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Abstract. We outline the elements of a mean-field density functional theory of inhomogeneous liquid crystals which is able to account for surface-enhanced smectic ordering (SESO) at a free surface. The theory generates SESO without requiring an external anchoring potential, and depending only on the properties (i.e., strengths and ranges) of the anisotropic intermolecular forces. Application of the theory to explaining recent experimental findings of layer-thinning transitions in freely suspended smectic-A films is briefly summarized.

1. Introduction

Smectic phases are highly anisotropic phases with layered structures. In particular, the symmetry of the smectic A (SmA) phase is characterized by a headless vector n, called the director, which is parallel to the mean molecular orientation and perpendicular to the layers. Interfaces between SmA and isotropic (I) phases are also affected by this anisotropy, showing a strong tendency to orient the interface perpendicular to the director. This effect, together with the layered nature of smectic phases, allows for the existence of freely suspended smectic films (FSSF), whose thicknesses can be varied mechanically from two up to an arbitrarily large number of layers. These films have been extensively studied over the past twenty years, mainly with respect to two-dimensional phase transitions within the films [1]. A feature commonly observed in such films is surface-enhanced smectic ordering (SESO), whereby, for example, the external layers of a film are more strongly ordered than the internal ones. Due to SESO, transitions to a more structured type of smectic phase may take place upon cooling, via a stepwise series of layer transitions starting at the surface layers [1]. A related example of SESO in liquid-crystal compounds is the observed formation of SmA layers at the free surface of an isotropic liquid phase at temperatures well above the bulk SmA–isotropic transition temperature [2].

The transitions usually reported in FSSF do not affect the number of layers in the film, but only the nature of ordering within some (or all) of the layers. Recently, however, unusual melting phenomena in FSSF have been observed. Termed *layer-thinning transitions*, these were first observed by Stoebe *et al* [3] as the stepwise thinning of a FSSF when its temperature was raised above the bulk SmA–I transition temperature T_{AI}. It is important to note that, as speculated previously [3], the existence of SESO is essential to account for these transitions. In the absence of SESO, the first smectic layers to become unstable would

be those at the surfaces. Analogous to the surface melting of most conventional crystals, this process would begin at temperatures *below* the bulk smectic spinodal temperature, $T_{AI}^{(S)}$, and, upon heating, would proceed inward from the surfaces until the whole film becomes destabilized on approaching $T_{AI}^{(S)}$. In contrast, SESO stabilizes the outer layers of the film relative to those in the bulk-like interior, and the successive thinning transitions can be interpreted as SmA–I transitions of the interior layers located at distances beyond some temperature-dependent penetration length from either of the film surfaces. These transitions appear to be fairly rare, having only been observed in two compounds out of more than fifteen examined [3, 4]. Recently, layer-thinning transitions have also been reported for compounds in which the bulk SmA phase transforms to a nematic (rather than isotropic) liquid [5]. The latter work suggested that thinning transitions in these cases might be *universal* phenomena, although this is contrary to the reports of reference [4].

    The theoretical study of these phenomena is difficult. Until now, all theoretical models have failed to account for SESO behaviour at free surfaces, as discussed in more detail below. In this paper we describe some modifications of an earlier theory of ours which now enables it to generate SESO. With this theory, we address the nature of layer-thinning transitions and give a possible explanation of these phenomena.

2. Theory

We use a density-functional theory based on an approximation to the grand potential Ω of an inhomogeneous molecular fluid. Details are given in [6]. The theory has two parts: (i) a weighted density functional approximation for the contribution of molecular hard-core interactions, where the cores are modelled by parallel spheroids of elongation ratio $\sigma_\parallel = 1.8\sigma$ (where σ is the mean hard-core diameter), and (ii) a mean-field approximation to the contribution of the long-range anisotropic pair potential $\tilde{V}_A(12)$:

$$\tilde{V}_A(12) = \epsilon_1 V_1(r_{12}) + \epsilon_2 V_2(r_{12}) P_2(\theta_{12}) + \epsilon_3 V_3(r_{12}) \left[P_2(\theta_1') + P_2(\theta_2') \right]. \tag{1}$$

Here P_2 denotes the second Legendre polynomial, $r_{12} \equiv |\boldsymbol{r}_{12}|$ is the intermolecular separation, θ_{12} is the angle between the symmetry axes of molecules 1 and 2 and θ_i' ($i = 1, 2$) is the angle between the molecule i and the intermolecular vector $\boldsymbol{r}_{12}$. In previous work, the functions $V_n(r_{12})$ were taken to be truncated Lennard-Jones potentials. The free parameters of the model are then the coupling constants ϵ_n, which determine the topology of the bulk phase diagram.

    In our previous work, the theory has been used to study SmA wetting and layering phenomena at liquid–vapour [6] and liquid–solid [7] interfaces, as well as to investigate the statistical mechanical conditions required for *metastability* of FSSF [8]. However, in common with several other theoretical studies of smectic-A interfaces [9, 10, 11], a degree of SESO sufficient to induce SmA wetting and layering transitions could only be achieved by applying a suitable *external* anchoring potential [7]. Thus, the theory could not generate these ordering effects at a true liquid–vapour interface [6] nor could it account for layer-thinning transitions in FSSF [8], as these systems are *not* in the presence of an anisotropic external field.

    Inspection of the attractive potential of equation (1) shows that the term responsible for surface-induced order is the third one, proportional to $\epsilon_3 V_3$. In mean-field theory, this term yields a non-zero contribution to Ω only if there are inhomogeneities in the number density $\rho(z)$ or orientational order parameter $\eta(z) \equiv \langle P_2(\cos\theta) \rangle / \rho(z)$ within the range of the term [12]. However, this term also favours bulk smectic order [6], which leads to difficulties in generating SESO. Generally we have found that increasing ϵ_3 increases the
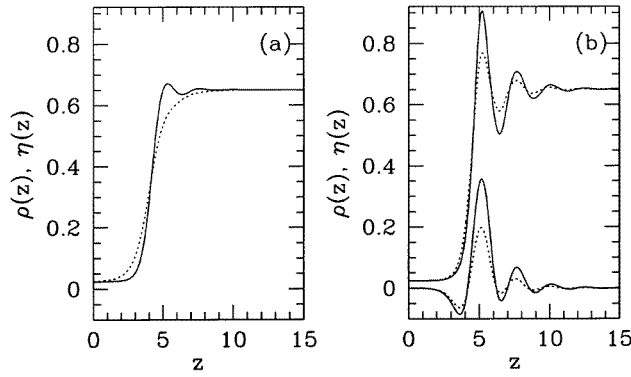
Figure 1. (a) The effect of varying λ_1 on the liquid–vapour interfacial structure. The solid line gives the density profile corresponding to $\lambda_1 = 5$ while the dotted line is for $\lambda_1 = 2$. The temperature has been rescaled to maintain the same bulk densities in both cases. Both ϵ_2 and ϵ_3 are zero. Since the potential is isotropic in this case, no orientational order parameter curves are shown. (b) The effect of varying λ_3 on the liquid–vapour interfacial structure at the vapour–isotropic–SmA triple point. $\lambda_1 = 5, \lambda_2 = 3, \epsilon_2/\epsilon_1 = 0.162$, and $k_B T = 0.049\,92$. The solid curves are for $\lambda_3 = 3.5$ while the dotted curves are for $\lambda_3 = 5$. ϵ_3 has been rescaled to maintain a constant triple point temperature. The two upper curves are the density profiles and the lower two are the order parameter profiles.

degree of surface-induced order, but we systematically reach a bulk smectic phase before encountering 'layering' at a liquid–vapour interface or SESO in a FSSF. In order to produce SESO, it is necessary to introduce additional features with more surface-specific ordering effects. With this purpose in mind, we have allowed each potential term V_1 to V_3 to have a different spatial range. For concreteness, we have modelled the functions $V_n(r_{12})$ by Yukawa potentials (although the precise functional form of these potentials is not expected to be crucial). Explicitly

$$V_n(r) = \begin{cases} 0 & r < 1 \\ \dfrac{-1}{r} e^{-\lambda_n(r-1)} & r > 1 \end{cases} \tag{2}$$

where distance r is expressed in units of the mean hard-core diameter σ.

The ability to produce SESO at a free surface in this model crucially depends on choosing *different* values for the inverse-range parameters λ_1–λ_3. This follows by considering the respective roles played by the interaction terms in equation (1). The function $\epsilon_1 V_1(r)$ describes isotropic attractive interactions which are responsible for inducing liquid–vapour phase separation and hence for the existence of a liquid–vapour interface. At such an interface (without other interaction terms), λ_1 plays the role of the inverse penetration length. Figure 1(a) shows the effect of increasing λ_1 on the interfacial density profile $\rho(z)$ (with an appropriate rescaling of temperature in order to maintain constant bulk densities). One sees that the interface becomes more abrupt and, as a result, oscillations in $\rho(z)$ are induced by hard-core effects.

The term $\epsilon_2 V_2(r) P_2(\theta_{12})$ is analogous to a Maier–Saupe interaction and therefore induces bulk nematic orientational ordering. Hence λ_2 is related to the inverse of the penetration length of the orientational order parameter profile $\eta(z)$. The third term, proportional to $\epsilon_3 V_3(r)$, describes coupling between rotational and translational degrees of freedom. For sufficiently large $|\epsilon_3|$, the third term is responsible for inducing nematic wetting at a vapour

(V)–isotropic liquid (I) interface [12] and, in conjunction with spatially anisotropic hard-core interactions [6], for stabilizing the bulk SmA phase. It can be shown that the direct contribution of this term to Ω is related to the density gradient $d\rho(z)/dz$ [12]. Hence, it is expected that SESO should be favoured by increasing λ_1 and λ_2 relative to λ_3. Figure 1(b) compares the profiles at the V–I interface for fixed values of λ_1 and λ_2 and two different values of λ_3, showing that oscillations in the profiles are increased on *reducing* λ_3.
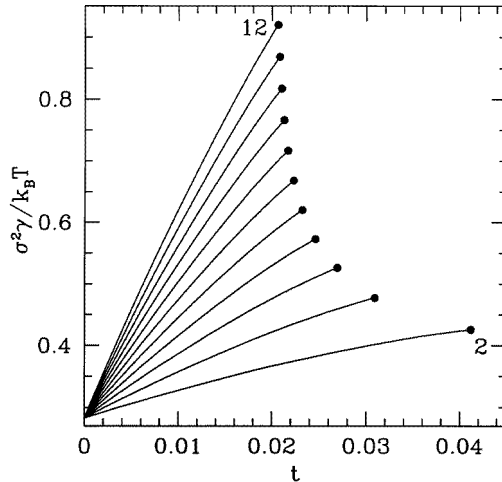
Figure 2. Reduced film tension versus temperature for the following set of parameters: $\lambda_1 = 5, \lambda_2 = 3, \lambda_3 = \lambda_4 = 3.5, \epsilon_2/\epsilon_1 = 0.225, \epsilon_3/\epsilon_1 = -0.110, \epsilon_4/\epsilon_1 = -0.8$. The number of smectic layers varies from 12 to 2 as indicated.

However, the latter recipe leads to an additional problem. The V_3-term induces a repulsive interaction between parallel molecules in the 'head–tail' configuration. Thus, if the range of $V_3(r)$ is much larger than that of the other two terms, the interaction between smectic layers becomes repulsive at large distances. Therefore, the stable smectic-A phase will have a very large period and, as a result, a very low mean density (lower than the nematic and even the isotropic liquid densities). Clearly this would not correspond to a real smectic phase (more properly it should be called a 'swollen lamellar' phase). In order to obtain SESO and at the same time physically realistic phase diagrams, we have found it necessary to introduce an additional term in the attractive potential, so that the latter becomes

$$V_A(12) = \tilde{V}_A(12) + \epsilon_4 V_4(r_{12})\Gamma_4(\theta_1', \theta_2', \theta_{12}) \tag{3}$$

where

$$\Gamma_4(\theta_1', \theta_2', \theta_{12}) = \frac{1}{2}(9\cos\theta_1'\cos\theta_2'\cos\theta_{12} - 3\cos^2\theta_1' - 3\cos^2\theta_2' - 3\cos^2\theta_{12} + 2).$$

This fourth term corresponds to the (222) component in a standard spherical harmonic expansion [13]. It plays a somewhat similar role to the third term, although it equally favours 'side-by-side' and 'T' configurations and, thus, is less effective in stabilizing bulk smectic order.

3. Results for layer thinning

With the new ingredients we are now able to study SmA wetting at a liquid–vapour interface and layer-thinning transitions in FSSF. A detailed discussion is given elsewhere [14]. We have considered different sets of potential parameters which produce SESO in the vicinity of T_{AI}. Typical results for the film tension of a FSSF as a function of temperature and number of layers is given in figure 2. Each curve for a given number of layers n terminates at a *spinodal* temperature (denoted T_n), the maximum temperature for which that film exists as a local minimum of the grand potential Ω. This figure suggests that layer-thinning transitions are possible due to the loss of metastability when films are heated beyond their spinodal temperatures. When an n-layer film becomes unstable, the $(n-1)$-layer film is still metastable. This appears to be a generic behaviour of films exhibiting SESO, and thus it is now necessary to understand why 'thinning' is not observed more often. We have found that when the interior film layers melt into isotropic liquid (the most stable bulk phase), the whole film tends to melt and results in its complete rupture. Instead, when the film interior tends to melt into a nematic state, full melting is prevented and 'thinning' is more probable [14].

We doubt that this is a complete story. According to the above results, true thinning transitions are restricted to parameter ranges which produce a nearby 'quadruple' point in the bulk phase diagram, i.e., involving proximity of the isotropic, nematic, SmA phases along the liquid–vapour phase boundary. Whether this proximity characterizes the systems in which layer-thinning transitions have been observed experimentally is not known. A closer look at dynamical influences on film evolution during layer thinning should also be considered.

Acknowledgments

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