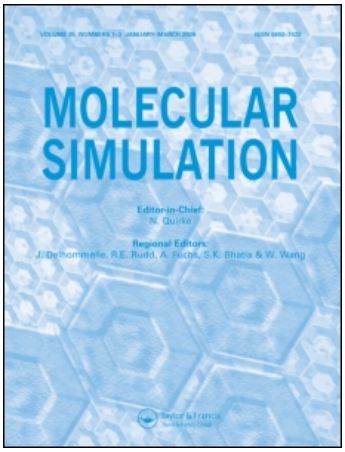
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Wetting of Planar Surfaces by a Gay-Berne Liquid Crystal

Erich A. Müller[a]; Inmaculada Rodríguez-Ponce†[b]; Abdelkrim Oualid[c]; José M. Romero-Enrique[c]; Luis F. Rull[c]

[a] Departamento de Termodinámica y Fenómenos de Transferencia, Universidad Simón Bolívar, Caracas, Venezuela [b] Lehrstuhl 5 für theoretische Physik, Physik Department, Technische Universität München, Munich, Germany [c] Departamento de Física Atómica, Molecular y Nuclear Area de Física Teórica, Universidad de Sevilla, Sevilla, Spain

Online publication date: 26 October 2010

To cite this Article Müller, Erich A. , Rodríguez-Ponce†, Inmaculada , Oualid, Abdelkrim , Romero-Enrique, José M. and Rull, Luis F.(2003) 'Wetting of Planar Surfaces by a Gay-Berne Liquid Crystal', Molecular Simulation, 29: 6, 385 — 391
To link to this Article: DOI: 10.1080/0892702031000117162
URL: http://dx.doi.org/10.1080/0892702031000117162

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, Vol. 29 (6–7), June 2003, pp. 385–391

Taylor & Francis
Taylor & Francis Group

Wetting of Planar Surfaces by a Gay–Berne Liquid Crystal

ERICH A. MÜLLER[a,*], INMACULADA RODRÍGUEZ-PONCE[b,†], ABDELKRIM OUALID[c], JOSÉ M. ROMERO-ENRIQUE[c] and LUIS F. RULL[c,‡]

[a]*Departamento de Termodinámica y Fenómenos de Transferencia, Universidad Simón Bolívar, Caracas 1080, Venezuela;* [b]*Lehrstuhl 5 für theoretische Physik, Physik Department, Technische Universität München, Munich, Germany;* [c]*Departamento de Física Atómica, Molecular y Nuclear Area de Física Teórica, Universidad de Sevilla 41080, Sevilla, Spain*

(Received September 2002; In final form September 2002)

Downloaded At: 18:38 14 January 2011

Molecular simulation of the wetting of an unstructured attractive wall by Gay–Berne liquid crystals are reported. Simulations are performed in the grand canonical ensemble on a wide pore at constant temperatures of $T^* = 0.53$ and 0.56, corresponding to temperatures below and above the nematic-isotropic-vapor triple point. Close to the coexistence chemical potential, a thick liquid film wets the solid surface. The film is composed of stratified layers of molecules parallel to the solid surface, which follow to a nematic domain at the lower temperature and an isotropic one at the higher temperature. In both cases, the film is in equilibrium with the corresponding vapor phase. Close to the liquid–vapor interface there is a manifest tendency for the molecules to orient themselves parallel to the interface. The adsorption on the wall varies continuously with the thermodynamic parameters considered and no evidence of a first order prewetting transition is observed.

Keywords: Monte Carlo; Adsorption; Film; Prewetting

INTRODUCTION

Computer simulations have allowed reasonable insight on the phase equilibria of bulk liquid crystals (LC), and both the structure and thermodynamics of these systems are known to some extent [1–3]. However, the effects of surfaces on the phase behavior of LC is far from being totally understood. Phase equilibria of confined LC is an area of ongoing interest since many industrial applications of LC crystals involve the direct interaction with surfaces. In this scenario, a myriad of new phenomena come into play, including, but not limited to, the appearance of new phases and wetting phenomena. Molecular simulation is an ideal tool to study the physical phenomena found at these nano-scales. This work focuses on studying the wetting of an unstructured attractive wall by a simple model of a LC.

Mostly, LC molecules are large molecules (when compared to industrial solvents and gases) with a rather rigid molecular backbone. Their complexity precludes an atomistic description, which when used within a molecular simulation, may become computationally expensive and require parallel hardware [4]. Furthermore, most of the singular behavior observed in LC does not seem to depend on the detailed molecular structure, but rather on the overall effect of the elongation and rigidity of the molecule. Thus, LC phase behavior seems to be appropriately modeled using either rigid (non attracting) models [5], or "soft" potentials such as the Kihara potential [6], simple non-flexible bead-chain potentials [7] and the Gay–Berne (GB) potential [8], among others. Of these, the latter has gained the most attention due to its ability to model a wide variety of phases (nematic, smectic, etc.), which have been observed experimentally. Phase diagrams have been published for several GB parameterizations [9–11] and some studies [12–14] have detailed the liquid–vapor interface, which exhibits several peculiarities, such as nematic ordering.

*Corresponding author. E-mail: emuller@usb.ve
†E-mail: irodrigu@ph.tum.de
‡E-mail: rull@us.es

ISSN 0892-7022 print/ISSN 1029-0435 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0892702031000117162

Downloaded At: 18:38 14 January 2011

Chalam *et al.* [15] have performed molecular dynamics (MD) studies of the changes that occur in a fluid of GB LC when confined in pores with parallel homeotropic walls (which favor a perpendicular alignment to the wall plane), showing how the confinement shifts the phase transitions to higher temperatures and stabilizes the LC phases. Stelzer *et al.* [16], Zhang *et al.* [17] and Wall and Cleaver [18] have performed MD studies on the effect of confinement of GB molecules in attractive smooth-walled pores. They have performed MD simulations on wide pores (such that it would be expected that no correlation exists between each wall). By varying the wall potential various smectic and planar layers were obtained near the wall, while the coexisting bulk phase (i.e. the middle of the pore) is either isotropic, nematic or smectic, depending on the thermodynamic parameter. Gruhn and Schoen [19] have performed grand canonical Monte Carlo (GCMC) simulations on confined GB fluids in pores formed by layers of spherical molecules. The bulk conditions corresponded to an isotropic fluid. However, upon confinement, the molecules near the walls developed either planar (ordered layers with parallel alignment to the wall) or homeotropic alignments. For a wide enough pore, the middle of the pore maintained an isotropic-like behavior. Palermo *et al.* [20] performed canonical (NVT) MC simulations of adsorption of GB molecules onto graphite-like walls. The opposing wall of the simulation cell was filled with a layer of either planar or homeotropic GB molecules fixed in space. These papers emphasize on the structure of liquid films near a single wall or within confinement. In all of them it is evident that the effect of the wall does not extend more than a few layers into the bulk (or middle of the pore) and that the film formed on the wall is more directly influenced by the nature of the substrate rather than on the thermodynamic conditions.

None of the above mentioned papers address explicitly the case of wetting of a surface (from a vapor) by a nematic LC. Experiments show that such a situation is possible, e.g. Sigel and Strobl [21] have observed the wetting of a solid surface by a homeotropically oriented nematic layer in the isotropic phase of a cyanobiphenyl CB8. It is expected that by varying the surface properties the nematic wetting might change its orientation, as it is the case for the wetting at the isotropic liquid–vapor interface by a nematic phase, (see for example, theoretical [22,23], computer simulation [12] and experimental [24–26] evidence of this). It is the purpose of this paper to determine if a simple attractive wall is sufficient to induce wetting by a nematic phase of a GB fluid, from a bulk phase isotropic fluid. Such wetting may or may not be accompanied by pre-wetting transitions, as observed in simple spherical fluids [27].

POTENTIAL MODEL AND SIMULATION DETAILS

The fluid–fluid intermolecular potential energy, U^{ff}, is modeled using an anisotropic GB [8] potential.

$$U_{ij}^{\mathrm{ff}}(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) = 4\varepsilon(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) \times \left\{ \left[\frac{\sigma_0}{r_{ij} - \sigma(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) + \sigma_0} \right]^{12} - \left[\frac{\sigma_0}{r_{ij} - \sigma(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) + \sigma_0} \right]^{6} \right\} \quad (1)$$

where $\hat{\boldsymbol{u}}_i$ and $\hat{\boldsymbol{r}}_{ij}$ are unit vectors which define the direction of the main symmetry axis of the molecule and intermolecular distance, respectively. Details on the particular functional form of the potential are given in detail elsewhere [1,2,8,11]. The potential requires four parameters: κ, the measure of the length-to-breadth ratio of the molecule; κ', the measure of the well-depth anisotropies; μ and ν which adjust the relative strengths of the intermolecular interactions. Additionally, two parameters σ_0 and ϵ_0 correspond to the characteristic length and energy. We have set the values $\mu = 2$, $\nu = 2$, $\kappa = 3$ and $\kappa' = 1.25$ which are the same used in the bulk phase simulations of de Miguel *et al.* [9] and correspond to the Bates–Luckhurst [11] notation of GB (κ, κ', μ, ν) = GB (3, 1.25, 2, 2). With this choice of parameters, the bulk liquid exhibits a vapor-nematic transition between $\mathrm{T}^* = kT/\varepsilon_0 = 0.53$ and 0.55, where T is the temperature and k is Boltzmann's constant. Above this temperature the isotropic liquid is in equilibrium with the vapor phase.

All distances considered in this paper are reduced with respect to the characteristic length of the potential, e.g. $z^* = z/\sigma_0$. The fluid is confined in a rectangular box of length $l^* = 15$ in the x and y directions and $l_z^* = 50$ in the z direction. The box has periodic boundary conditions in the x and y directions and walls in the $z^* = 0$ and $z^* = 50$ plane. The walls in the z direction are hard with respect to the GB molecules, i.e. GB molecules act as ellipsoids with a length to width ratio of 3:1. However, on the $z^* = 0$ plane we have superimposed an attractive potential of the form.

$$U_i^{\mathrm{wf}} = -10\varepsilon_0 \exp\left(-\frac{z_i}{0.9\sigma_0}\right) \quad \text{for } (z_i/\sigma_0) \geq 0 \quad (2)$$

where z_i is the normal distance of center of mass to the $z^* = 0$ plane. The ratio of the well

depth (potential minima) between the side–side (i.e. parallel configuration) fluid–fluid interaction and the fluid–solid interaction is chosen to be roughly equivalent to the ratio found between bulk fluid argon and the argon–graphite interactions. This latter system, modeled as a Lennard–Jones fluid adsorbing unto on a 9:3 wall, serves as a test case for simple adsorption studies and has shown to have a first order prewetting transition [27]. The attraction (Eq. (2)) is not present in the $z^* = 50$ plane in order to avoid capillary condensation effects. The full potential U is thus a superposition of the fluid–fluid interactions, the interactions of the molecules with the attractive wall at $z^* = 0$ and the hard wall at $z^* = 50$,

We have run GCMC molecular simulations, where the temperature, T, chemical potential, μ and volume V are fixed. Each MC cycle consists of a total of N translation and rotation steps on a randomly chosen particle (where N is the number of molecules in the system) and between 10 and 100 insertion/deletion steps. The reader is referred to standard textbooks [28,29] for a full description of the GCMC procedure.

The volume of the box is fixed at $(15 \times 15 \times 50)\sigma_0^3$ and initially is set up with 10 randomly placed molecules. The potential is cut off and shifted at a distance of $4\sigma_0$ and no long range corrections are applied. At the end of the simulations it exhibited a maximum mean occupation of O (10^3) molecules. For averaging purposes, the box has been divided in the z direction into slices of width $\Delta z = 0.1\sigma_0$ with the exception of the calculation of the orientational order where slices of $\Delta z = 0.5\sigma_0$ were used. The area, A, of a slice is $A = (15\sigma_0)^2$. The systems were run for up to 4.5×10^6 cycles and statistics collected during the last 0.5×10^6 cycles.

RESULTS

We have studied two temperatures, a lower one, $T^* = 0.53$, in which one encounters a nematic liquid at bulk saturation and a higher one, $T^* = 0.56$, chosen such that the isotropic liquid is expected at bulk condensation conditions, i.e. temperatures chosen to be below and above the nematic-isotropic-vapor triple point [9]. We have performed a complete adsorption isotherm in both cases, e.g. made a series of constant temperature simulations in which the chemical potential was varied.

We define the adsorption, Γ, as

$$\Gamma = \int_0^{50} [\rho^*(z^*) - \rho_b^*] \mathrm{d}z^* \tag{3}$$

where ρ_b^* is the reduced bulk number density and $\rho^*(z^*)$ is the density profile in the z direction

$$\rho^*(z^*) = \frac{\langle N \rangle \sigma_0^3}{A \Delta z} \tag{4}$$

and $\langle N \rangle$ is the average number of molecules in a given slice. For practical purposes, since there is a low density in the vapor, the bulk density of the integral in Eq. (3) is taken to be null, as compared to liquid-like density found in the adsorbed films. Figure 1 corresponds to the adsorption isotherm at $T^* = 0.56$. One observes a continuous growth of the liquid film. A continuous increase in chemical potential (pressure) allows a monotonous increase in the film thickness until a fully developed thick film is formed. There is no evidence of first order prewetting phase transitions at this temperature. In Fig. 2, we show some density profiles $\rho(z^*)$ in the z direction (the x and y directions are infinitely replicated due to the periodic boundary conditions) which correspond to the above mentioned isotherm.

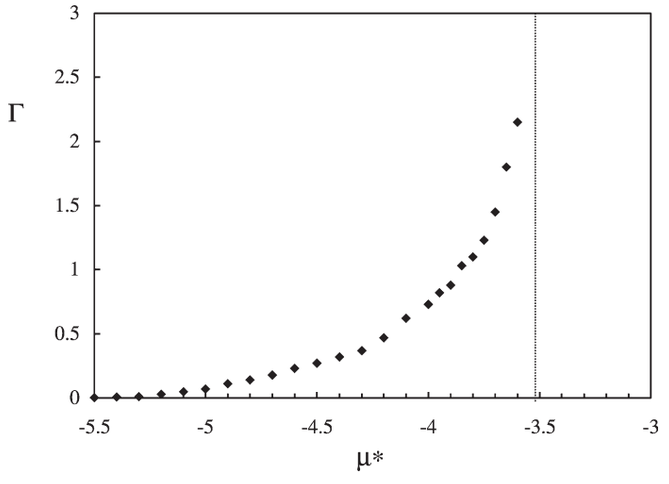


FIGURE 1 Adsorption isotherm for a temperature of $T^* = 0.56$ as a function of the reduced chemical potential, μ^*. Dashed line is a guide to the eye and corresponds to $\mu^* = -3.52$, the approximate bulk saturation condition. Error bars are smaller than the symbols.

Downloaded At: 18:38 14 January 2011

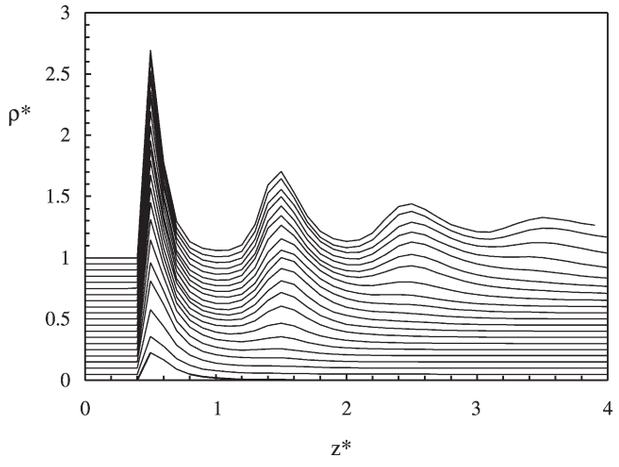


FIGURE 2 Density profiles ρ^* (z^*) as a function of μ^* for a temperature of $T^* = 0.56$. Bottom curve corresponds to $\mu^* = -5.0$. Subsequent curves correspond to increments of $\Delta\mu^* = 0.5$ and are shifted 0.05 for clarity. Top curve corresponds to $\mu^* = -3.5$.

Downloaded At: 18:38 14 January 2011

No "jump" is seen in the film thickness, rather a continuous buildup is observed.

In light of some controversy [27] about the GCMC method being or not able to detect prewetting transition, we have performed some isothermic–isobaric Monte Carlo (NPTMC) simulations, as described by Finn and Monson [27]. Results for these runs show a continuous increase from a thin film to a thick one with no discontinuity. The density profiles agree with the GCMC results and confirm the absence of first order (discontinuous) transition between the thin and thick wetting film. Analogous results were found for the lower temperature isotherm.

From the two isotherms, two conditions are further analyzed here, $T^* = 0.53$, $\mu^* = \mu/\varepsilon_0 = -3.625$ and $T^* = 0.56$, $\mu^* = -3.52$. The chemical potentials are chosen so that the system is close to saturation at bulk conditions. In Fig. 3, we plot the density profiles for both conditions. The values for the lowest temperature are shifted one unit in the vertical direction for clarity. From the figure there is an evident stratification close to the attractive wall ($z^* = 0$), up to a distance of approximately $z^* = 5$. A bulk liquid is apparent at distances farther away from the wall until a gas–liquid interface forms at distances of $17 < z^* < 22$ and $22 < z^* < 27$ for the low and high temperatures, respectively. The remainder of the box, until a distance of $z^* = 50$ is reached, is filled with a gas phase. The insert of Fig. 3 is a close-up of the region near the wall, where the stratification is apparent. The liquid and vapor densities, corresponding to the plateau in the films coincide with the reported values [9] for the bulk case.

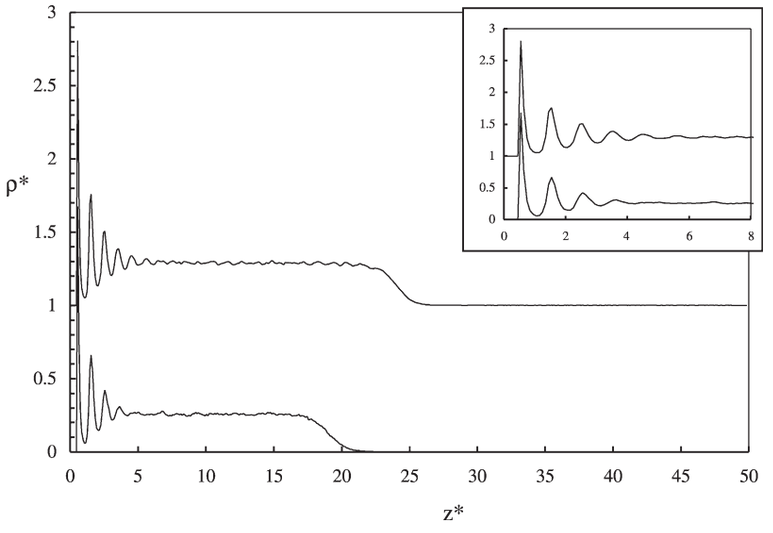


FIGURE 3 Density profiles ρ^* (z^*) as a function of the distance from the wall z^*. Bottom curve corresponds to $T^* = 0.56$, $\mu^* = -3.52$. Top curve corresponds to $T^* = 0.53$, $\mu^* = -3.625$ and is shifted up one unit for clarity. Insert shows the detail for small values of z^*.

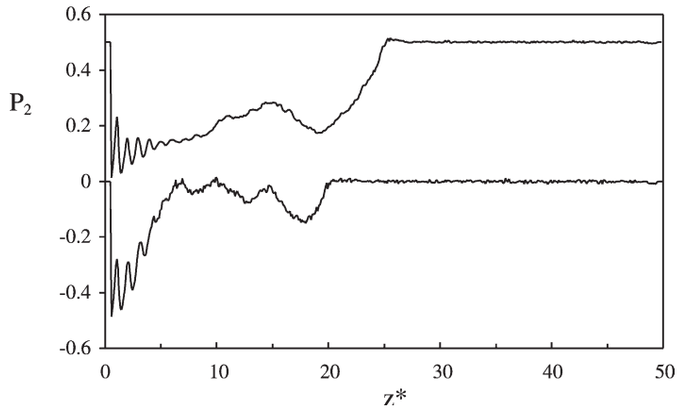


FIGURE 4 P_2 (z^*) order parameter as a function of the distance from the wall z^*. Bottom curve corresponds to $T^* = 0.56$, $\mu^* = -3.52$. Top curve corresponds to $T^* = 0.53$, $\mu^* = -3.625$ and is shifted up 0.5 units for clarity.

Downloaded At: 18:38 14 January 2011

In Fig. 4, we show the P_2 order parameter,

$$P_2(z^*) = \left\langle \frac{3}{2}\cos^2\theta_i(z^*) - \frac{1}{2} \right\rangle \tag{5}$$

where θ_i is the angle formed by $\hat{\boldsymbol{u}}_i$, the molecular axis, $\hat{\boldsymbol{n}}$, the unit vector normal to the attractive wall and the brackets correspond to an ensemble average over a given slice in the z direction. Values of $P_2 = -0.5$ correspond to molecules parallel to the wall while values of $P_2 = 1$ correspond to molecules perpendicular to the wall. The plot confirms the layering of the nematic-like wetting film close to the wall. An interesting feature is observed in the vapor–liquid interface, where a certain alignment is observed at the interface (the plot of P_2 shows a dip in the vicinity of the interface). This tendency of the molecules to align themselves with the plane of the interface has been reported in bulk liquid–vapor studies of LC [12,13] and is due to the constraints imposed by the interfacial tension. Plots of P_4 (not shown here) reconfirm these observations.

Considering the order tensor Q, defined as

$$Q_{\alpha\beta} = \frac{1}{2}\left\langle 3u_{i\alpha}u_{i\beta} - \delta_{\alpha\beta} \right\rangle \tag{6}$$

where $u_{i\alpha}$ is the $\alpha = x, y, z$ component of the axial unit vector of molecule i. Figure 5 shows the nematic order parameter S, defined as the ensemble average of the largest eigenvalue of the order tensor. Values of S close to unity correspond to a perfect orientationally ordered phase. It is clear form the figure that the wetting liquid layer has nematic characteristics at the lower temperature and it shows no ordering at the higher one.

Figure 6 are snapshots of final configurations for the lower and higher temperatures, respectively. It is visually observed how the attractive wall is wetted by planar layers. This stratification, of approximately three layers at high temperature, is induced by the wall potential, and has an interface with a bulk isotropic fluid. At the lower temperature it is seen how this wall-induced ordering extends further into the bulk fluid and interfaces with a nematic liquid.

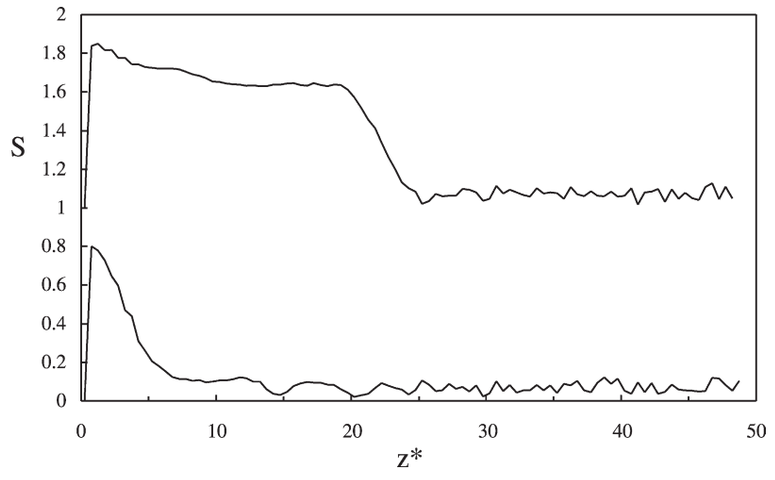


FIGURE 5 Order parameter S as a funtion of the distance from the wall z^*. Bottom curve corresponds to $T^* = 0.56$, $\mu^* = 3.52$. Top curve corresponds to $T^* = 0.53$, $\mu^* = -3.625$ and is shifted up one unit for clarity.

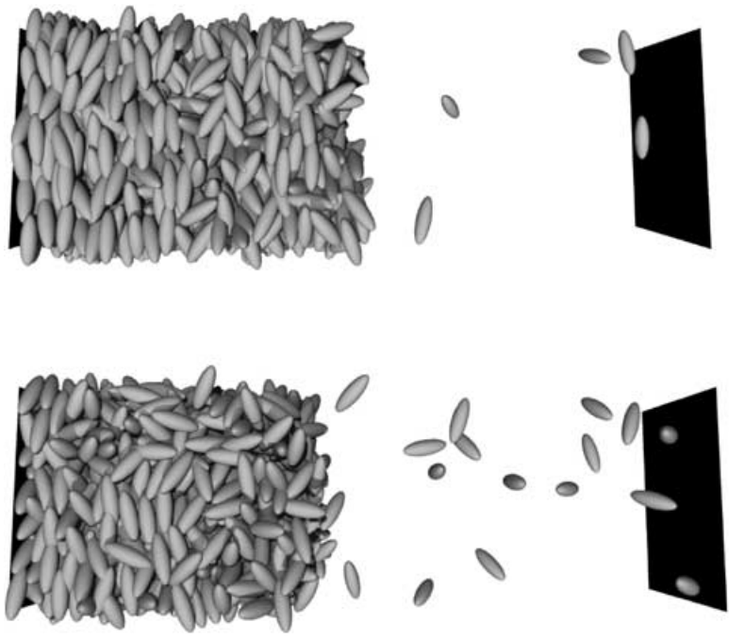


FIGURE 6 Snapshots of final equilibrium configurations. The attractive wall ($z^* = 0$) is to the left of the figure, the hard wall is to the right. Molecules are despicted by their hard cores. Top figure corresponds to $T^* = 0.53$, $\mu^* = -3.625$, bottom is $T^* = 0.56$, $\mu^* = -3.52$.

Downloaded At: 18:38 14 January 2011

The planar alignment at the liquid–vapor interface is observed in both snapshots.

CONCLUSIONS

In this work, we have performed GCMC simulations of a system of GB molecules in contact with an attractive planar wall. A thick film is monotonically formed with no indication of any first order prewetting transition.

In both temperatures studied, the attractive wall induces a stratification, more pronounced at the lower temperature, which evolves into the corresponding bulk phase, nematic or isotropic, depending on the temperature. The properties of the liquid–vapor interface are similar to those encountered under bulk conditions. Other than the layering effect on the first layers, the wall does not seem to have a pronounced effect on the properties of the thick film.

We note that the buildup of the film is continuous, i.e. no pre-wetting transition is detected. However, such transition is not discarded given a suitable choice of wall potential and parameters. Further study of this phenomena is currently under way.

References

[1] Allen, M.P. (1995) "Simulations and phase behaviour of liquid crystals", In: Baus, M., Rull, L.F. and Ryckaert, J.-P., eds, *Observation, Prediction and Simulation of Phase Transitions in Complex Fluids* (Kluwer, Dordrecht) pp 557–591.

[2] Zannoni, C. (2001) "Molecular design and computer simulations of novel mesophases", *J. Mater. Chem.* **11**, 2637.

[3] Rull, L.F. (1995) "Phase diagram of a liquid crystal model: a computer simulation study", *Phys. A* **220**, 113.

[4] Ilnytskyi, J.M. and Wilson, M.R. (2001) "Molecular models in computer simulation of liquid crystals", *J. Mol. Liquids* **92**, 21.

[5] McGrother, S.C., Williamson, D.C. and Jackson, G. (1996) "A re-examination of the phase diagram of hard spherocylinders", *J. Chem. Phys.* **104**, 6755.

[6] Kihara, T. (1963) "Convex molecules in gaseous and crystalline states", *Adv. Chem. Phys.* **5**, 147.

[7] Tian, P., Bedrov, D., Smith, G.D. and Glaser, M. (2001) "A molecular dynamics simulation study of the behavior of an ensemble of rigid bead-necklace molecules", *J. Chem. Phys.* **115**, 9055.

[8] Gay, J.G. and Berne, B.J. (1981) "Modification of the overlap potential to mimic a linear site–site potential", *J. Chem. Phys.* **74**, 3316.

[9] de Miguel, E., Martín del Rio, E., Brown, J.T. and Allen, M.P. (1996) "Effect of the attractive interactions on the phase behavior of the Gay–Berne crystal model", *J. Chem. Phys.* **105**, 4234.

[10] Brown, J.T., Allen, M.P., Martín del Rio, E. and de Miguel, E. (1998) "Effects of elongation on the phase behavior of the Gay–Berne", *Phys. Rev. E* **57**, 6685.

[11] Bates, M.A. and Luckhurst, G.R. (1999) "Computer simulation studies of anisotropic systems. XXX. The phase behavior and structure of a Gay–Berne mesogen", *J. Chem. Phys.* **110**, 7087.

[12] Martín del Rio, E., de Miguel, E. and Rull, L.F. (1995) "Computer simulation of the free liquid–vapor interface in liquid crystals", *Phys. A* **213**, 138.

[13] Martín del Rio, E. and de Miguel, E. (1997) "Computer simulation study of the free surfaces of a liquid crystal model", *Phys. Rev. E* **55**, 2916.

[14] Mills, S.J., Care, C.M., Neal, M.P. and Cleaver, D.J. (1998) "Computer simulation of an unconfined liquid crystal film", *Phys. Rev. E* **58**, 3284.

[15] Chalam, M.K., Gubbins, K.E., de Miguel, E. and Rull, L.F. (1991) "Molecular simulation of a liquid-crystal model: bulk and confined fluid", *Mol. Simulat.* **7**, 357.
[16] Stelzer, J., Galatola, P., Barbero, G. and Longa, L. (1997) "Molecular dynamics simulations of surface-induced ordering in a nematic liquid crystal", *Pys. Rev. E* **55**, 477.
[17] Zhang, Z., Chakrabarti, A., Mouritsen, O.G. and Zuckerman, M.J. (1996) "Substrate-induced bulk alignment of liquid crystals", *Phys. Rev. E* **53**, 2461.
[18] Wall, G.D. and Cleaver, D.J. (1997) "Computer simulation studies of confined liquid-crystal films", *Phys. Rev. E* **56**, 4306.
[19] Gruhn, T. and Schoen, M. (1998) "A grand canonical ensemble Monte Carlo study of confined planar and homeotropically anchored Gay–Berne films", *Mol. Phys.* **93**, 681.
[20] Palermo, V., Biscarini, F. and Zannoni, C. (1998) "Abrupt orientational changes for liquid crystals adsorbed on a graphite surface", *Phys. Rev. E* **57**, R2519.
[21] Sigel, R. and Strobl, G. (2000) "Light scattering by fluctuations within a nematic wetting layer in an isotropic phase of a liquid crystal", *J. Chem. Phys.* **112**, 1029.
[22] Martín del Rio, E., Telo da Gama, M.M., de Miguel, E. and Rull, L.F. (1995) "Surface-induced alignment at model nematic interfaces", *Phys. Rev. E* **52**, 5028.
[23] Martín del Rio, E., Telo da Gama, M.M., de Miguel, E. and Rull, L.F. (1996) "Wetting and interfacial order at nematic free surfaces", *Europhys. Lett.* **35**, 189.
[24] Bouchiat, M.A. and Langevin-Cruchin, D. (1971) "Molecular order at free surface of a nematic liquid crystal from light reflectivity measurements", *Phys. Lett.* **34A**, 331.
[25] Chiarelli, P., Faetti, S. and Fronzoni, L. (1984) "Critical-behavior of the anchoring energy of the director at the free-surface of a nematic liquid-crystal", *Phys. Lett.* **101A**, 31.
[26] Kasten, H. and Strobl, G. (1995) "Nematic wetting at the free surface of 4-cyano-4′-*n*-alkyl-biphenyls", *J. Chem. Phys.* **103**, 6768.
[27] Finn, J.E. and Monson, P.A. (1989) "Prewetting at a fluid–solid interface via Monte-Carlo simulation", *Phys. Rev. A* **39**, 6402.
[28] Allen, M.P. and Tildesley, D.J. (1987) *Computer Simulation of Liquids* (Clarendon Press, Oxford).
[29] Frenkel, D. and Smit, B. (2002) *Understanding Computer Simulation*, 2nd Ed. (Academic Press, San Diego).

Downloaded At: 18:38 14 January 2011