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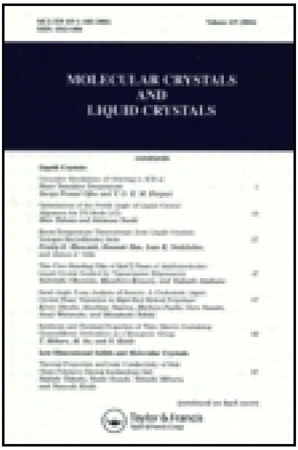

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Thin Nematic Films between Curved Subtrates

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Thin Nematic Films between Curved Subtrates

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The impact of macroscopically curved surfaces on the microscopic structure of confined molecularly thin liquid crystalline films is investigated in grand canonical ensemble Monte Carlo simulations (GCEMC), in which the thermodynamic state is determined by the temperature T and the chemical potential μ. This corresponds to experiments employing the surface forces apparatus (SFA), in which a fluid is confined between two crossed cylinders of macroscopic radius R. The thermodynamic state of the film is chosen such that a corresponding bulk liquid crystal is nematic. The film's microscopic structure is correlated with the normal stress $T_{zz}(s_z)$. The normal stress is used to calculate the solvation force per cylinder radius $F(h)/R$ applied by the film on the crossed cylinders of the SFA setup.

Keywords: liquid crystals; thin films; surface forces apparatus; statistical physics; Gay-Berne potential

INTRODUCTION

The properties of a liquid-crystal film confined by solid substrates to spaces of molecular dimensions are in general significantly different from those of a bulk liquid crystal. The rheological behavior of such films has been studied experimentally with the help of the surface forces apparatus (SFA) [1,2]. In the SFA a thin film is confined between the surfaces of two cylinders arranged such that their axes are at right angles[3]. In an alternative setup the fluid is confined between the surface of a macroscopic sphere and a planar substrate [4]. Crossed-cylinder and sphere-plane configurations can

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be mapped onto each other[5]. The surface of each macroscopic object is covered by a thin mica sheet with a silver backing, which permits measurement of the separation h between the surfaces by optical interferometry[3]. The radii are macroscopic so that the surfaces may be taken as parallel on a *molecular* length scale around the point of minimum distance. In addition, they are *locally* planar, since mica can be prepared with atomic smoothness. The setup is immersed in a bulk reservoir of the same fluid of which the film consists. Thus, at thermodynamic equilibrium T and μ are equal in both subsystems (i.e., film and bulk reservoir). By applying an external force in the direction normal to both substrate surfaces, the thickness of the film h can be altered. Plotting the normal force per radius R, F/R, as a function of h yields a damped oscillatory curve in many cases[2].

The normal force $F(h)/R$ can be related to the normal stress $T_{zz}(s_z)$ that a liquid-crystal film of thickness s_z applies to confining plane-parallel walls[5]. In this work molecularly thin films are investigated in grand canonical ensemble Monte Carlo (GCEMC) simulations at a temperature T and a chemical potential μ for which a corresponding bulk liquid crystal would be nematic. The behavior of the normal stress curve $T_{zz}(s_z)$ is related to the microscopic structure of the film. By generating pseudo-experimental $F(h)/R$ curves from $T_{zz}(s_z)$ one finds that the dependence of T_{zz} on s_z is linked in a nontrivial way to that of $F(h)/R$.

THEORETICAL DESCRIPTION

In the following the sphere-plane geometry is considered (see Fig. 1). Since the radius of the sphere is macroscopic, the sphere-plane arrangement can *locally* be viewed as that of two plane-parallel solid substrate surfaces.

Films between planar walls

In the grand canonical ensemble, infinitesimal, reversible transformations of thermodynamic states are governed by the grand potential Ω. For a film confined between planar walls the exact differential of Ω is given by[6]

$$d\Omega = -SdT - Nd\mu + \gamma' dA + T_{zz}Ads_z \quad , \qquad (1)$$

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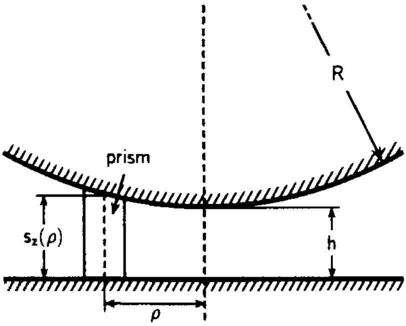

FIGURE 1 Side view of film confined between a sphere of macroscopic radius R and a planar substrate surface.

where S denotes entropy, N is the number of film molecules, γ' is a film-wall interfacial tension, A is the area of film-wall contact, and T_{zz} is the average stress applied normally to A. By convention, $T_{zz} < 0$ if the z component of the force on the substrate points outward. From Eq. (1) one obtains for a film composed of linear molecules[7]

$$\begin{aligned} AT_{zz} &= \left(\frac{\partial\Omega}{\partial s_z}\right)_{T,\mu,A} = \left(\frac{\partial(-kT\ln\Xi)}{\partial s_z}\right)_{T,\mu,A} \\ &= -\frac{1}{\beta A\Xi}\sum_{N=0}^{\infty}\frac{1}{N!\Lambda^{5N}}\left(\frac{I}{m}\right)^{N}\exp\left(\beta\mu N\right)\left(\frac{\partial Z}{\partial s_z}\right)_{T,\mu,A} \\ &= \left\langle F_z^{[2]}\right\rangle = -\left\langle F_z^{[1]}\right\rangle, \end{aligned} \tag{2}$$

where $F_z^{[k]}$ is the z component of the total force exerted by (a particular configuration of) the film on the upper ($k = 1$) and lower ($k = 2$) planar substrate and angular brackets signify the grand canonical ensemble average. The last equation in (2) is a consequence of the principle of mechanical stability. If the separation between the substrates becomes sufficiently large, one has $\lim_{s_z \to \infty} T_{zz}(s_z) = -P_{\text{bulk}}$.

Films between curved surfaces

In SFA experiments the confining surfaces are only locally parallel. Thus, T_{zz} becomes a local quantity which varies with the vertical distance $s_z =$

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$s_z(x,y)$ between the substrate surfaces (see Fig. 1). Since the setup is immersed in bulk fluid at pressure P_{bulk}, the total force exerted on the sphere by the film in the z direction can be expressed[8]

$$\begin{aligned} F(h) &= -\int dx \int dy \left[T_{zz}\left(s_z(x,y)\right) + P_{\text{bulk}}.\right] \\ &= 2\pi \int\limits_{h}^{h+R} ds_z \left(R - s_z - h\right) f\left(s_z\right) \quad . \end{aligned} \tag{3}$$

where $f(s_z) := -T_{zz}(s_z) - P_{\text{bulk}}$ is the excess normal pressure and the local distance $s_z = h + R - \sqrt{R^2 - x^2 - y^2}$ (see Fig. 1). Since $f(s_z)$ differs significantly from zero only for $s_z \ll R$, the upper integration limit in Eq. (3) may be taken to infinity to give

$$\frac{F(h)}{2\pi R} = \int_h^{\infty} ds_z f\left(s_z\right) \quad . \tag{4}$$

RESULTS

In GCEMC simulations liquid-crystal films between two plane parallel substrates are investigated for different wall separations s_z. The film consists of ellipsoidal molecules which interact with each other via the modified Gay-Berne potential introduced in Ref. [9]. The simulations are performed for a thermodynamic state for which a corresponding bulk liquid crystal is nematic. The interaction between film molecules and wall atoms is chosen such that a homeotropic alignment of molecules is favored[9].

Plots in Fig. 2 show that the excess pressure is a damped oscillatory function of wall separation. Over the range $4.0 \leq s_z \leq 20.0$, $f(s_z)$ exhibits five maxima separated by a distance $\Delta s_z \simeq 3.2$, which is slightly smaller than the large diameter of a film molecule (≈ 3.5). Therefore, it is plausible to associate oscillations in $f(s_z)$ with the formation of individual strata parallel with the walls. However, $f(s_z)$ also exhibits shoulders at characteristic values of s_z separated by the same distance $\Delta s_z \approx 3.2$ as the maxima. Portions of $f(s_z)$ between neighboring minima (i.e., $s_z < 6.80$, $6.80 \leq s_z \leq 10.00$, $10.00 \leq s_z \leq 13.20$, and $13.20 \leq s_z \leq 16.40$) are

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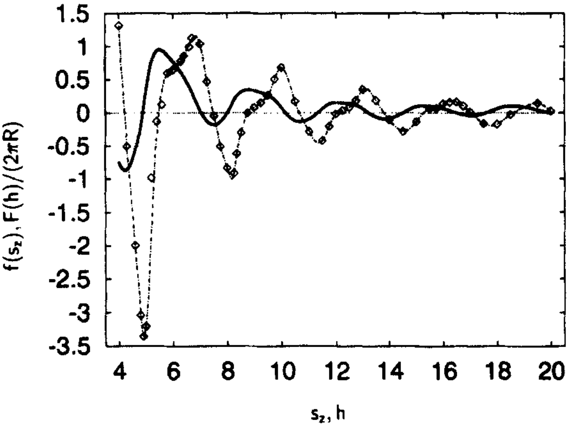

FIGURE 2 The excess pressure $f(s_z)$ (◇, dashed line) and the solvation force per radius $F(h)/R$ (full line) as functions of s_z and h, respectively, for an "nematic" film between homeotropically orienting substrates.

remarkably similar. In order to correlate the microscopic structure of the confined film with features of $f(s_z)$, it is convenient to label these portions as "decrease", "increase", and "shoulder" zones[9].

"Snapshots" in Fig. 3 illustrate the change of spatial and orientational order with increasing wall separation. For simplicity we shall restrict the discussion here to the first decrease ($s_z < 4.9$), increase ($4.9 \leq s_z \leq 5.8$), and shoulder ($5.8 \leq s_z \leq 6.8$) zones and the second decrease zone ($6.8 \leq s_z \leq 8.2$). A more detailed discussion is given in Ref. [9].

In the first decrease zone the film consists of a homeotropic monolayer (see Fig. 3a). In the adjacent increase zone substrate separations are too large to accommodate a homeotropic monolayer conveniently, but too small for a fully developed homeotropic bilayer film (see Fig. 3b). Therefore, molecules contact either wall with a more diffuse, but still preferentially homeotropic, orientation. This, however, leaves limited space which can accommodate a few additional molecules that lie parallel with the walls

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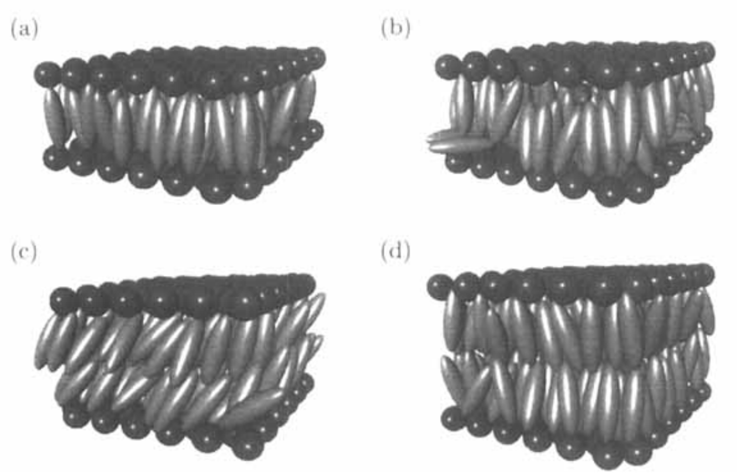

FIGURE 3 "Snapshots" of configurations of "nematic" Gay-Berne films with walls at various separations. (a) $s_z = 4.6$; (b) $s_z = 5.4$; (c) $s_z = 6.3$; (d) $s_z = 7.5$. (See Color Plate XVIII at the back of this issue)

(see Fig. 3b). As the wall separation increases beyond $s_z \simeq 5.8$ (first shoulder zone), the structure of the film changes dramatically (see Fig. 3c). In this range of wall separations the film comprises two well-defined strata in which molecules appear to be tilted. If s_z increases further in the shoulder zone, molecules in the bilayer film gradually change their orientation from tilted to homeotropic and a smectic, homeotropically anchored bilayer film eventually forms (see Fig. 3d). In a similar fashion variations in the film's microscopic structure can be correlated with variations of T_{zz} in decrease, increase, and shoulder zones for higher values of s_z [9].

The corresponding pseudo-experimental solvation-force $F(h)/R$ can be obtained by numerically solving Eq. (4) [i.e., by numerically integrating $f(s_z)$]. $F(h)/R$ is not as regular as a corresponding curve for a "simple" fluid (see Ref. [8]) and is not simply $f(s_z)$ shifted. Furthermore, $F(h)/R$ is free of any shoulders. Height and width of its maxima in Fig. 2 exceed those of its minima considerably. Thus, $F(h)/R$ oscillates around a repulsive background force. This observation seems to agree with exper-

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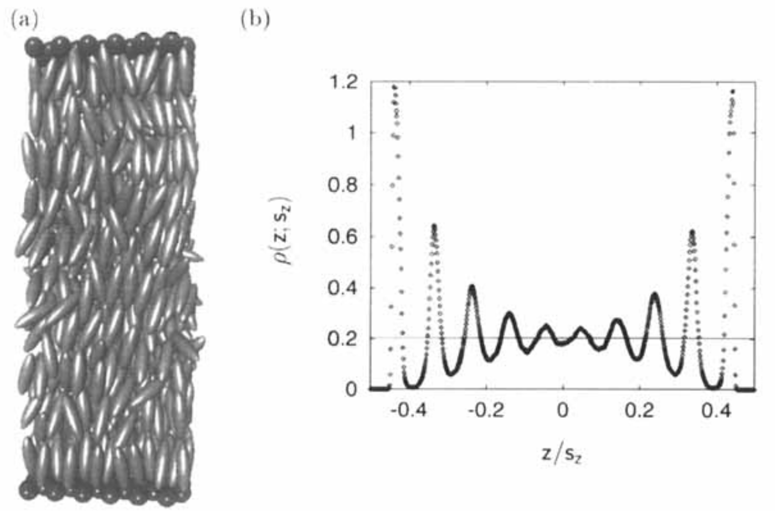

FIGURE 4 Film with wall separation $s_z = 32.0$. (a): "Snapshot" of a configuration. (b): The local density $\rho(z; s_z)$ as a function of the distance z/s_z from the walls located at $z/s_z = \pm 0.5$. The horizontal line demarcates the density of a corresponding bulk liquid crystal.

(See Color Plate XIX at the back of this issue)

imental data (see Fig. 4(a) in Ref. [2]), as far as "nematic" films of 8CB between homeotropically anchoring walls are concerned. It is furthermore interesting to note that the slope of $F(h)/R$ in the experimentally inaccessible regions (where $d[F(h)/R]/dh > 0$ [8]) is substantially larger than in the accessible regions (where $d[F(h)/R]/dh < 0$), which seems to be in agreement with the plot in Fig. 4(a) of Ref. [2].

In Fig. 4 a "snapshot" and a plot of the local density $\rho(z; s_z)$ is shown for a film with wall separation $s_z = 32.0$. Even for this comparably large film thickness the smectic order induced by the walls extends across the whole film. The height of the maxima of $\rho(z; s_z)$ decays exponentially towards the middle of the film where $\rho(z; s_z)$ is close to the bulk density. This is in accord with analytical results for films consisting of spherically symmetric molecules[10]. The negative normal stress $-T_{zz} = 1.037$ for $s_z = 32.0$ is insignificantly higher than the bulk pressure $P_{\text{bulk}} = 1.028$.

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CONCLUSIONS

The macroscopically curved substrate surfaces of the SFA setup may be taken as plane-parallel on a molecular lengthscale while for the measurable force $F(h)/R$ the substrate curvature must be considered. Molecularly thin nematic liquid crystal films confined between homeotropically orienting planar planar substrates exhibit smectic-A like structures. The number of strata increases with growing wall separation; at $s_z = 32.0$ ten such strata are observed. The transition from k strata to $k+1$ strata is accompanied by an intermediate reorientation of molecules. This is reflected by characteristic shoulder zones in $f(s_z)$. By numerical integration a pseudo-experimental force curve $F(h)/R$ was obtained which is in qualitative agreement with SFA data. Provided $F(h)/R$ can be measured with sufficiently high precision and resolution, similar molecular reorientations should be detectable in SFA experiments.

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