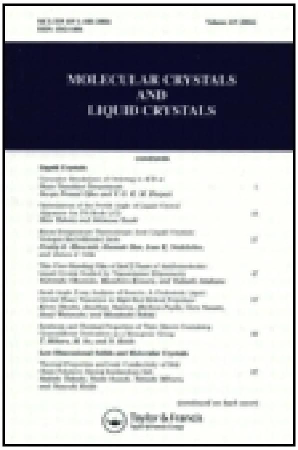

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

ATOMISTIC COMPUTER SIMULATIONS OF TERRACED WETTING OF MODEL 8CB MOLECULES AT CRYSTAL SURFACES

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Version of record first published: 07 Jan 2010

To cite this article: Andrew J. McDonald, Simon Hanna & H. H. Wills (2004): ATOMISTIC COMPUTER SIMULATIONS OF TERRACED WETTING OF MODEL 8CB MOLECULES AT CRYSTAL SURFACES, Molecular Crystals and Liquid Crystals, 413:1, 135-144

To link to this article: http://dx.doi.org/10.1080/15421400490437222

Mol. Cryst. Liq. Cryst., Vol. 413, pp. 135/[2271]–144/[2280], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490437222

ATOMISTIC COMPUTER SIMULATIONS OF TERRACED WETTING OF MODEL 8CB MOLECULES AT CRYSTAL SURFACES

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Results are shown from computer simulations of droplets of model 8CB-like liquid crystal molecules in contact with a crystal surface. It is shown that the type of wetting observed depends on the strength of the interaction energy between the liquid crystal molecules an the substrate. For a low energy surface, partial wetting is found, and the liquid crystal forms a sessile droplet. However, for higher energies, the droplet spreads rapidly, forming a percursor layer and clearly defined molecular terraces. These results are qualitatively in line with experimental findings. The dynamics of spreading of the precursor layer have been examined, and the experimentally observed proportionality of the film radius on $\sqrt{t}$ *has been reproduced. However, on examining the structure of the spreading layer, it is found that, at temperatures corresponding to a bulk smectic A phase, the spreading layer has a diamond shape, with edges perpendicular to the [110] directions in crystal surface. At higher temperatures, when the bulk system is in the isotropic phase, the spreading layer reverts to a radial symmetry.*

Keywords: 4′-n-octy1-4-cyanbipheny1; computer simulation; liquid crystal; terraced wetting

INTRODUCTION

Terraced wetting in a simple or light polymeric fluid occurs when a fluid droplet completely wets a planar surface. A microsocopic precursor film spreads radially outwards, preceding the macroscopic fluid edge. The precursor film, comprised of a few molecular monolayers, is arranged in a characteristic terrace structure. The layer closest to the surface leads

The authors wish to thank the EPSRC and British Council for financial support, Prof. M.P. Allen for helpful discussions and for generous assistance with computer time, and Dr. D.R. Binger for computational support.

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the radial spreading, followed by the next monolayer and so on. The remaining fluid molecules of the macroscopic droplet act as a reservoir for the expansion of the terraced precursor film.

The precursor film mechanism of complete wetting was first observed by Leger *et al.* [1] in ellipsometry experiments on poly (dimethylsiloxane) droplets spreading on smooth silicon wafers. Subsequently, Heslot *et al.* [2] performed the same experiment analysing profiles down to the monolayer and submonolayer regimes. They observed that the precursor film was of a uniform thickness, corresponding to a single monolayer. Under certain conditions multiple terraced monolayers were also observed at smaller radii. This went contrary to the belief that droplets adopted a smooth pancake-like structure during spreading and showed that any theory of complete wetting must take short range forces and molecular dynamics into account. In a more recent study, two distinct terraced wetting regimes were identified for high-energy and low energy surfaces [3]. For a high energy surface, corresponding to a low surface tension, wetting occurred through the terraced spreading of a few monolayers. For a low energy surface, corresponding to a higher surface tension, wetting occurred through just a single terrace or monolayer. In both cases, the radius of the wetting monolayer, $R(t)$, was proportional to $\sqrt{t}$. Thus, the precursor film evolved over the surface in a diffusive manner, overcoming the liquid cohesion to behave like a 2-D gas.

Considerable experimental and theoretical literature has appeared regarding terraced wetting since it was first observed. A semi-continuum theoretical model proposed by de Gennes and Cazabat treats the monolayers as elastic sheets [4]. Other theoretical analyses have been largely numerical, being based on molecular-kinetic theories of partial wetting and contact angle dynamics [5–7]. Several simulation studies of the spreading of simple fluids and chain molecules on solid surfaces have been performed [8–12]. The focus has been on reproducing the characteristic diffusive dynamics of the precursor film radius, $R(t) \sim \sqrt{t}$, observed in experiment. The main conclusion is that the registry of the fluid atoms or molecules with the surface is critical to the spreading dynamics of the monolayer.

Recently, experiments have been performed on the liquid crystal 4′-n-octyl-4-cyanbipheny1 (8CB) undergoing terraced wetting [13]. The authors concluded that the structure of the spreading droplet appears not to be a direct reflection of the long-range phase structure in the bulk liquid crystal at the same temperature, but again appears to be induced by short range forces and the fluid-surface interaction. Several simulation studies have explored the interactions of 8CB liquid crystals with substrates [14–16]. However, to the best of our knowledge no direct molecular simulations have been performed of liquid crystal molecules spreading on surfaces.

In this paper we present a simulation study of terraced wetting of a liquid crystal fluid on a crystalline surface. To model the liquid crystal fluid we use an atomistically detailed representation of 8CB, which however lacks hydrogen atoms and electrostatic interactions. The surface is the (100) face of a generic face-centred cubic crystal. The results are prefaced by a brief study of the behaviour of the model 8CB system in the bulk, and in isolated droplets.

METHODS

As indicated above, we employ a model liquid crystal molecule based on the chemical structure of 8CB. The model 8CB differs from real 8CB because it is (a) a united atom representation, meaning that the hydrogen atoms have been subsumed into the carbon atoms, and (b) there are no electrostatic interactions. The effect of these modifications is to enhance the speed of simulations by approximately a factor of ten. However, the consequence is that the simulated phase transition temperatures differ from experimental values by ten's of degrees, and the well-known structural dimerisation of 8CB is not observed.

All simulations were performed using molecular dynamics methods, performed using a modified version of the DL_POLY molecular dynamics code [17]. Energy parameters for bonds lengths, angles, dihedral angles and van der Waals interactions were obtained from the Amber force field [18], and from the work of Cross and Fung [19]. Preliminary simulations were performed on small systems with periodic boundary conditions, in the isobaric isothermal ensemble, in order to establish the bulk phase behaviour of the model 8CB. Further simulations were performed on isolated droplets in the canonical ensemble, to confirm that the same phase behaviour was observed in the absence of periodicity.

For the spreading simulations, the surface was represented by a generic face-centred cubic crystal. Three layers of surface atoms were employed, with the coordinates of the lowest layer being fixed. Each atom of the solid was connected to its twelve nearest neighbours by harmonic bond potentials, with stiffness constant set equal to the average intra-molecular bond stiffness constant of the liquid crystal molecules. The lattice constant of the crystal was chosen so that the nearest neighbour separation, in the [110] direction, was equal to the average minimum energy separation between non-bonded atoms in the liquid crystal fluid. The interaction between surface and fluid atoms was represented by a Lennard-Jones energy term:

$$U = \sum_{j=1}^{n\_surface} 4\varepsilon_{fs}\left[\left(\frac{\sigma_{fs}}{\gamma_{ij}}\right)^{12} - \left(\frac{\sigma_{fs}}{\gamma_{ij}}\right)^{6}\right]$$

where the range parameter, σ_{fs}, was set equal to the r.m.s. inter-fluid atom range parameter, and the strength of the fluid-surface interaction was controlled by ε_{fs}. Simulations were performed in the canonical ensemble, with thermostatting applied to the surface atoms only.

RESULTS AND DISCUSSION

Bulk Simulations of Model 8CB. Simulations were performed on systems of 595 molecules of model 8CB, in a periodic box at ambient pressure. Equilibration periods of up to 12 ns were employed, and the orientational order parameters determined (see Fig. 1). It can be seen that there is a steady decrease in order, as temperature increases, with a transition to a disordered, isotropic, state above 400 K.

In order to determine the type of liquid crystal phase present, the pair distribution function was calculated, resolved parallel to the system director (see Fig. 2). At temperatures below 400 K, the pair distribution function indicates clear layering of the molecules, corresponding to a smectic phase. The layer spacing is around 20 Å, which is consistent with the mean molecular length of 8CB, for which reason the mesophase is assigned to be smectic A. There is a slight increase in layer spacing with

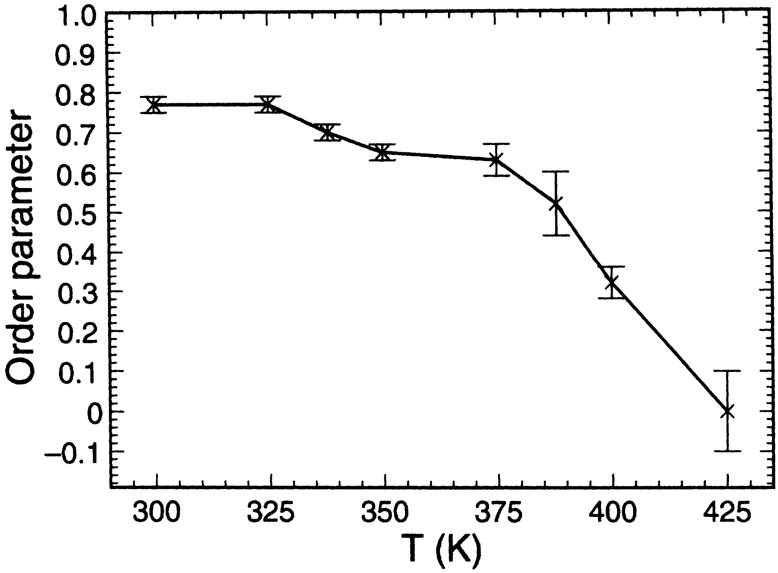

FIGURE 1 Orientational order parameter versus temperature for systems containing 595 molecules of model 8CB molecules with periodic boundary conditions.

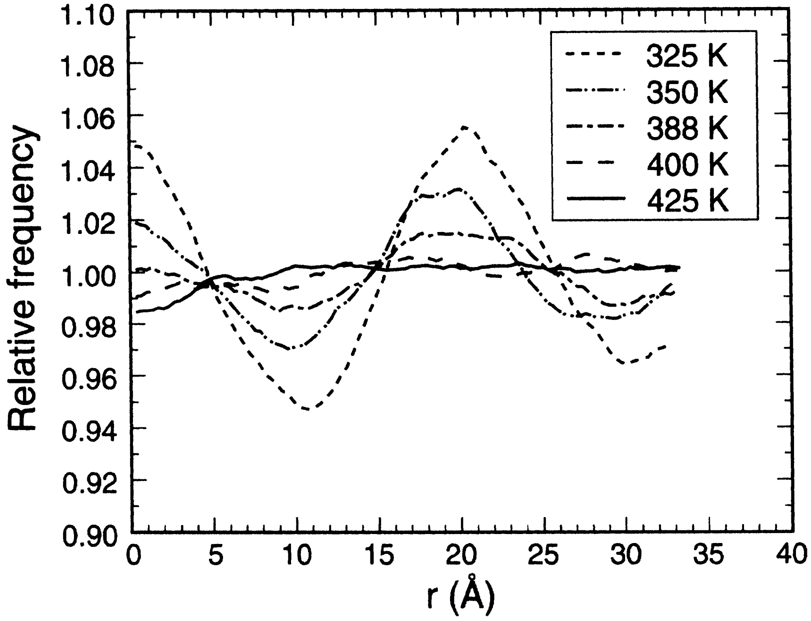

FIGURE 2 The pair distribution function resolved parallel to the system director.

decreasing temperature, which is due to a straightening of the alkyl tails. The layering disappears at 400 K, although some orientational ordering is still present, indicating a nematic region in the phase diagram.

Isolated Droplets of Model 8CB. Droplets of model 8CB molecules were prepared containing either 595 or 1593 molecules. The droplets were equilibrated in the smectic A phase (350 K for 8 ns) and the isotropic phase (425 K for 4 ns). In all cases, the droplets became near spherical after about 50 ps. The droplets were found to be relatively non-volatile, with only occasional molecules evaporating into the vapour phase. Figure 3 shows example configurations of droplets at each temperature, with the molecules drawn as equivalent ellipsoids, to aid the visualization.

For the system at 350 K, there is a predominantly radial alignment of molecular directors in the droplet, as homeotropic anchoring is strongly favored at the liquid - vapour interface. Antagonism is apparent however, between the spherical droplet shape and the requirements of the smectic-A bulk phase. Layers appear to form in planes normal to the local director, as in the smectic-A phase. However, due to the spherical symmetry imposed by the surface tension, the layer normals must align themselves at an angle to one another. The internal structure, and indeed the shape of the droplet, changes repeatedly over timescales of about a

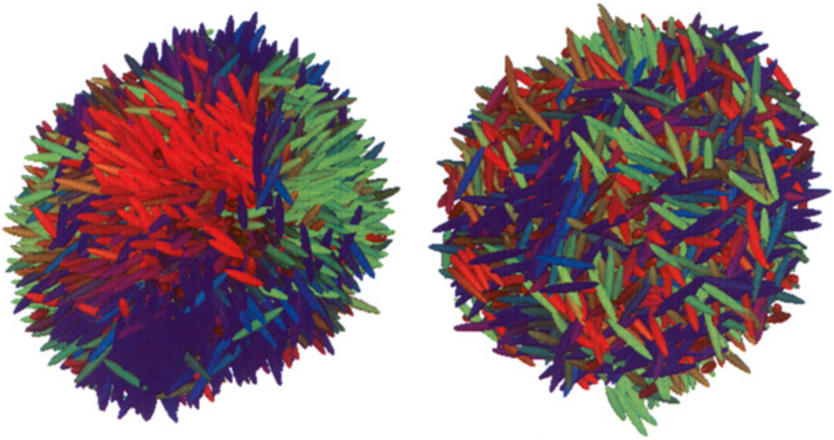

FIGURE 3 Large droplets of 8CB containing 1953 molecules (42966 atoms) at 350 K (left) and 425 K (right). The molecules are represented by ellipsoids, colour-coded so that molecules lying parallel to the coordinate axes appear either red, green or blue. Molecules pointing in other directions have intermediate colours. (See COLOR PLATE XIV)

nanosecond, indicative of a frustrated configuration. The shape fluctuations are more pronounced in the 595 molecule systems than in the 1953 molecule systems, but the structures are qualitatively similar. The droplet at 425 K displays no orientational order, and little deformation of the spherical shape.

Terraced Wetting of Model 8CB Droplets. The equilibrated droplets of liquid crystal molecules were placed in contact with the (100) surface of the crystal substrate, and allowed to spread under the influence of the surface - fluid interaction. Different values of ε_{fs} were used. Snapshots of the 350 K (smectic A) system, taken after 4 ns, are shown in Figure 4, for $\varepsilon_{fs} = 2.0$ and 2.5. In both cases layering is visible, parallel to the surface, which is similar to that seen in simple fluids. It can be seen that the wetting characteristics depend sensitively on the value of ε_{fs}. For the weaker fluid – surface interaction ($\varepsilon_{fs} = 2.0$), there is only partial wetting, and the profile of the droplet is essentially static. However, for the stronger interaction ($\varepsilon_{fs} = 2.5$), complete wetting occurs, with the droplet continuing to spread through the simulation. A precursor layer is clearly visible in contact with the substrate, and a less distinct second terrace may also be seen. The behaviour of the 425 K (isotropic) system is qualitatively similar.

Spreading of Model 8CB Droplets. The dynamics of radial spreading of the precursor layer was examined for systems at 350 K and 425 K, with $\varepsilon_{fs} = 2.5$. The results are shown in Figure 5. The diffusive nature of the spreading is clear from the graphs, with the experimental relationship

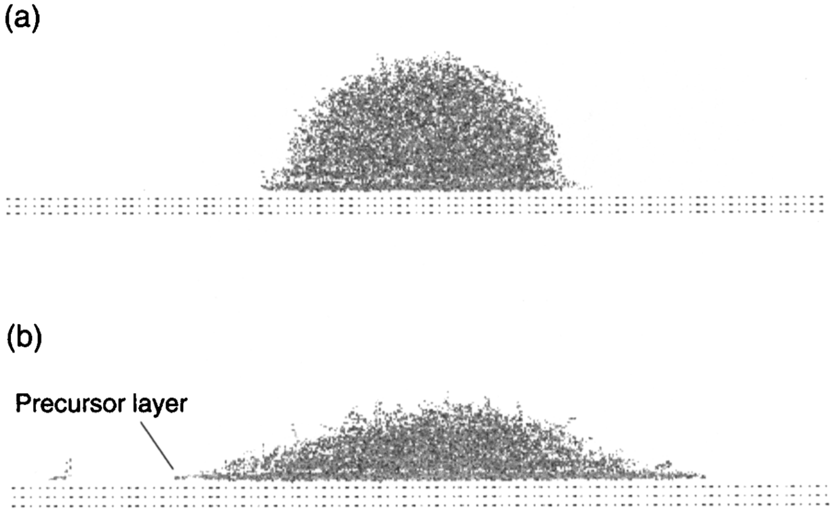

FIGURE 4 Examples of wetting in systems containing 595 model 8CB molecules at 350 K. In (a), $\varepsilon_{fs} = 2.0$ and partial wetting occurs. The liquid crystal molecules form a sessile droplet. In (b), $\varepsilon_{fs} = 2.5$ and complete wetting is observed with the formation of a precursor layer and molecular terraces. All liquid crystal atoms are shown.

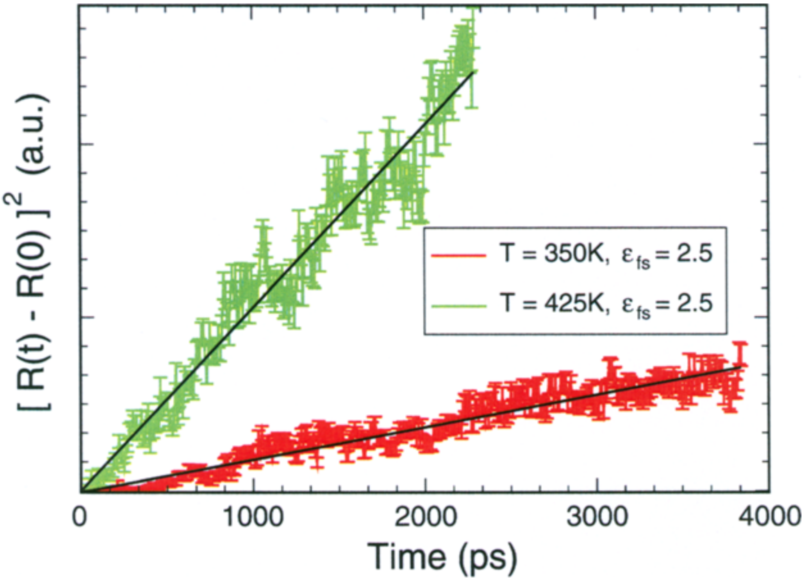

FIGURE 5 Radial growth of the precursor wetting monolayer over time. Error bars reflect fluctuations in the calculated radius of the monolayer over short time scales. (See COLOR PLATE XV)

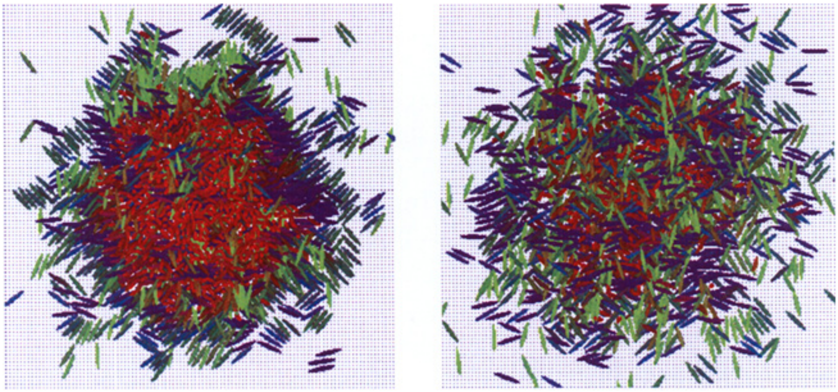

FIGURE 6 Coarse-grained snapshots of droplet spreading at 350 K (left) and 425 K (right), with $\varepsilon_{fs} = 2.5$, and 1953 molecules. Here, a red colour indicates the molecules are perpendicular to the page, while blue and green molecules lie in the plane of the page. (See COLOR PLATE XVI)

$R(t) \sim \sqrt{t}$ being reproduced. It is also apparent that the diffusion constant is much greater at 425 K than at 350 K.

Figure 6 shows snapshots of the structures of the spreading precursor films at 350 K and 425 K. It can be seen that there is a pronounced difference between the behaviour at the two temperatures. At 350 K, the precursor layer is not radially symmetric, but is tending to form a diamond shape as it spreads. There is a tendency for the directors of molecules wetting the surface to lie along the [110] directions of the crystal. There is also evidence of smectic-like layering in the wetting film, and a homeotropic alignment of the molecules at the liquid vapour interface in the middle of the droplet. At 425 K, on the other hand, the spreading film has a radial symmetry, and no obvious homeotropic tendencies. Thus, at both temperatures, the orientational order observed in the precursor film is consistent with that of the bulk at the same temperature.

CONCLUSIONS

The model 8CB system described above displays the same sequence of phases in the bulk as real 8CB, i.e. smectic A, nematic and isotropic. However, the transition temperatures are higher in the model system, as a consequence of the simplifications introduced. Simulations of isolated droplets of liquid crystal molecules show regions of localised order consistent with the phase structure of the bulk system at the same temperatures. Long range order in these systems appears to be frustrated by the spherical symmetry of the droplet imposed by the surface tension and the tendency to favour homeotropic (radial) alignment at the liquid vapour interface.

It has been possible, with a relatively simple atomistic model, to simulate the spreading of a droplet of liquid crystal on an atomically detailed surface. For suitable values of the surface–fluid interaction strength, terraced wetting has been observed experimentally in simple fluids. Under certain conditions a diamond shaped wetting monolayer was observed, which is attributed to weak smectic-like liquid cohesion, orientational coupling of molecular directors along the [110] direction in the crystal surface, and a surface–fluid interaction just strong enough to produce complete wetting. Orientational anchoring with the surface occurs through alignment of molecules along natural corrugations in the (100) surface.

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