PHYSICAL REVIEW E VOLUME 56, NUMBER 6 DECEMBER 1997

Pathway to surface-induced phase transition of a confined fluid

Ka Lum and Alenka Luzar*
Department of Chemistry, University of California at Berkeley, Berkeley, California 94720-1460

(Received 15 May 1997; revised manuscript received 22 August 1997)

We perform Glauber dynamics Monte Carlo simulations of a lattice gas confined between drying walls to model the dynamics that leads to the evaporation of water between extended hydrophobic surfaces. We find direct evidence that the long and short wavelength fluctuations are the important features involved in the evaporation process. These fluctuations correspond to capillary wave fluctuations in the emerging liquid-vapor interfaces and to the formation of vapor tubes that bridge across the interfaces. [S1063-651X(97)51512-1]

PACS number(s): 68.10.Jy, 64.70.Fx, 64.60.My

Confinement affects the phase behavior of a liquid. For example, at ambient conditions, water at an extended and ideal hydrophobic surface (no forces of attraction between molecules and the surface) is predicted to exhibit a drying transition [1]. Drying of a wall is tied to the physics of phase transition, i.e., it is akin to evaporation, making the liquid move away from the surface with a density profile much like that of the free vapor-liquid interface. Indeed, one expects from general thermodynamic arguments that a liquid confined between two drying walls will be replaced by vapor, due to competition between bulk energetics (favoring the liquid phase), and surface energetics (favoring the vapor). Below some threshold separation the surface energetics will dominate over the bulk energetics. The reduction of liquid density between two solvated inert surfaces will lead to attraction between them. This effect is of importance to the hydrophobic attraction, especially if the tendency to evaporate can be induced by widely separated hydrophobic surfaces.

A comparison of bulk to surface energetics provides an estimate of the range of surface separation where this effect of confinement will become significant. The critical distance D between planar walls of lateral size L, below which vapor represents the stable phase is given by [2]

$$D \sim 2\Delta\gamma/(\rho\Delta\mu + b\gamma/L), \tag{1}$$

where $\Delta\gamma \equiv \gamma_{wl} - \gamma_{wv} = -\gamma\cos\theta_c$, and we make use of Young-Dupré equation for relating the difference in wall/vapor and wall/liquid surface tension to the surface tension of the free liquid-vapor interface, γ, and the contact angle θ_c. ρ is the number density of a liquid, $\Delta\mu$ is the difference of the chemical potential of bulk liquid from liquid-gas coexistence, and b is a geometry dependent constant of the order of unity. For macroscopic surfaces, Eq. (1) reduces to the well known result [3,4] $D \sim 2\Delta\gamma/\rho\Delta\mu$. For hydrophobic surfaces (large θ_c) in water at ambient conditions, vapor becomes the thermodynamically stable phase at separations of the order of 100 nm. The magnitude of the length at which confinement becomes relevant is a consequence of water's large surface tension, and the proximity to the liquid-vapor coexistence line (i.e., the smallness of $\Delta\mu$).

Others have noted that physics of evaporation and surface drying is pertinent to the interaction between extended hydrophobic surfaces separated at distances large compared to a typical bulk correlation length of a liquid. Macroscopic thermodynamics [5], and mean field approach [6] were used in these works. Molecular simulation studies are still restricted to small simulation box, where a tendency of water to escape from the hydrophobic environment has been observed at very small separations, up to two molecular layers. Note that, for specific conditions of the calculations, grand canonical Monte Carlo (GCMC) simulations of simple potential of water [7] and constant pressure molecular dynamics of RER water [8] captured spontaneous evaporation at distances consistent with Eq. (1). The simulations confirm the pertinent physics at small separations of large hydrophobic objects [9]: liquid confined to one molecular layer, which prevents the molecules from having neighbors, vaporizes.

Clearly, evaporation induced by confinement is a real phenomenon, but its extent and time scale can vary appreciably depending upon the size and shape of the confining hydrophobic surfaces. Recent reports on hysteresis in surface force measurements [3] indicate metastabilities associated with first-order phase transitions. Macroscopic thermodynamics predicts [5] that for a vapor bridge to grow to its equilibrium size, a very high potential barrier must be overcome, leading to astronomical time scales for the evaporation to be observed in experiments [10]. Yet, the phenomenon does occur: at separations of about 10–20 nm, the two surfaces jump into contact, indicating the occurrence of spontaneous cavitation [11]. Hence, there must be an alternative pathway for evaporation to occur. In this paper, we give evidence for a different mechanism for spontaneous cavitation: we argue that it is the interfacial fluctuations that are essential for relatively fast cavitation.

Our results are based upon an analysis of Glauber dynamics GCMC simulation of simple lattice gas model with nearest-neighbor attractive interactions [12]. We consider only systems in which vapor represents the stable phase. Beginning with a slit filled with metastable liquid, we use simulations to study the dynamics of cavitation. Because of apparently very long range nature of the interaction, which is experimentally observed only between *macroscopic* surfaces [13], any simulation would have to be carried out on systems

---

*Author to whom correspondence should be addressed. Present address: Hilgard Hall-3110, UC Berkeley, CA 94720-3110.

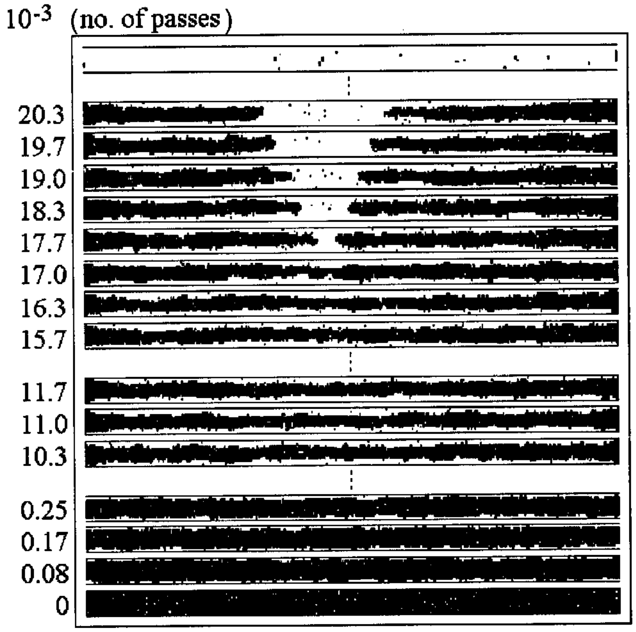

FIG. 1. Cross sections of the $D\times L\times L$ lattice gas system ($D=12$, $L=512$) confined between drying walls ($\epsilon_s=0.01\epsilon$, values of the parameters given in Ref. [16]). Cells are black when occupied, and white when empty. Initial system (0 passes) is a slab of metastable liquid with density 0.95. The drying surfaces induce evaporation by the pathway illustrated in the progression of cross section ''snapshots'' taken from a Glauber dynamics Monte Carlo simulation. Number of passes is given on the left-hand side of each snapshot.

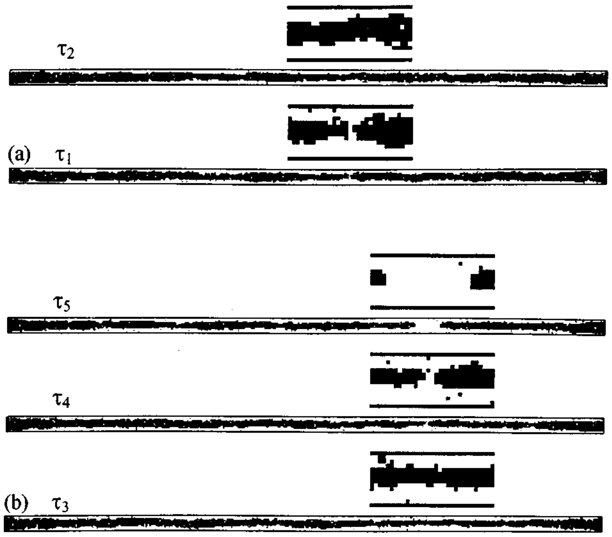

FIG. 2. Cross sections of lattice gas confined by drying walls at consecutive times, τ (see text). Enlarged portions of the cross sections show the appearance (b) and disappearance (a) of a microscopic vapor tube, discussed in the text. System size and parameters as in Fig. 1.

with prohibitively large *lateral* dimensions of surfaces. In such a geometry even the fastest computers cannot currently handle the necessary number of particles. Since a density profile associated with surface drying [1] contains a free liquid-vapor interface, the dynamics may involve interfacial capillary wave fluctuations [4]. Therefore, periodic boundary conditions cannot resolve the problem because they cannot capture density fluctuations with wavelength exceeding the dimensions of the simulation cell. When studying the dynamics of phase transitions in a slit geometry, we must have a model with lateral dimensions much larger than the separation between the confining surfaces for the transition to be seen in a finite time of simulation.

Lattice gas models provide a conventional framework for computations at large length scales where molecular details become unimportant [14]. The existing lattice gas simulations of a confined fluid have examined the equilibrium phase behavior properties [15]. However, the way the phase transition occurs, i.e., the mechanism of induced cavitation, has never been studied. The present calculations focus on the kinetic pathway of the liquid-gas phase transition of a confined fluid close to liquid-gas coexistence. Specifically, we follow the evaporation process and try to identify the important fluctuations that lead to cavity formation.

The lattice-gas Hamiltonian is given by

$$\mathcal{H}=-\epsilon\sum_{\langle ij\rangle\in\text{bulk}} n_i n_j-\epsilon_s\sum_{i\in\text{surface}} n_i\;-\mu\sum_i n_i, \qquad (2)$$

where the first term represents the interparticle interaction for a given set of occupation numbers n. $n_i=1$ if the cell at position i is occupied (liquid), and is equal to zero if it is empty (gas). ϵ_s denotes the lattice gas surface-particle interaction, and μ is chemical potential. $\Sigma_{\langle ij\rangle}$ runs over all nearest-neighbor pairs, and $\Sigma_{i\in\text{surface}}$ over all $2\times L^2$ surface sites. The lattice gas parameters, namely, the nearest-neighbor interaction ϵ, the chemical potential μ, and the lattice spacing a, are chosen such that at room temperature the corresponding lattice gas exhibits high surface tension, close proximity to vapor-liquid coexistence, and high incompressibility. These are the three features that seem most pertinent for a liquid such as water at ambient conditions [16].

The space between the parallel surfaces is filled by a simple cubic lattice with volume $D\times L\times L$. In most of our calculations we have used a simulation box of size $12\times512\times512$ (in units of a). The boundary conditions are chosen to mimic the experimental setting in the surface force apparatus [13]. In the x-y direction, the confined region is surrounded by the bulk liquid ($n_i=1$ at the boundary in the lateral direction). The system is simulated under the conditions of constant temperature and chemical potential, using the Glauber [17] single spin-flip Monte Carlo algorithm, with surface fields that correspond to strongly hydrophobic surfaces, $\epsilon_s=[(1+\cos\theta_c)/2]\epsilon=0.01\epsilon$.

In our simulation, Fig. 1, the system is initially occupied, i.e., filled with liquid. Because vapor is thermodynamically stable in the confined region at this separation [18], this initial configuration corresponds to metastable liquid. A film of vapor quickly develops between the liquid and each wall in about 200 passes (1 pass corresponds to 1 single-flip trial at each cell for the entire system). In the present case the formation of vapor film merely reflects the fact that liquid tends to escape from interfacial region to the bulk phase in GCMC. These newly created liquid-gas interfaces undergo thermal fluctuations. The fixed boundary conditions pin the interfaces at the edges. We identify long wavelength fluctuations (capillary waves) that contribute to the thermal roughness of the

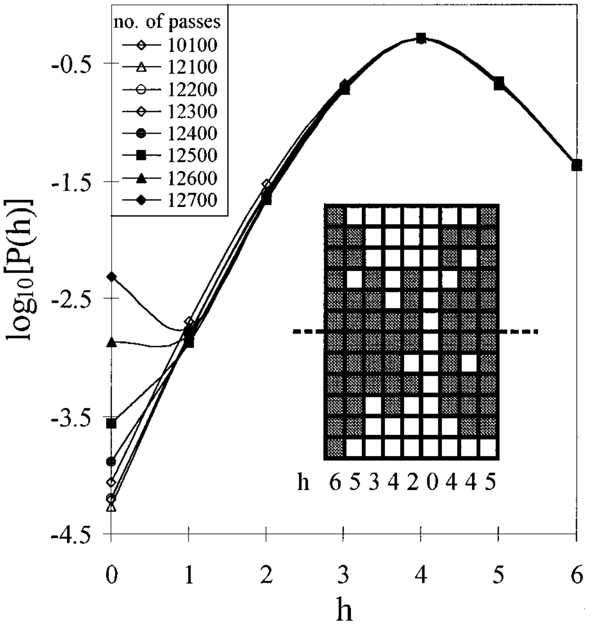

FIG. 3. Logarithm of the probability of finding h occupied sites in half-columns extending from either of the walls to the midplane (dashed line in the inset; counting for the lower-half columns is illustrated). Different symbols denote different times of the simulation; lines are guides to the eye. System size and parameters of the lattice gas model are given in Fig. 1.

water-vapor interfaces [19]. After 10^4 passes the liquid-gas interfaces are still fluctuating. When the two interfaces finally touch each other (after about 18 000 passes), a vapor cavity bridges across the surface and then expands to fill the confined region. The system then evolves to its thermodynamic stable state [20].

In Fig. 2 we show additional features that lead to evaporation by presenting liquid density cross sections at consecutive times, from a different run than presented in Fig. 1. At τ_1, a microscopic vapor ''tube'' forms across the two fluctuating liquid-vapor interfaces. At τ_2, the tube closes up and disappears [Fig. 2(a)]. At τ_4, the tube forms at another position. This time, the tube expands and evaporation occurs at τ_5 [Fig. 2(b)]. We identify these short wavelength fluctuations as important features involved in the evaporation process: microscopic vapor tubes appear across the interfaces, and disappear at later times. When they expand the evaporation takes place. The appearance of vapor tubes gives rise to the interaction decaying exponentially with separation, as predicted by Fishers [21]. These tubes contribute to the communication between the two liquid-gas interfaces [22], especially when the system is close to the transition state, i.e., just before the evaporation occurs. To study the formation of such tubes quantitatively let us define $P(h)$ as the probability that h sites in a half column are occupied (Fig. 3, inset):

$$P(h)=1/L^2\sum_{x,y}\ \delta\left(\sum_{z=z_1}^{z_2} n(x,y,z)-h\right), \tag{3}$$

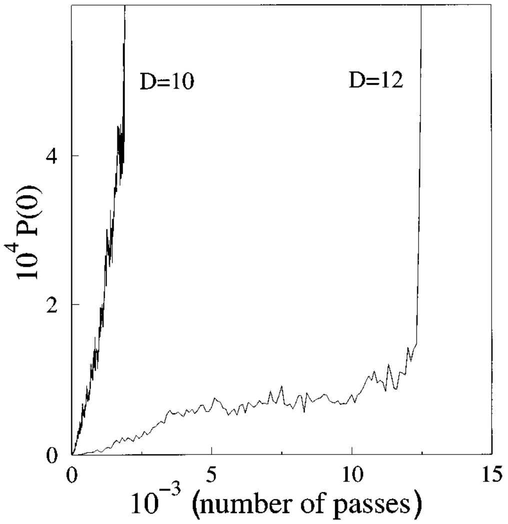

FIG. 4. Probability of observing empty half-columns (see Fig. 3), $P(0)$, as a function of the time of simulation for specified separation D.

where $n(x,y,z)=0,1$ and $(z_1,z_2)=$ $(1, D/2)$ or $(D, D/2+1)$. Figure 3 contains the data for log$P(h)$ vs h in a system before evaporation (from a different run than presented in Fig. 1). The peaks of the distributions are Gaussian. The peak positions and the widths do not change with time (number of passes), which means that the average interfacial positions and fluctuations do not change significantly. Prior to evaporation, for $h\leqslant 2$, the distributions are approximately exponential (linear on the logarithmic scale). When evaporation begins to occur (12 400 passes), only the probability of observing half-empty columns, $P(0)$, increases. When two half columns join, they form a vapor tube [Fig. 2(b)].

Figure 4 shows the effect of interfacial separation on evaporation. The probability of observing half empty columns increases with decreasing separation between surfaces. log$P(0)$ scales as $-\epsilon D/kT$ [21]. When the two vapor-liquid interfaces are close enough that the occurrence of vapor tubes becomes more frequent, evaporation occurs [sudden increase in $P(0)$] when one of these tubes expands and fills the confined region.

In conclusion, our findings suggest the pathway to evaporation of a metastable liquid between drying walls is driven by fluctuations of the liquid-gas interfaces that necessarily exist [1] at drying surfaces [23]. The early long-wavelength stage [24], corresponding to a detachment of the fluid from the surface, is followed by short wavelength fluctuations essential for the evaporation process, so the evaporation pathway cannot be fully captured with interfacial models [24] in which short wavelength fluctuations are integrated out. Due to the incompressibility of water, the long wavelength fluctuations of the two liquid-gas interfaces that we observe can be correlated even at large distances, an effect relevant to interpretations of long-ranged interaction between surfaces separated by metastable liquid.

We are grateful to D. Chandler, M. E. Fisher, S. Marcelja, V. A. Parsegian, and J. C. Wheeler for very helpful discussions. This work was supported by the ONR and the NSF.

[1] F. H. Stillinger, J. Solution Chem. **2**, 141 (1973).

[2] This is essentially the Kelvin equation for a fluid between finite plates. It is derived by equating the grand potential of a confined liquid $\Omega_l \sim -PV + 2A_w\gamma_{wl}$ and that of a confined vapor $\Omega_v \sim -P_v V + 2A_w\gamma_{wv} + A\gamma$, where $V \simeq A_w D$ is the volume of the confined region, $A_w \propto L^2$ the area of the wall, and $A \propto LD$ the area of the liquid-vapor interface. The $A\gamma$ term is relevant because of the finite lateral size of the cavity. For an incompressible fluid the difference in the bulk pressure, P, and the pressure of the coexisting vapor, P_v, is approximated by $\rho\Delta\mu$. For a derivation of an analogous equation for a particular geometry, see Ref. [3].

[3] L. J. Parker *et al.*, J. Phys. Chem. **98**, 8468 (1994).

[4] R. Evans, in *Liquids at Interfaces*, Proceedings of the Les Houches Summer School of Theoretical Physics, Les Houches, 1988, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (North Holland, Amsterdam, 1990), and references therein.

[5] V. V. Yaminski *et al.*, J. Colloid Interface Sci. **96**, 307 (1983); V. V. Yaminski and B. W. Ninham, Langmuir **9**, 3619 (1993).

[6] G. Gompper *et al.*, J. Chem. Phys. **101**, 3378 (1994); D. R. Berard *et al.*, J. Chem. Phys. **98**, 7236 (1993).

[7] A. Luzar *et al.*, J. Chem. Phys. **86**, 2955 (1987).

[8] A. Wallqvist and B. J. Berne, J. Phys. Chem. **99**, 2893 (1995).

[9] B. J. Berne, Proc. Natl. Acad. Sci. USA **93**, 8800 (1996); A. Luzar, Faraday Discuss. **103**, 205 (1996).

[10] The height of the free energy barrier ($\sim D^2$; Ref. [5]) is of the order of 1000 kT, when the two surfaces are 10 nm apart. The rate of nucleation can be estimated from $\sim \nu \times \exp(-\Delta F_a/kT)$, where ΔF_a is the activation free energy to form a nucleus, and ν is the prefactor frequency. In water, the prefactor is bound by the scale of microscopic motions, $1/\tau_{HB}$, where τ_{HB} is the hydrogen bond lifetime ~ 1 ps [Teixeira *et al.*, Phys. Rev. A **31**, 1913 (1985); A. Luzar and D. Chandler, Phys. Rev. Lett. **76**, 928 (1996)].

[11] H. K. Christenson and P. M. Claesson, Science **239**, 390 (1988); J. Wood and R. Sharma, Langmuir **11**, 4797 (1995); Y. I. Rabinovich and B. V. Derjaguin, Colloids Surface **30**, 243 (1988).

[12] With an Ising system that is equivalent to lattice gas models of fluids, one can reproduce the high surface tension of water.

[13] For a review until 1992, see H. K. Christenson, in *Modern Approaches to Wettability: Theory and Applications*, edited by M. E. Schreder and G. Loeb (Plenum Press, New York, 1992); R. H. Yoon and S. A. Ravishankar, J. Colloid Interface Sci. **179**, 391 (1996).

[14] Note that at large length scales, evaporation of a fluid confined between two drying walls is mathematically isomorphic to the condensation of a vapor between two wetting walls. In the latter case, the phenomenon is known as ‘‘capillary condensation.’’ Extensive discussions on the topic as applied to lattice-gas models are found in the reviews by A. O. Parry and R. Evans [Physica A **181**, 250 (1992)].

[15] K. Binder *et al.*, Ber. Bunsenges. Phys. Chem. **98**, 304 (1994), and references therein.

[16] $\epsilon = 1.653 k_B T$, $\mu = \mu_{\text{coex}} + \Delta\mu$, $a = 0.22$ nm. These values are correspond to the surface tension, $\gamma = \epsilon/2a^2$, for water at $T = 298$ K: $\gamma = 70$ mN/m, $\kappa_T = 4.58 \times 10^{-10}$ Pa^{-1}. Chemical potential at coexistence, $\mu_{\text{coex}} = -6\epsilon/2$, and $\Delta\mu$ is determined by the pressure: $\Delta\mu = \Delta P/\rho = 2.589 \times 10^{-4} k_B T$, with $\Delta P \sim 10^5$ Pa, $\rho = 1/a^3$.

[17] R. J. Glauber, J. Math. Phys. **4**, 294 (1963).

[18] For our system ($L \gg D$ and $\Delta\gamma = 0.98\gamma$), Eq. (1) predicts evaporation for $\Delta\mu < \epsilon/D = 0.13 k_B T$.

[19] X-ray scattering results suggest that capillary waves with wavelengths as small as 40 nm contribute to the roughness of pure water-vapor interface [D. K. Schwartz *et al.*, Phys. Rev. A **41**, 5687 (1990)].

[20] To deal with chemical inhomogeneity characteristic for real systems (interference fringe patterns, measuring refractive index on 0.1 nm distance, do not reveal a dry surface, because $\gamma_{\text{water/air}} > \gamma_{\text{water/oil}}$) the above simulations were repeated for some representatives of nonuniform hydrophobic surfaces, by randomly distributing hydrophilic patches (with patch size 8×8 in units of lattice spacing; ϵ_s on the patches was 1.01 ϵ) on drying surfaces. As expected, hydrophilic patches lengthened the time for the evaporation to occur, because the pinning fields (attractive sites) quench the long wavelength fluctuations.

[21] M. E. Fisher and D. S. Fisher, Phys. Rev. B **25**, 3192 (1982).

[22] M. E. Fisher (private communication).

[23] In view of the present results, we can understand why recent molecular simulation studies [J. Forsman *et al.*, J. Phys. Chem. **100**, 15 005 (1996)] failed to reproduce experimentally observed and thermodynamically predicted cavitation at large separations. These studies are restricted to small, periodically replicating hydrophobic plates which act to suppress capillary-wave fluctuations (Ref. [19]).

[24] W. Helfrich, in *Liquids at Interfaces*, Proceedings of the Les Houches Summer School of Theoretical Physics, Les Houches, 1988, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (North Holland, Amsterdam, 1990); L. V. Mickeev and J. D. Weeks, Physica A **177**, 495 (1991).