Lattice study of a Janus interface

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A lattice gas simulation of water between a hydrophobic plate and a hydrophilic plate (a Janus interface) shows large fluctuations in the number of liquid cells in contact with the hydrophobic plate, and a power spectrum similar to the experimental results that Zhang, Zhu, and Granick found [X. Y. Zhang, Y. X. Zhu, and S. Granick, Science **295**, 663 (2002)] when measuring viscous response in a Janus system. Study of the spatial Fourier modes of the liquid-vapor interface suggests that interface fluctuations with length scales between approximately 1.5 and 20 nm cause the effects observed in the simulation.

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I. INTRODUCTION

The interactions between water and hydrophobic and hydrophilic surfaces are important in many areas of research, including such diverse fields as lubrication and protein folding. In order to study hydrophobic effects with as few additional complications as possible, the behavior of water confined between two hydrophobic plates has been the subject of many experimental and theoretical studies [1–7]. More recently, experimentalists and theorists have also examined the behavior of water confined between one hydrophobic and one hydrophilic plate [8,9], the so-called Janus interface, to learn how water reacts to the competing effects of the plates.

While performing experiments to study the response of water in a Janus system to shear deformations, Zhang *et al.* [8] found that the fluctuations about the mean value of the viscous response were typically 25–50 % of the mean value, but ranged up to 100%. These fluctuations are extraordinarily large compared to the fluctuations observed when both plates are hydrophilic, and it is surprising that they do not average out over the plates, which are approximately 10 μm on a side. When the time series of the viscous response was Fourier analyzed, it was found that the resulting power spectrum is independent of frequency at low frequencies, but at approximately $f=0.001$ Hz, the power spectrum crosses over to power-law dependence on frequency, with an apparent exponent near f^{-2}. For frequencies greater than $f=0.01$ Hz, the power spectrum again levels off and becomes seemingly independent of frequency.

It has been predicted [10] that when water encounters a large hydrophobic solute, such as the hydrophobic plate in a Janus system, it forms a semi-free liquid-vapor interface near the hydrophobic surface. The surface is unable to form hydrogen bonds with the water, and the formation of an interface allows the water to form a more energetically favorable hydrogen bonding network. Zhang *et al.* suggested that their results are caused by fluctuations of such an interface. They further identified the time scale of $\sim 10^3/2\pi$ s, the inverse of the frequency at which power-law behavior begins in their power spectrum, as the lifetime of vapor or a vapor bubble.

This paper presents the results of a simulation designed to test the hypothesis that fluctuations in the liquid-vapor interface are the source of the large fluctuations and power spectrum seen experimentally. We chose to study a lattice gas because it is a simple model system that can be used to examine the large length scale behavior of a liquid between competing solvophobic and solvophilic plates, and can also describe interface fluctuations. After describing the details of the simulation in Sec. II, results are presented in Sec. III, and the paper is concluded with a brief discussion.

II. SIMULATION DETAILS

The system in the simulation is an $L\times L\times R$ cubic lattice gas, where L is the side length of the hydrophobic and hydrophilic plates in the x and y directions in units of the lattice spacing a, and R is the distance between the plates, in the z direction, as shown in Fig. 1. L and R were chosen to be 128 and 8, respectively. Each cell i has an associated variable n_i which labels the cell as liquid ($n_i=1$) or vapor ($n_i=0$). The cells around the edges of the system are constrained to have $n_i=1$ in order to ensure that there is no evaporation between the plates. The cells in the $z=0$ and $z=7$ layers represent the hydrophobic and hydrophilic plates, respectively, and are constrained to have $n_i=1$ at all times so that liquid in the bulk always interacts with the plates. The remaining unconstrained cells in the bulk obey the Hamiltonian

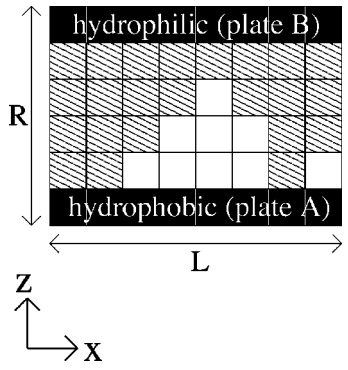

FIG. 1. Cross section of the lattice in the simulation. A possible configuration of vapor (white) cells and liquid (shaded) cells is also shown.

$$\beta H = -\beta\epsilon \sum_{\langle ij \rangle} n_i n_j - \beta\mu \sum_i n_i - \beta\sigma_A \sum_{i\ \mathrm{nn}A} n_i - \beta\sigma_B \sum_{i\ \mathrm{nn}B} n_i, \tag{1}$$

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann's constant, $\langle ij \rangle$ indicates a sum over nearest neighbors, and $i\ \mathrm{nn}A$ and $i\ \mathrm{nn}B$ indicate sums over cells adjacent to plate A (the hydrophobic plate) or B (the hydrophilic plate).

The parameters $\beta\epsilon$ and $\beta\mu$ have the same values as in the simulation of Luzar and Leung [7], $\beta\epsilon = 1.26$ and $\beta\mu = -6\epsilon/2 + 1.84 \times 10^{-4}$, chosen to match the surface tension and isothermal compressibility of water at 300 K. With these parameters, the lattice spacing a corresponds to 0.193 nm, so the plates are approximately 1.5 nm apart, within the range studied by Zhang *et al.* However, the plates in the simulation have a side length of approximately 25 nm, which is significantly smaller than the experimental plates. The interactions with the plates are $\beta\sigma_B = \beta\epsilon$ and $\beta\sigma_A = 0.1\beta\epsilon$, which gives a contact angle of 143° at the hydrophobic plate, comparable to the contact angle of approximately 120° in the experimental system.

Zhang *et al.* were careful to show that although they applied shear forces to the hydrophobic plate and measured the response of the water in their experiments, the system was still in the linear response regime, so fluctuations present in the nonequilibrium experiment should be present at equilibrium as well. To make the simulation as simple as possible, we chose to study an equilibrium lattice gas propagated by Metropolis Monte Carlo, according to the Hamiltonian in Eq. (1) for approximately 140 000 passes through the lattice. The contact density, defined to be the number of liquid cells in contact with the hydrophobic plate,

$$c(t) = \sum_{i\ \mathrm{nn}A} n_i(t) \tag{2}$$

was calculated as a function of time, where time is measured in units of Monte Carlo passes through the lattice. $c(t)$ should be related to the viscosity of water near the hydrophobic plate, because the viscosity measured at the plate should increase with the amount of liquid (rather than vapor) in contact with the plate.

The distance of the liquid-vapor interface h from the hydrophobic plate, as a function of (x,y) and time, was also calculated in the simulation. The interface in the (x,y) column is defined to be located at the average of the distances of the liquid cell closest to, and the vapor cell farthest from, the hydrophobic plate in that column, reminiscent of Weeks' derivation of the capillary wave model [11,12]:

$$h(x,y) = \tfrac{1}{2}\{\max_{(x,y)}[z_i(1-n_i)] + \min_{(x,y)}[z_i n_i]\}. \tag{3}$$

The value of h when liquid is in contact with the hydrophobic plate is $h = (0+1)/2 = 0.5$, and increases in increments of 1 to its maximal value of $h = (6+7)/2 = 6.5$, for vapor in contact with the hydrophilic plate.

The fact that the edges of the system are constrained to be liquid for all z leads to a boundary region of approximately 12 cells from each edge where the fluctuations of h are smaller than those in the middle of the lattice. Results reported below for the $104 \times 104 \times 8$ lattice resulting from ignoring the outer perimeter of 12 cells are virtually indistinguishable from results with a boundary of 32 cells, so the lattice seems to be large enough to study a Janus interface.

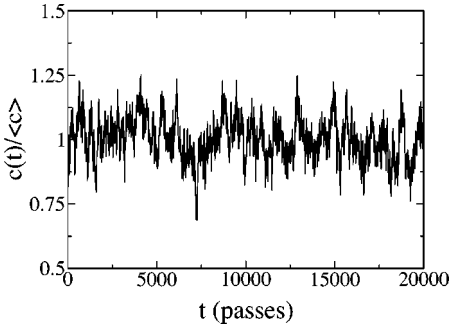

FIG. 2. A portion of the time series of the contact density, normalized by the time-averaged value $\langle c \rangle = 2673$. The value of the average contact density indicates that approximately 25% of cells in the $z = 1$ layer have $n_i = 1$ at any given time.

Inside the boundary region, the time- and space-averaged interface position is $\langle h \rangle = 2.0$, which means that on average, the first one or two layers in contact with the hydrophobic plate are vapor. Because the plate is so significantly dewetted, changes in the amount of liquid in contact with the plate in our simulation are caused largely by fluctuations of the liquid-vapor interface, rather than by spontaneously forming vapor bubbles. To the extent that this lattice gas is an accurate description of the experimental Janus system, spontaneously forming vapor bubbles do not seem to be important contributors to the results.

III. RESULTS

The contact density $c(t)$ and interface $h(x,y;t)$ were saved every ten passes through the lattice during the simulation. A section of the time series for the contact density measured over the central $104 \times 104 \times 8$ lattice is shown in Fig. 2. The fluctuations in $c(t)$ range up to approximately 25% of the mean, which is within the range seen experimentally. The power spectrum resulting from the time Fourier transform of $c(t)$, $S(f) = |\tilde{c}(f)|^2$, where

$$\tilde{c}(f) = (\Delta t) \sum_{t=0}^{t_{max}} c(t) \exp[2\pi f t / t_{max}] \tag{4}$$

and Δt is the time between samples (ten passes in our simulation) is shown on a log-log plot in Fig. 3. The power is independent of frequency until approximately $f = 0.001$ passes^{-1}, where it begins to drop off. The best-fit line to the data between $f = 0.001$ passes^{-1} and $f = 0.015$ passes^{-1} has a slope of -1.48 ± 0.04, less than the apparent power law of f^{-2} seen experimentally. There seems to be a slight leveling off of the power as a function of frequency at high f, but the data are so noisy that it is diffi-

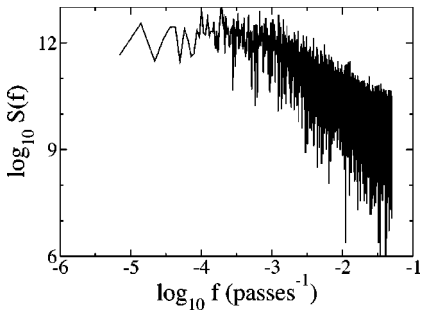

FIG. 3. The power spectrum $S(f)$ resulting from the time Fourier transform of $c(t)$.

cult to quantify. The contact density $c(t)$ thus exhibits behavior surprisingly similar to the viscous response in the experiments of Zhang *et al.*

In order to try to understand the cause of the fluctuations and power spectrum of $c(t)$, the dynamics of the liquid-vapor interface were studied. The characteristic length scales of fluctuations of the liquid-vapor interface relevant to fluctuations in the contact density can be inferred from an analysis of the spatial Fourier modes of the interface. The Fourier modes $\hat{h}(k_x,k_y;t)$ of the interface can be defined with the equation

$$\hat{h}(k_x,k_y;t) \equiv (\Delta x)^2 \sum_{x,y=0}^{N} h(x,y;t) e^{-2\pi i(k_x x + k_y y)}, \quad (5)$$

where Δx is the spatial resolution (a in the simulation) and N is the number of cells in each dimension (104 in the simulation).

Figure 4 shows the time autocorrelation function of the $\mathbf{k}=(0,0)$ spatial Fourier mode of the interface,

$$F(t) = \langle \delta\hat{h}(0,0;0)\, \delta\hat{h}(0,0;t) \rangle, \quad (6)$$

where $\delta\hat{h}(k_x,k_y;t) = \hat{h}(k_x,k_y;t) - \langle \hat{h}(k_x,k_y;t) \rangle$, as a function of time. $F(t)$ decays on a time scale of approximately 1000 passes, which is the inverse of the frequency near which power-law behavior begins in $S(f)$. In the sense that fluctuations of the whole interface correspond to changes in the amount of vapor near the hydrophobic plate, $f \sim 0.001$ passes^{-1} corresponds to the lifetime of vapor fluctuations, similar to the conclusion of Zhang *et al.* The fact

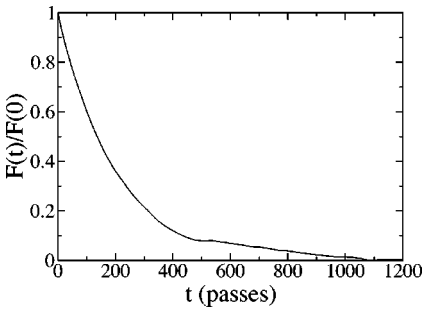

FIG. 4. The time autocorrelation function for fluctuations in the $\mathbf{k}=(0,0)$ spatial Fourier mode of the liquid-vapor interface.

that the relaxation time of fluctuations of the entire interface corresponds to the frequency at which power-law behavior begins in $S(f)$ suggests that interface fluctuations, rather than spontaneously forming vapor bubbles, are the cause of the fluctuations in $c(t)$.

If D is the smallest length scale of fluctuations in the interface relevant to fluctuations in the contact density, then contributions to $h(x,y;t)$ from Fourier modes with wavelengths smaller than D should be minimal. A new function, $h_D(x,y;t)$, with no contributions from short-wavelength Fourier modes, can be created by taking the inverse transform of Eq. (5), but cutting off the sum over wave vectors at $k_D = 1/D$:

$$h_D(x,y;t) = \frac{1}{N^2} \sum_{k_x=0}^{k_D} \sum_{k_y=0}^{k_D} \hat{h}(k_x,k_y;t) e^{2\pi i k_x x} e^{2\pi i k_y y}. \quad (7)$$

When the small-wavelength Fourier modes are not included, $h_D(x,y;t)$ is no longer restricted to take on discrete values. The lack of high-frequency Fourier modes also smoothes out the interface sufficiently that it seldom comes in contact with the hydrophobic plate, so the definition of $c(t)$ in Eq. (2) is no longer useful in the context of fluctuations of $h_D(x,y;t)$. Instead, a clipping function is used to create a function $c_D(t)$,

$$c_D(t) \equiv \sum_{x,y} \Theta[\lambda - h_D(x,y;t)], \quad (8)$$

where Θ is the Heaviside function, and the smooth interface $h_D(x,y;t)$ is considered to be in contact with the hydrophobic plate when $h_D(x,y;t) \leqslant \lambda$. λ is chosen for each D so that the time average of $c_D(t)$ equals the time average of the total contact density $c(t)$.

To estimate the smallest-wavelength fluctuations of the interface relevant to the fluctuations in the $c(t)$ time series that was collected during the simulation, the functions $h_D(t)$ with $D=6a$, $7a$, $8a$, $9a$, $10a$, $12a$, $14a$, and $16a$ were computed from the time series of $h(x,y;t)$ collected during the simulation, and the corresponding λ's ranged from $\lambda = 1.50$ for $D=6a$, to $\lambda = 1.67$ for $D=16a$. The power spectra $S_D(f) = |\tilde{c}_D(f)|^2$ were computed, and the slope of each curve was measured on a log-log plot between $f = 0.001$ passes^{-1} and $f = 0.015$ passes^{-1}, to see how many Fourier modes could be removed from $h(x,y;t)$ but still obtain a slope statistically indistinguishable from the slope of $S(f)$ over the same frequency range. It should be noted that this calculation was carried out as a technique to analyze the data collected during the simulation, and not to make a statement about the exact power-law behavior of $S(f)$, since the data are quite noisy. The value of the slope for each D is displayed in Table I. The largest value of D with a slope still within one standard deviation of the true slope of $S(f)$, -1.48 ± 0.04, is $D=8a$, which suggests that fluctuations with wavelengths smaller than $8a$ are not important to the fluctuations in $c(t)$.

When a similar calculation was performed where the small-$|\mathbf{k}|$ (large-wavelength) Fourier modes of the interface

TABLE I. Slope of the linear regime on a log-log plot of $S_D(f)$ for different values of D (the units of D are lattice spacings a). The slopes have a standard deviation of approximately 0.04.

D	Slope
6	−1.50
7	−1.48
8	−1.46
9	−1.42
10	−1.41
12	−1.40
14	−1.36
16	−1.34

were progressively removed from the sum in Eq. (5), the slope of the resulting power spectrum was far outside of the standard deviation of the true slope. In order to estimate the largest length scale of interface fluctuations relevant to fluctuations in $c(t)$, a short simulation was run on a larger lattice. A simulation identical to that described in Sec. II, but with $L=1024$, was run for approximately 2000 Monte Carlo passes through the lattice. The power spectrum of the interface fluctuations, $|\hat{h}(k_x,k_y;t)|^2$ was calculated every ten passes, and the time-averaged power spectrum is shown in Fig. 5, plotted versus $k=|\mathbf{k}|$. The power begins to depend on k at approximately $k=0.01a^{-1}$, which suggests that fluctuations over length scales up to approximately $100a$ are relevant in the simulation. Thus, it seems that interface fluctuations over length scales between $8a$ ($\sim$1.5 nm) and $100a$ ($\sim$19 nm) cause the fluctuations in $c(t)$ in the simulation.

Additional simulations were performed to determine the effects of the parameters of the model upon the results described above. Simulations at higher and lower temperatures (corresponding to physical temperatures between 290 and 320 K), and with different values of $\beta\sigma_A$, were carried out. $\beta\epsilon$ and $\beta\mu$ were not varied independently so that the system would remain close to liquid-vapor coexistence, and $\beta\sigma_B$ was not varied because the interface is so far from the hydrophilic plate that the results would be unchanged.

The results of these parameter changes were consistent with physical intuition. As temperature increases, the interface fluctuates more, causing larger-magnitude fluctuations in $c(t)$ and also causing $\langle h\rangle$ to increase (that is, the interface moves farther from the hydrophobic plate). The power in the spatial Fourier modes of the interface increases, and the leveling off of the power spectrum at small k moves to smaller k, indicating that larger length-scale interface fluctuations are important, as would be expected. The behavior of $S(f)$ does not change noticeably over the temperature range studied, and the linear regime begins at approximately the same value of f.

$\beta\sigma_A$ was varied from 0.0 to $0.2\beta\epsilon$. Increasing $\beta\sigma_A$ corresponds to making the hydrophobic plate more hydrophilic, and as would be expected, doing so decreases $\langle h\rangle$ and the magnitude of the fluctuations in $c(t)$, and increases $\langle c\rangle$. The power in the interface Fourier modes decreases substantially, and the power spectrum levels off at much larger values of k, indicating that large-wavelength Fourier modes become less important in the interface dynamics, which is reasonable since the interface is so close to the plate and thus has little room in which to move. When $\beta\sigma_A$ is increased to $0.2\beta\epsilon$, $\langle h\rangle=0.89$, indicating that the hydrophobic plate is almost completely wetted, and the linear regime in $S(f)$ disappears.

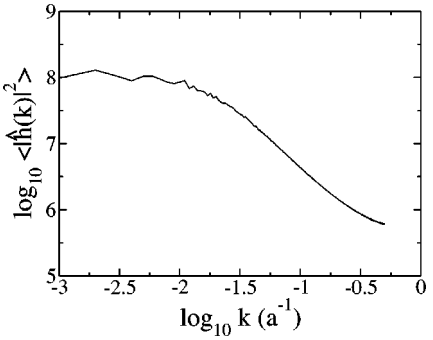

FIG. 5. Time averaged power spectrum of interface fluctuations as a function of $k=|\mathbf{k}|$.

IV. DISCUSSION

The results of the simulation described above are very similar to the experimental behavior of water at a Janus interface, and support the hypothesis that the large fluctuations and power spectrum of viscous response that were seen experimentally can be attributed to the fluctuating liquid-vapor interface interacting with competing hydrophobic and hydrophilic walls. The power spectrum of fluctuations in $c(t)$ has apparent power-law behavior at intermediate frequencies, but the power law is a less rapidly decaying function of frequency then the apparent experimental value of f^{-2}. However, the combination of the noise in the power spectrum from the simulations, and the lack of a precise experimental value, means there is no firm basis for a detailed discussion of the exact value of the exponent. Regardless of that exact value, a Fourier analysis of the liquid-vapor interface suggests that fluctuations of the interface over length scales between 1.5 and 19 nm cause the fluctuations in $c(t)$ that were observed in the simulation. It is probable that fluctuations over these length scales would be averaged out in a simulation of a system with the much larger plates studied experimentally, but it is interesting that such large fluctuations could be observed in such a simple system.

ACKNOWLEDGMENTS

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