Monte Carlo study of the prewetting supercritical phase

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Abstract.   By means of Monte Carlo simulations, we investigate prewetting and its supercritical phase. First, we discuss the general properties of prewetting and obtain global phase diagrams. Secondly, we study the prewetting supercritical phase, in which density fluctuations in a film play an important role. We derive isotherms of two-dimensional compressibility from structure factors of the first adsorption layer, and find that the extension of the prewetting line is given by the location of the maxima of the isotherms. Our results complement recent mercury-on-sapphire experiments.

1. Introduction

Recently, Hensel and Yao found, by observing an anomaly in the optical reflectivity, that a mercury-on-sapphire system exhibits prewetting [1, 2]. An interesting point as regards their experiments is that this anomaly persists even in the temperature region above the prewetting critical temperature T_{cpw} [2]. They assume that this behaviour arises from the increase of the two-dimensional (2D) compressibility in the prewetting supercritical one-phase region. In this article, we report the results of our Monte Carlo (MC) simulations, on the basis of which we confirm that their interpretation accounts for the above-described behaviour.

2. The model and method

As the interparticle interaction, we choose a familiar Lennard-Jones (LJ) 12–6 potential with the cut-off distance of 2.5σ. The particle–substrate interaction is also chosen in an LJ potential form:

$$\phi(z_i) = \frac{3\sqrt{3}\varepsilon_w}{2}\left[\left(\frac{\sigma_w}{z_i}\right)^9 - \left(\frac{\sigma_w}{z_i}\right)^3\right] \tag{1}$$

where z_i denotes the distance from the solid surface to the ith particle. It is true that these potentials are not realistic for a mercury-on-sapphire system; however, our assertion as regards this point is that the behaviour as observed in a mercury-on-sapphire system is a general property, which is in some way independent of the details of the potential form, and even these LJ potentials give the essential aspects. The number of particles $N = 12\,500$, and the size of the simulation box is $50\sigma \times 50\sigma \times L_z$. In the off-lattice isobaric–isothermal MC method adopted in this work, L_z is varied at each MC step according to the temperature and pressure of the system [3]. We locate an attractive surface at $z = 0$ which interacts with
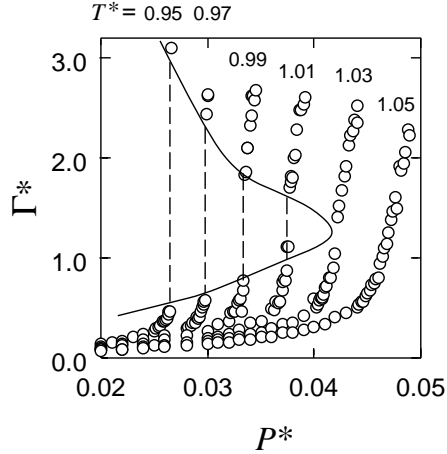
Figure 1. Adsorption isotherms for $\varepsilon_w^* = 2.0$.

a particle through equation (1), and a repulsive wall at $z = L_z$, and we apply a periodic boundary condition in the x–y direction. Each run is performed for 2×10^3–8×10^4 MC steps. Hereafter, an asterisk is added to a quantity normalized with respect to the LJ parameters ε and σ.

3. Prewetting

From measurements of the density profile $\rho^*(z^*)$, we calculate the adsorption excess density, defined as

$$\Gamma^* \equiv \int_0^{L_z^*} \mathrm{d}z^* \, [\rho^*(z^*) - \rho_b^*] \tag{2}$$

where ρ_b^* is the gas density estimated for the range $15 < z^* \leqslant L_z^* - 15$ as long as $L_z^* > 50$, and we derive adsorption isotherms as shown in figure 1. It is found that the adsorption isotherms in the temperature range $0.95 \leqslant T^* \leqslant 1.03$ change discontinuously along the broken lines, which implies that prewetting takes place. The magnitude of the jump gets smaller with temperature, and the change is continuous for $T^* > 1.03$. From this observation, we can determine the wetting temperature $T_w^* \simeq 0.95$ and the prewetting critical temperature $T_{cpw}^* \simeq 1.03$. The solid curve is the boundary of two-phase regions, i.e., thin-film and liquid phases for $P^* < 0.0264$, and thin-film and thick-film phases for $0.0264 < P^* < 0.0422$, where $P^* = 0.0264$ is the saturation pressure corresponding to T_w^*. A film is unstable inside the curve.

4. The prewetting supercritical phase

Since the adsorption isotherms increase continuously in the prewetting supercritical region, we divide a film into adsorption layers and observe the 2D structures to make a more detailed analysis. In order to see whether the substrate is wet or not, it is important to investigate the structure of the first adsorption layer. To this end, we calculate a 2D structure factor of the first layer:

$$S_2^{(1)}(q^*) \equiv \left\langle \frac{1}{N^{(1)}} \left[\left(\sum_i \cos q^* \cdot R_i^* \right)^2 + \left(\sum_i \sin q^* \cdot R_i^* \right)^2 \right] \right\rangle \tag{3}$$
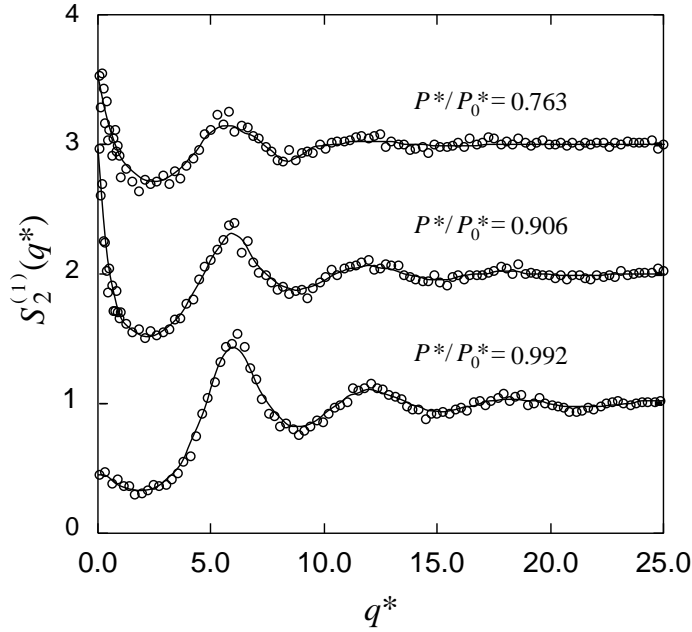
Figure 2. Structure factors of the first adsorption layer for $\varepsilon_w^* = 2.0$, $T^* = 1.06$, and $P^*/P_0^* = 0.763, 0.906, 0.992$. The curves are shifted by 2 and by 1 for lowest and middle pressures, respectively.

$$q^* \equiv \frac{2\pi}{L^*}(\nu_1, \nu_2) \qquad \nu_1, \nu_2 \text{: integer}$$

where $N^{(1)}$ is the number of particles in the first layer, $L^* = L_x/\sigma = L_y/\sigma = 50$, and $R_i^* \equiv (x_i^* \equiv x_i/\sigma, y_i^* \equiv y_i/\sigma)$ is the x–y coordinate of the ith particle. In figure 2, we show typical results for structure factors for different pressures for $T^* = 1.06 > T_{cpw}^*$. Here, the small-q^* behaviour for the intermediate pressure is noteworthy. A simple way to analyse this behaviour is to use the Ornstein–Zernike form [4, 5]

$$S_2^{(1)}(q^*) = \frac{S_2^{(1)}(0)}{1 + \xi_{\parallel}^{*2} q^{*2}} \tag{4}$$

even though a number of approximates have been proposed in the 2D Ising system [6]. By means of least-mean-square fitting, we determine the 2D compressibility $S_2^{(1)}(0)$, which is found to be at its largest for intermediate pressure.

By performing the same analysis, we obtain isotherms of $S_2^{(1)}(0)$ for $1.03 \leqslant T^* \leqslant 1.08$ as shown in the inset of figure 3. The physical picture given by this figure is as follows. When the pressure is increased, the size of the droplets and the density of the first adsorption layer increase, so the compressibility starts to decrease when the first layer is filled up. In the case of mercury-on-sapphire experiments, the filling up of the first adsorption layer is expected to lead to an anomalous increase of the optical reflectivity. The broken line in the inset of figure 3 connects the positions of the maxima of the isotherms. By locating these positions in the phase diagram, we obtain the squares plot shown in figure 3. If we draw a guiding line from the prewetting critical point (CPW) to the circles as well as one to the squares, we find that the two lines bend at the CPW, and this feature is in qualitative agreement with the mercury-on-sapphire result. Similar phase diagrams are derived for
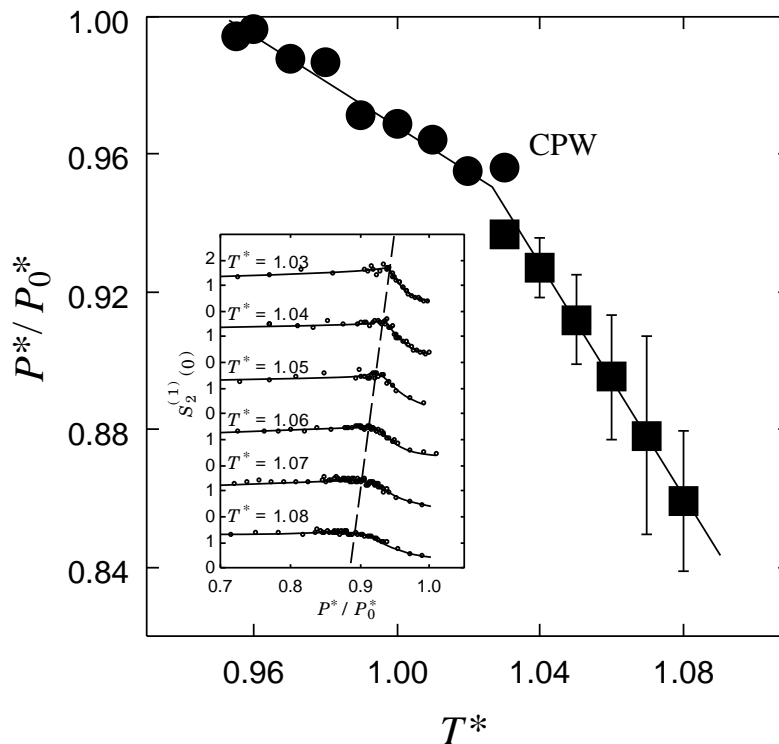
Figure 3. The phase diagram on a P^*/P_0^*–T^* surface for $\varepsilon_w^* = 2.0$. The circles and squares are determined from adsorption isotherms (figure 1) and $S_2^{(1)}(0)$ isotherms (inset), respectively.

the range $1.8 \leqslant \varepsilon_w^* < 3.0$. From the above microscopic analysis, we can conclude that the extension of the prewetting line marks the maximum of the compressibility in the prewetting supercritical phase.

Acknowledgments

References

[1] Hensel F and Yao M 1994 *Elementary Processes in Dense Plasmas* ed S Ichimaru and S Ogata (Tokyo: Addison-Wesley)
    Hensel F and Yao M 1996 *J. Non-Cryst. Solids* **205–207** 231
    Hensel F 1995 *Adv. Phys.* **44** 3
[2] Yao M and Hensel F 1996 *J. Phys.: Condens. Matter* **8** 9547
[3] Finn J E and Monson M P 1989 *Phys. Rev.* A **39** 6402
[4] Tarazona P and Evans R 1983 *Mol. Phys.* **48** 799
[5] Lipowsky R 1985 *Phys. Rev.* B **32** 1731
[6] Tracy C A and McCoy B M 1975 *Phys. Rev.* B **12** 368