0.07$. In this region, the surface transition temperature is always lower than the bulk transition temperature. As pointed out before, the effect of the incomplete interaction is to favor the destabilization of the homeotropic pattern near the wall, working in our model as an extra repulsive interaction that tends to destroy the ordering in the vicinity of the interface. For $\mu > \mu^*$, the discontinuous transition disappears and $S_0(T)$ becomes a continuous function of the temperature.

In Fig. 3 the surface tension, in $\gamma_0 = \rho v r_0/2$ units, versus

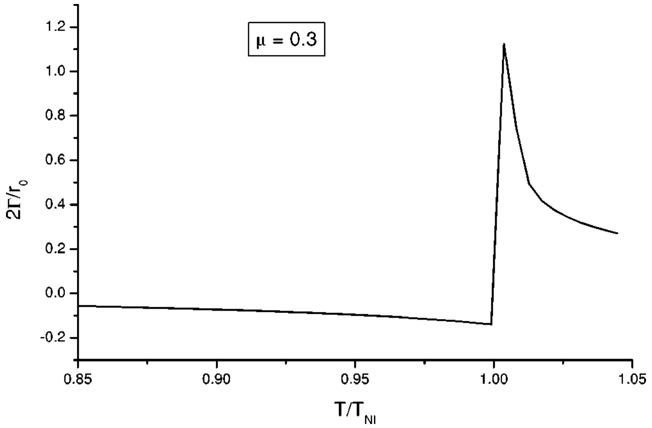

FIG. 5. Adsorption function Γ versus T/T_{NI}. This function is a measure of the extra order near the wall [13]. For $T/T_{NI} > 1$ from our analysis one can also obtain the induced birefringence in the isotropic phase, defined as $\Delta\phi = \int_0^\infty S(z)dz$ [8]. This quantity presents a sharp variation close to T_{NI}. By assuming $r_0 \approx 20$ Å and $\mu \approx 1$ (which corresponds to the experimental situation analyzed in Ref. [8], where the NLC was strongly homeotropically oriented by a surfactant) one obtains $\Delta\phi$ of the order of several angstroms, as experimentally detected.

the reduced temperature for different values of μ is reported. The case of $\mu=0$ corresponds to nematic liquid crystals in contact with the vacuum. This case is not important from the experimental point of view, for obvious reasons. By assuming $\rho\approx 2.5\times 10^{21}$ cm^{-3} [16], $v=k_B T_{NI}/0.220\,19\approx 2.6\times 10^{-13}$ erg [11], and $r_0\approx 20$ Å, we obtain $\gamma_0\approx 65$ erg/cm^2, for PAA. In this case, γ is estimated one order of magnitude smaller than the surface tension detectable by experimental techniques [16].

In Fig. 4, we show the surface tension $\gamma(T)$ predicted by our model and compare it with the experimental data concerning the PAA (*p*-azoxyanisole) liquid crystal in contact with its vapor, as reported in Ref. [15]. For the fit we have assumed that close to T_{NI} ($t=0.22019v/k_B$), the isotropic part of the surface tension [$\gamma_i(T)$] is practically temperature independent, which represents a rough approximation. As it is evident in this framework, the agreement is rather good for $T/T_{NI}<1.04$. For large temperatures, the disagreement between our theory and the experimental data is probably connected to the hypotheses of a constant density of the liquid crystal, and of a γ_i temperature independence that do not work well in this temperature range. It is possible to compare our theory with the data of $\gamma(T)$ for different liquid crystals as reported in Ref. [16], showing a different behavior in the low-temperature region. As shown in Fig. 3, it is connected to the different values of μ. Note, in particular, that for $\mu>0.3,\gamma(T)$ presents a minimum in the nematic phase and it starts to increase just close to T_{NI}. We underline that, as pointed out in p. 84 of Ref. [16], our model represents one of the first successful attempts to interpret the experimental data of $\gamma(T)$, obtained long ago.

Finally, in Fig. 5 we present the trend of the adsorption function $\Gamma(T)$ versus the temperature $\mu=0.3$. Γ presents a pronounced variation in the vicinity of the transition point, as experimentally observed in Ref. [8].

In conclusion, we have developed a Maier-Saupe model for the surface phase transition in nematic liquid crystals. The new ingredients of the model are: (i) the delocalized surface interaction; (ii) the incomplete nematic-nematic interaction. By means of the presented model, we have demonstrated the existence of a surface phase transition and we have been able to interpret, in a molecular statistical approach, the temperature dependence of the surface tension in nematic liquid crystals.

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