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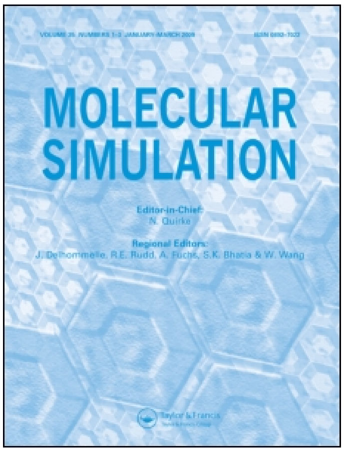

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STRUCTURAL CHARACTERIZATION OF CURVED INTERFACIAL FILMS OF T AND S-LJ FLUID BY MOLECULAR SIMULATION

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The structure of curved interfacial films formed by the adsorption of the simple T and S-LJ fluid between two structureless planar surfaces was investigated by the means of Grand Canonical Ensemble Monte Carlo (GCEMC) simulation. Our specific aim was to study the formation of a semi-spherical droplet on the planer surface. The surfaces were simulated using Steele's $U_{10\text{-}4\text{-}3}(z)$ potential. The droplet was created by truncating the surface potential with a sharp circular cut-off. The remainder of the surface consists of an infinitely hard reflective wall, with rectangular periodic boundary conditions (PBCs) in the *xy*-plain. This system produced three distinct stages in the structure adsorbed curved films, over an increasing range of relative pressure, p': at low p' the film consists of circular monolayers with decreasing radii the farther from the surface; at mid range p', the film closes to semi-spherical interface with a cap of liquid-like fluid at the pole, at p' low p' the film consists of circular monolayers with decreasing radii the farther from the surface; at mid range p', the film closes to semi-spherical interface with a cap of liquid-like fluid at the pole, at p' above the saturated vapour pressure of the bulk fluid, a liquid–gas (LG) film of cylindrical symmetry forms an "hour-glass" interface bridging the droplets on opposite surfaces.

Keywords: Droplet formation; Curved interfacial films; Monte Carlo simulation

INTRODUCTION

The physics driving the formation of highly curved interfacial fluid films, confined to spaces of molecular dimension is of increasing interest to both

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scientists and technologists, particularly in the new field of microfluidics. Results from early researches in adsorption science [1] form a basis for current work, which aims to elucidate the central role of film curvature in nucleation, capillary condensation (cc) and wetting phenomena.

Essentially, two unique mechanisms give rise to the creation of a droplet or wetting film on a surface [2]: (i) a phase transition viewed as, adsorption, cc, and evaporation or (ii) the dynamical processes of spreading, retraction and diffusion which are driven by the hydrodynamics of the fluid.

Recently, Talanquer and Oxtoby [3] have applied density functional theory to study nucleation within a slit pore. Their results indicate that a critical nucleus can either be attached as a droplet to each of the opposing planes or form a bridge like film across the planes.

In this preliminary note, we describe a simple method where the GCEMC simulation technique can be used to create highly curved interfacial film on a structureless planar surface.

METHOD AND SYSTEM

To create a highly curved interface consisting of a fluid–solid (FS) region at each of the planar surfaces and a liquid–gas (LG) interface bridging the two surfaces, we used the GCEMC simulation technique [4–6], to generate equilibrium configurations of the confined fluid. The total configurational energy of N molecules in the Monte Carlo (MC) cell of dimension $XL \times YL \times ZL$ is

$$\Phi_h = \sum_{i<j}^{N} \phi(r_{ij}) + \sum_{i}^{N} [U_{fw}(z_i) + U_{fw}(h - z_i)] \tag{2.1}$$

where $h = ZL$ is the spacing between the two structureless plane parallel solid surfaces. The truncated and shifted. Lennard–Jones (T and S-LJ) potential represents the fluid–fluid interaction, viz.

$$\phi(r) = \begin{cases} \phi_{LJ}(r) - \phi_{LJ}(r_\mathrm{c}) & \text{If } r \leq r_\mathrm{c} \\ 0 & \text{If } r > r_\mathrm{c} \end{cases} \tag{2.2}$$

with $\phi_{LJ}(r) = 4(r^{-12} - r^{-6})$ and $r_\mathrm{c} = 2.5$. The fluid–wall interaction potential for the slit-like pore is given by Ref. [7]

$$U_{fw}(z) = 4\pi A \left\{ \frac{2\alpha^{10}}{5z^{10}} - \frac{\alpha^4}{z^4} - \frac{\alpha^4}{3\Delta z(z + 0.61\Delta z)^3} \right\} \tag{2.3}$$

for details of the parameters A and α see van Megen [4–6]. The droplet was created by truncating the surface potential with a sharp circular cut-off. The remainder of the surface consists of an infinitely hard reflective wall, with rectangular periodic boundary conditions (PBCs) in the *xy*-plane. This is best represented by viewing a configuration from its base viz, Fig. 1. This system creates a finite capillary space of cylindrical symmetry which is surrounded by a bulk gas reservoir. As pointed out by Papadopoulou *et al.* [8], the reservoir fluid is in thermal, chemical, and mechanical equilibrium with the capillary confined fluid. The infinitely hard reflective wall is completely dry and isolated the FS and LG interfaces from any disturbance due to the PBCs, therefore, properties such as, the surface tension can be correctly determined. Since the bulk and confined

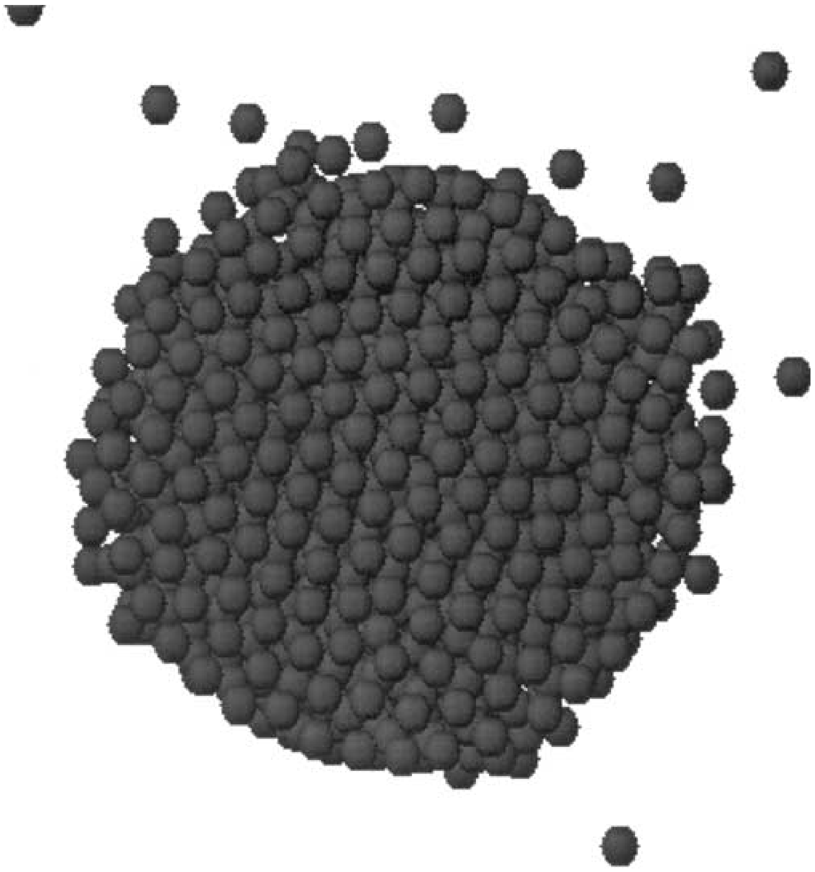

FIGURE 1 This snapshot of a configuration, viewed from the base of the MC cell, clearly represents the sharp circular truncation of the fluid–wall interaction potential.

fluid chemical potentials are equivalent, we use bulk simulation to determine the relative pressure, p', of the pore fluid. The bulk equation of state for several isotherms of the T and S-LJ fluid is represented in Fig. 2. We report herein measurements of several quantities at the reduced temperature $T^* = 0.6$ for the system described. Firstly, the adsorption isotherm is plotted as a function of the excess number density, Γ, given by,

$$\Gamma = \frac{\langle N \rangle - \langle N \rangle_\mathrm{b}}{2A} \tag{2.4}$$

versus, the relative pressure, p'. Where $A = XL \times YL$s is the entire surface area of the wall. The excess number density of the bulk, $\langle N \rangle_\mathrm{b}$ is determined in a separate bulk simulation and scaled to the appropriate pore volume. Secondly, the average configurational energies U_{ff} and U_{fw}, given by,

$$U_{ff} = \frac{1}{\langle N \rangle} \sum_{i<j}^{N} \phi(r_{ij}), \tag{2.5}$$

$$U_{fw} = \frac{1}{\langle N \rangle} \sum_{i}^{N} U_{fw(h)}(z_i), \tag{2.6}$$

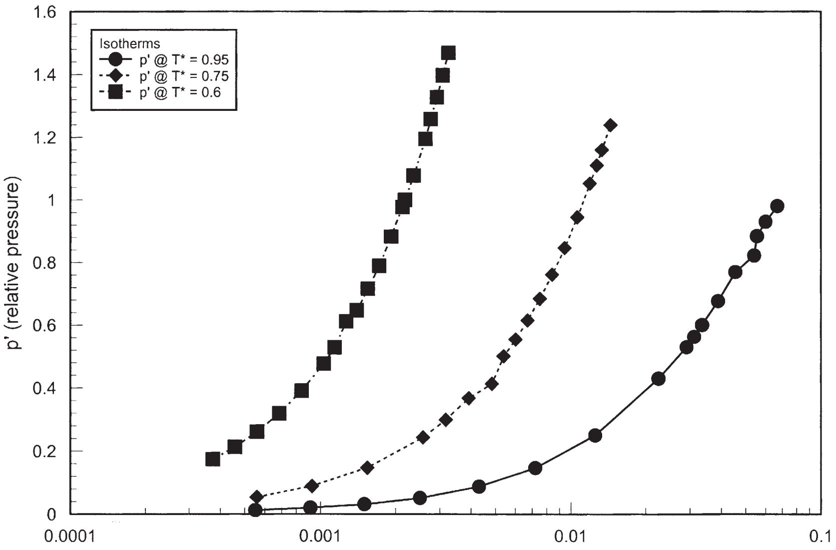

FIGURE 2 The bulk equation of state for several isotherms depicted in paper.

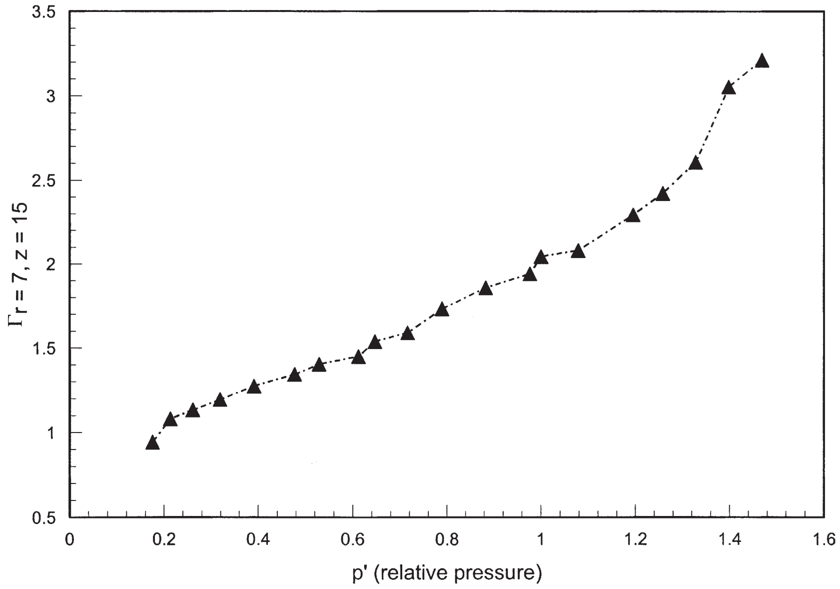

FIGURE 3 The adsorption excess, Γ, versus relative pressure, p' at the reduced temperature, $T^* = 0.6$.

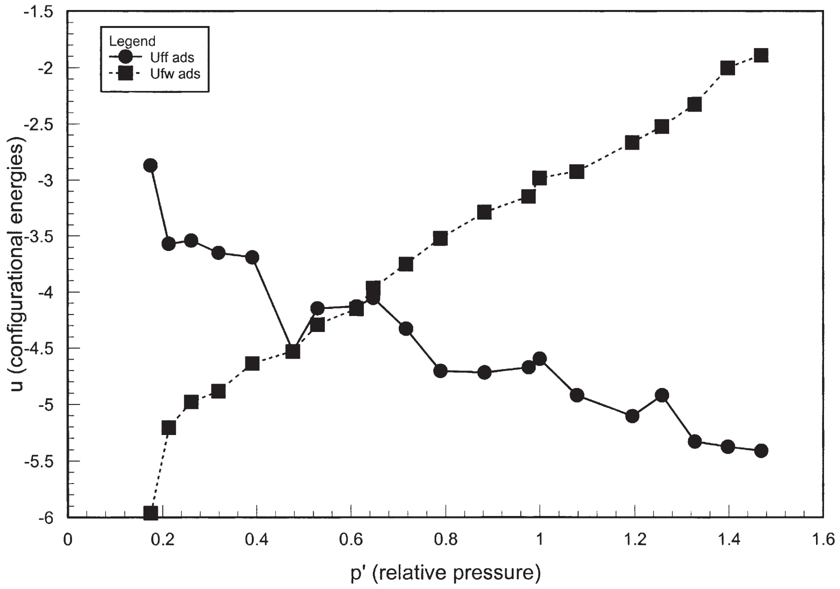

FIGURE 4 The configurational energies, U, versus relative pressure, p' at the reduced temperature, $T^* = 0.6$.

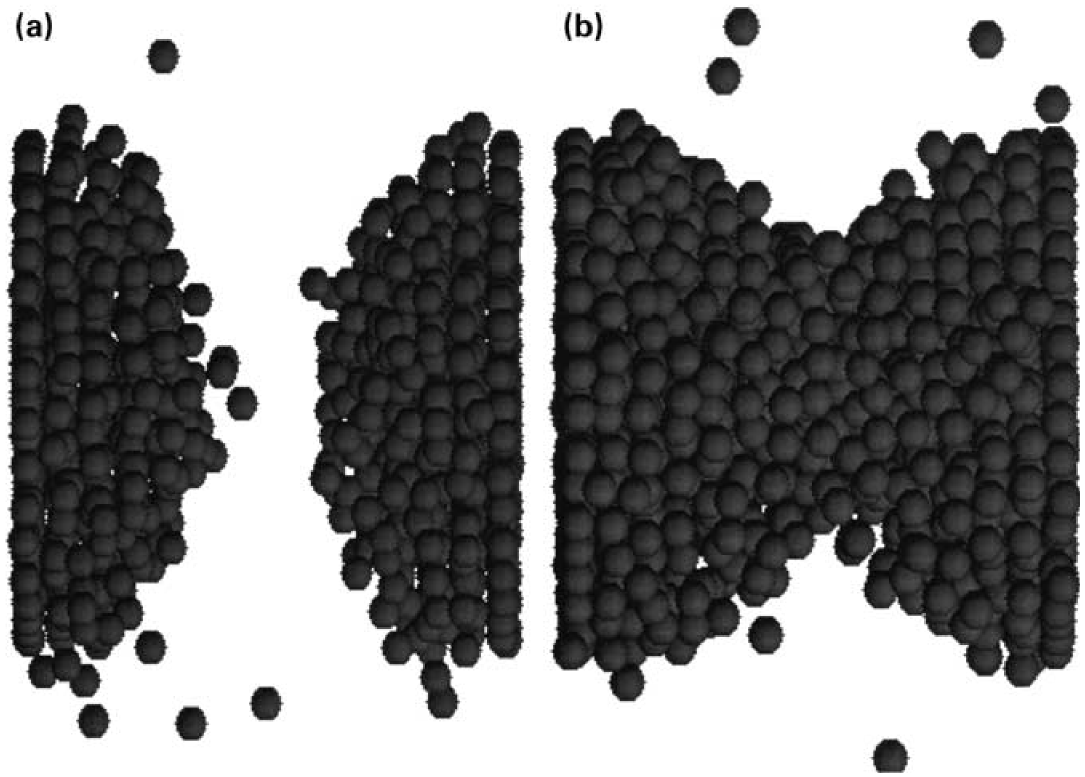

FIGURE 5 Snapshots after 20 million MC configurations at $T^* = 0.6$ the triple point of the T and S-LJ fluid, where $p_{\mathrm{sat}} = 0.00128$. With (a) the droplet state at $p' = 1.195$ and (b) the bridge-like state at $p' = 1.258$.

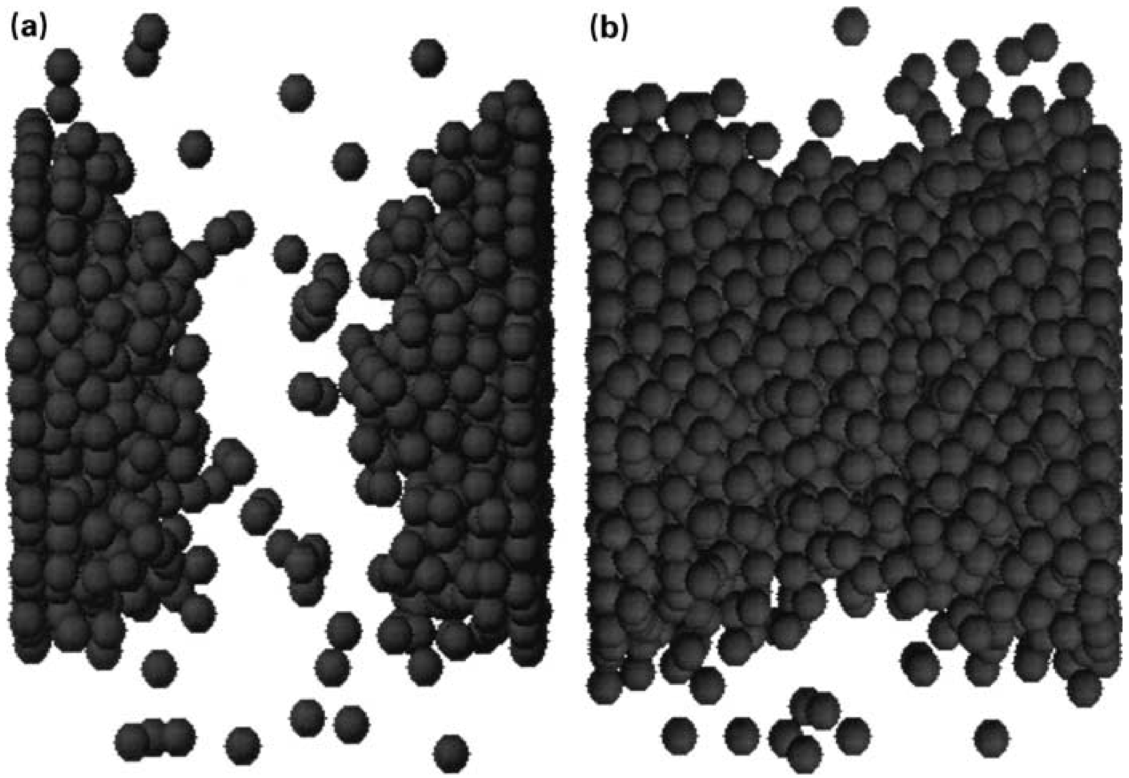

FIGURE 6 Snapshots after 20 million MC configurations at $T^* = 0.75$ where $p_{\mathrm{sat}} = 0.0078$. With (a) the droplet state at $p' = 1.160$ and (b) the bridge-like state at $p' = 1.239$.

where plotted versus relative pressure, p'. Here the so-called cavity potential, $U_{fw(h)}$, includes the interaction energy of the fluid with both surfaces,

$$U_{fw(h)}(z_i) = U_{fw}(z_i) + U_{fw}(h - z_i). \tag{2.7}$$

RESULTS AND DISCUSSION

Firstly, the system was simulated at the reduced temperature, $T^* = 0.6$, which is the triple point of the T and S-LJ fluid. The distance between the wall was set at $h = 15$ molecular diameters. The results indicate that the effect capillary confinement in a system with cylindrical symmetry. Plotting the adsorption excess, Γ, versus relative pressure, p', Fig. 3, and average configurational energies, U, at the corresponding relative pressures, Fig. 4, reveals that increasing p' below the saturated vapour pressure, P_{sat}, results in layer by layer wetting of the surface, with each contiguous layer of decreasing radius. These terrace-like wetting transitions are particularly prominent in the plot of U_{ff} versus p' of Fig. 4. Above P_{sat}, the supersaturated gas condenses to form an hour-glass shaped film which bridges the two micro-droplets, see Fig. 5b. The system was also simulated at the reduced temperature, $T^* = 0.75$, with the same radius of truncation, $r = 7$, in the fluid–wall interaction potential. The snapshots represented in Fig. 6, indicate that in this more volatile system, the droplet interface is less well defined and the bridging film is much broader.

CONCLUSION

Using the GCEMC simulation technique and a simple sharp circular truncation in the FS interaction potential of a slit-like pore, we have been able to generate a stable droplet and hour-glass shaped LG interfacial films. The films are highly curved and are inhomogeneous in the direction normal to the structureless planar surfaces.

Following this preliminary work, we propose to make a systematic study of the microscopic structure of the confined liquid–gas interface. We also with to investigate dynamical properties such as surface diffusion by implementing a molecular dynamics program using the same circular truncation of the fluid–wall interaction potential.

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