Prewetting Boundary Tensions from Monte Carlo Simulation

Jeffrey R. Errington* and David W. Wilbert

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260-4200, USA

(Received 12 July 2005; published 23 November 2005)

We examine the boundary tension of a model system along the prewetting saturation line. Boundary tensions are evaluated through a combination of finite-size scaling and grand canonical Monte Carlo simulation. The model system consists of Lennard-Jones particles interacting with a single structureless surface. After scaling our dimensionless results with a characteristic force, we obtain a value of 2×10^{-11} N for the boundary tension at the system's wetting temperature. This estimate is consistent with theoretical and recent experimental values.

DOI: 10.1103/PhysRevLett.95.226107 PACS numbers: 68.03.Cd

Prewetting transitions represent one of the many interesting and diverse surface phase transformations observed when a fluid is in the presence of a substrate. Phase equilibrium is characterized by coexistence between thin and thick films absorbed on a substrate. These phase transitions are often observed with substrates of moderate strength and occur at a pressure below the bulk saturation value at a given temperature. Akin to bulk vapor-liquid saturation lines, prewetting lines terminate at critical end points. At the low temperature end, prewetting saturation lines terminate at a wetting temperature, which denotes the point at which fluid adsorption switches from partial to complete wetting. The existence of these transitions was first predicted theoretically by Cahn [1] and Ebner and Saam [2]. Since their pioneering work, the prewetting transition has been the subject of numerous theoretical and computational studies. Experimentally, these transitions have been observed for systems such as ^{4}He on Cs [3,4] and the mixture water-2, 6-lutidine on silica [5].

Prewetting transitions are inherently two dimensional in nature. As a result, the boundary between two coexisting phases is a one-dimensional structure (a line), defined by the edge-on meeting of a thin and a thick film. Such a boundary is associated with an inhomogeneity in density, which gives rise to an excess free energy. The magnitude of this quantity, per unit length of the interfacial line, defines the boundary tension. Conceptually, this property is analogous to the surface tension between two bulk phases [6]. Using theoretical arguments, Schick and Taborek have shown that boundary tension plays an important role in determining the lifetime of wetting films [7]. Relative to the determination of prewetting surface phase properties, this interfacial quantity has proven particularly challenging to characterize. Although theoretical estimates for the boundary tension have been obtained, direct experimental measurement and calculation through molecular simulation have proven difficult.

In this Letter, we use a combination of Monte Carlo simulation and finite-size scaling techniques to obtain estimates of the boundary tension for a model system. We utilize a model in which monatomic particles interact with a single structureless surface. The energy of interaction u_{ff} between any two fluid particles separated by a distance r is given by the truncated Lennard-Jones 12-6 potential,

$$u_{\mathrm{ff}}(r) = \begin{cases} 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] & \text{for } r < r_c \\ 0 & \text{for } r > r_c \end{cases}, \tag{1}$$

where ε and σ are energy and size parameters, respectively, and the cutoff distance r_c has a value of 2.5σ. The energy of interaction u_{sf} between the substrate and a fluid particle separated by a distance z is given by the Lennard-Jones 9-3 potential,

$$u_{\mathrm{sf}}(z) = \frac{2\pi}{15}\rho_{\mathrm{w}}\sigma_{\mathrm{w}}^3\varepsilon_{\mathrm{w}}\left[\frac{2}{15}\left(\frac{\sigma_{\mathrm{w}}}{z}\right)^9 - \left(\frac{\sigma_{\mathrm{w}}}{z}\right)^3\right] \tag{2}$$

with $\rho_{\mathrm{w}}\sigma_{\mathrm{w}}^3 = 0.988$, $\varepsilon_{\mathrm{w}}/\varepsilon = 1.2771$, and $\sigma_{\mathrm{w}}/\sigma = 1.0962$. From this point forward, all quantities are made dimensionless using ε and σ as characteristic energy and length scales, respectively. The model parameters adopted in this work were originally introduced by Ebner and Saam to describe the adsorption of argon on a solid carbon dioxide surface [2]. Since its introduction, this model has been used in numerous theoretical [8–11] and simulation [12–17] studies to investigate prewetting phenomena. These studies indicate that the model system exhibits prewetting phase behavior over a relatively broad range of temperatures, with a wetting temperature of $T_{\mathrm{w}} = 0.581$ [17,18] and critical prewetting temperature of $T_{\mathrm{pwc}} \approx 0.92$ [14].

The finite-size scaling formalism of Binder [19] is used to determine boundary tension values. In this approach, a true boundary tension value τ_b at a given inverse temperature $\beta = 1/kT$ (k is the Boltzmann factor) is related to a set of apparent system-size-dependent boundary tension values $\tau_{b,L}$, obtained through a series of molecular simulations with varying substrate area $A = L^2$, through the scaling relationship,

$$\beta\tau_{b,L} = c_1\frac{1}{L} + c_2\frac{\ln L}{L} + \beta\tau_b, \tag{3}$$

where c_1 and c_2 are constants. The expression suggests that the term $\beta\tau_{b,L}$ becomes linear in the scaling variable $\ln(L)/L$ as the system size approaches infinity. The formalism enables one to extrapolate the true infinite-system-size interfacial tension from a series of finite-system-size calculations.

Apparent system-size-dependent boundary tensions are directly related to the free energy barrier a system must traverse when transforming from one surface phase to another. For a prewetting transition, the relevant macrostate variable that connects two coexisting phases is the surface density. It follows that the magnitude of the free energy barrier F_L can be written in terms of the probability Π of finding the system with a surface density corresponding to one of the two saturated phases (Π_{thin} and Π_{thick}), relative to the probability of the least likely macrostate along the path connecting the saturated states (Π_{min}),

$$\beta F_L = \tfrac{1}{2}(\ln\Pi_{\text{thin}} + \ln\Pi_{\text{thick}}) - \ln\Pi_{\text{min}}. \tag{4}$$

The system-size-dependent boundary tension is given by the magnitude of the free energy barrier put unit length of the interfacial line, $\tau_{b,L} = F_L/2L$, where the 2 appears in the denominator due to the presence of two interfaces within a given simulation cell. Provided an algorithm can be identified that produces a surface density probability distribution over a range of states that includes both coexisting phases, we now have a means to calculate boundary tensions.

Surface density probability distributions are obtained using grand canonical transition-matrix Monte Carlo simulation [20]. Simulations are conducted in a standard grand canonical ensemble [21] where the volume $V = AH$, chemical potential μ, and temperature T are held constant and the particle number N and energy E fluctuate. The surface density is given by N/A, and is therefore directly proportional to the particle number. During a simulation, probabilities of accepting attempted transitions between states with different values of the particle number are monitored [22]. At regular intervals throughout a simulation, this information is used to obtain an estimate of the particle number (surface density) probability distribution $\Pi(N)$. To ensure that all densities are sampled adequately, a multicanonical sampling procedure [23] is used to drive the simulation towards low probability states. Over time, all densities of interest are sampled with roughly uniform frequency. The end result is an efficient self-adaptive method for determining a surface density probability distribution over a specified range of densities (typically a range that corresponds to the densities of two potentially coexisting phases). Once a probability distribution has been collected at a given value of the chemical potential, histogram reweighting [24] is used to obtain the probability distribution at other values of the chemical potential. At conditions close to coexistence, the two coexisting phases appear as distinct peaks within the distribution. The saturation point is determined by identifying a chemical potential that produces equal areas under the peaks of the bimodal distribution. This approach has been used recently to accurately determine the prewetting phase behavior of the model studied in this work [17].

The method outlined above is used to calculate the boundary tension at temperatures spanning from just above the wetting temperature to the prewetting critical temperature. Simulations are conducted with a rectangular parallelepiped cell with periodic boundary conditions applied in the x and y directions. The cell is closed at each end of the z axis, with an adsorbing wall at one end and a hard wall at the other. For a given temperature, a series of grand canonical transition-matrix Monte Carlo simulations are completed in which the substrate area is varied between $A = 49$ (7×7) and $A = 400$ (20×20). For a given series of substrate areas, the distance between the adsorbing and hard walls is kept constant at a value between $H = 20$ and $H = 40$.

Representative surface density probability distributions for a range of system sizes at $T = 0.75$ are displayed in Fig. 1. For relatively small system sizes and high temperatures, the probability varies relatively smoothly with density. As the system size increases or the temperature is lowered, distinct regions begin to emerge within the distribution. Similar to the bulk liquid-vapor case [25], each of these regions corresponds to a different structural geometry. For the prewetting system studied here, one may observe a variety of inhomogeneous two-dimensional structures, including circular-shaped droplets in an otherwise homogenous vapor, system-spanning rectangular-shaped slabs, and circular-shaped voids in an otherwise homogenous surface film.

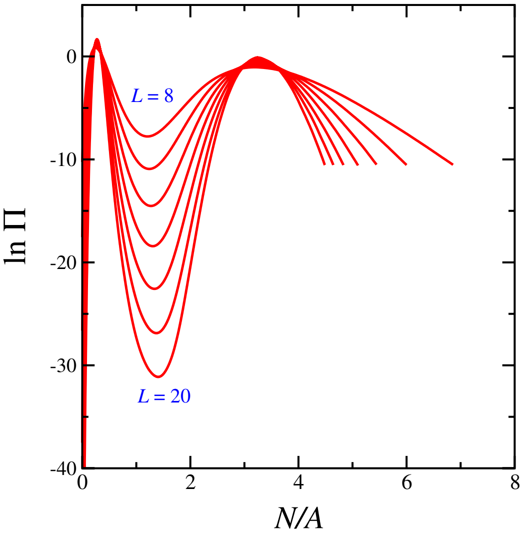

FIG. 1 (color online). The logarithm of the probability of observing a system with a given surface density under saturation conditions at $T = 0.75$. Curves from top to bottom are for $L = 8$ through $L = 20$ in increments of 2.

The system-size dependence of apparent boundary tension values is shown in Fig. 2. At temperatures sufficiently below the prewetting critical temperature, these values monotonically increase with system size. In contrast, for near-critical conditions, the apparent boundary tensions decrease with increasing system size. Similar behavior is observed for the system-size dependence of bulk interfacial tensions [25]. We find that the apparent boundary tensions vary linearly with the scaling variable $\ln(L)/L$ for systems with surface areas of $A = 144$ and larger. A total of five data points are used to extrapolate infinite-system-size values.

Our estimates of the boundary tension are provided as a function of temperature in Fig. 3. As pointed out by Indekeu [26], the prewetting critical temperature is identified as the first point at which the boundary tension reaches a value of zero from below. It is at this temperature where the two coexisting phases become indistinguishable. Our results indicate that the prewetting critical temperature is $T_{\mathrm{pwc}} = 0.875$. This value is approximately 5% lower than the recent estimate of Shi *et al.* [16], $T_{\mathrm{pwc}} \approx 0.92$, and in good agreement with the estimate of Bojan *et al.* [14], $T_{\mathrm{pwc}} \approx 0.88$. Shi *et al.* located the critical point by examining finite-system-size density probability distributions, generated using multiple-histogram reweighting, to identify the first temperature at which the free energy barrier between coexisting phases vanishes. Bojan *et al.* located the critical point by determining the first temperature at which adsorption isotherms, obtained from grand canonical simulations, cease to display a jump discontinuity. Both groups indicate the importance of finite-size effects in locating the critical point and describe their results as approximate. In this work, we obtain an accurate value for the prewetting critical temperature by rigorously accounting for the influence of system size.

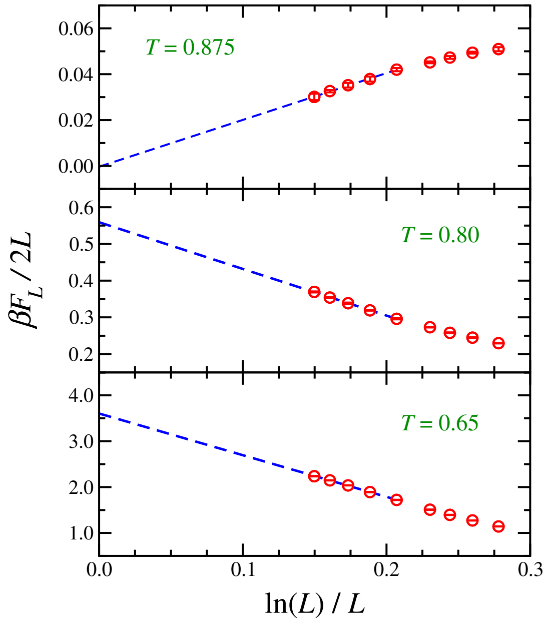

FIG. 2 (color online). Apparent system-size-dependent boundary tensions as a function of system size. The plots from top to bottom are for $T = 0.875$, $T = 0.80$, and $T = 0.65$. Circles represent simulation data and the dashed lines provide an extrapolation to the true infinite-system-size boundary tension. Extrapolations are performed using data from systems with $12 \leq L \leq 20$.

The wetting temperature represents the second terminal point on the prewetting line. To approximate the boundary tension at the wetting temperature $\tau_{b,\mathrm{w}}$, we fit the data to a functional form developed by both Indekeu [26] and Blokhuis [27], $\tau_b = \tau_{b,\mathrm{w}} - a(T - T_{\mathrm{w}})^{1/2} + b(T - T_{\mathrm{w}})$, where a and b are fitting parameters. This approach leads to a value of $\tau_{b,\mathrm{w}} = 5.1$, which is in reasonably good agreement with theoretical estimates. Using a mean-field free energy model and a van-der-Waals-based theory, Perković *et al.* obtained a limiting reduced boundary tension of $\tau_{b,\mathrm{w}} = 1.57$ [28]. Scaling our dimensionless estimate by a characteristic force kT/σ, using a temperature of 300 K and length scale of 10 Å [29], gives a value of 2×10^{-11} N for the boundary tension at the wetting temperature. This estimate is roughly an order of magnitude larger than the value of 4×10^{-12} N obtained by Dobbs, who used a Cahn-type theory to predict the limiting value of the boundary tension of n-pentane on water [30].

Although direct experimental measurements of the boundary tension have not been completed, one can obtain an estimate of $\tau_{b,\mathrm{w}}$ by considering the line tension related to the three-phase contact line associated with the formation of liquid droplets on a solid substrate below the wetting temperature. Theoretical arguments, first described by Widom [31,32] and later supported by mean-field calculations [28], indicate that the values of the line and boundary tensions are equivalent at the wetting temperature. This

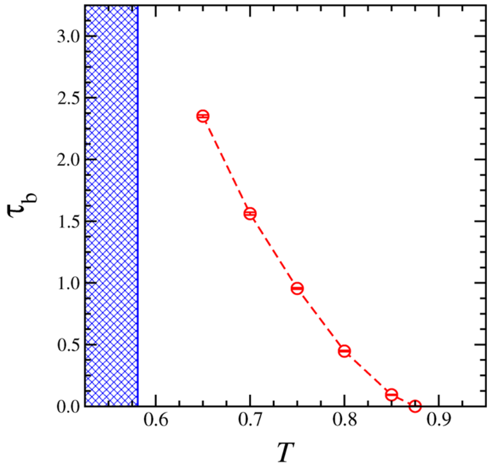

FIG. 3 (color online). Boundary tension as a function of temperature. The hatched region corresponds to states below the wetting temperature. The dashed line connecting the points simply serves as a guide to the eye. Complete boundary tension curves span between the wetting and critical prewetting temperatures.

finding enables one to estimate the value of $\tau_{b,\mathrm{w}}$ through measurement and subsequent extrapolation of the line tension. While a wide range of estimates for $\tau_{b,\mathrm{w}}$ have been generated using this approach (spanning from 10^{-12} to 10^{-5} N), recent measurements with carefully characterized surfaces suggest that experimental values for $\tau_{b,\mathrm{w}}$ lie close to the simulation value obtained in this work. For example, Wang *et al.* found a limiting value of 1.2×10^{-9} N for the line tension when studying the wetting behavior of *n*-octane and 1-octene on a hexadecyltriclorosilane coated silicon wafer [33,34]. In another recent study, focusing on the adsorption of hexaethylene glycol on a silicon wafer, Pompe obtained a value of 7.8×10^{-11} N for $\tau_{b,\mathrm{w}}$ [35].

The results presented here are satisfying in that it appears that there is reasonable agreement between experimental, theoretical, and now simulation estimates of the boundary tension. This study also suggests that molecular simulation could play an important role in providing a better understanding of many of the outstanding issues related to the interfacial properties of surfaces phases. For example, with an appropriate means to vary the roughness of a model surface, one could systematically investigate the influence of surface molecular roughness on line and boundary tensions. It is this factor that is often cited as the reason for the early experimental line tension values that are orders of magnitude larger than theoretical predications. Given that one can precisely specify the intermolecular forces in a molecular simulation, this tool could provide insight into how wetting behavior evolves with the range of intermolecular interactions. Finally, simulation could help to resolve the relationship between the line tension and droplet contact angle, an area where theory and experiment are not in complete agreement [34].

In summary, we have used molecular simulation to calculate the boundary tension for a model system along the prewetting saturation line. Finite-size scaling techniques are used to determine true boundary tension values from system-size-dependent free energy barriers, which are obtained from grand canonical transition-matrix Monte Carlo simulations. Our boundary tension values are within the same order of magnitude as mean-field theoretical results and are in relatively good agreement with a number of recent experimental values. Collectively, the results from this and previous studies suggest that the magnitude of the boundary tension for systems with short-range interactions is in the vicinity of 10^{-11} N.

This material is based upon work supported by the National Science Foundation under Grant No. CTS-0238772. We also gratefully acknowledge the donors of the American Chemical Society Petroleum Research Fund for their support under Grant No. 43452-AC5. Computational resources were provided in part by the University at Buffalo Center for Computational Research.

*Electronic address: jerring@buffalo.edu

[1] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).
[2] C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).
[3] J. E. Rutledge and P. Taborek, Phys. Rev. Lett. **69**, 937 (1992).
[4] K. S. Ketola, S. Wang, and R. B. Hallock, Phys. Rev. Lett. **68**, 201 (1992).
[5] L. Ghaicha, M. Privat, L. Tenebre, R. Bennes, E. Tronel-Peyroz, and J. M. Douillard, Langmuir **4**, 1326 (1988).
[6] B. Widom, Mol. Phys. **96**, 1019 (1999).
[7] M. Schick and P. Taborek, Phys. Rev. B **46**, 7312 (1992).
[8] R. Evans and P. Tarazona, Phys. Rev. A **28**, 1864 (1983).
[9] T. F. Meister and D. M. Kroll, Phys. Rev. A **31**, 4055 (1985).
[10] E. Velasco and P. Tarazona, J. Chem. Phys. **91**, 7916 (1989).
[11] F. Ancilotto and F. Toigo, Phys. Rev. B **60**, 9019 (1999).
[12] J. E. Finn and P. A. Monson, Phys. Rev. A **39**, 6402 (1989).
[13] Y. Fan and P. A. Monson, J. Chem. Phys. **99**, 6897 (1993).
[14] M. J. Bojan, G. Stan, S. Curtarolo, W. A. Steele, and M. W. Cole, Phys. Rev. E **59**, 864 (1999).
[15] M. B. Sweatman, Phys. Rev. E **65**, 011102 (2002).
[16] W. Shi, X. Zhao, and J. K. Johnson, Mol. Phys. **100**, 2139 (2002).
[17] J. R. Errington, Langmuir **20**, 3798 (2004).
[18] We use a slightly lower value for T_{w} than originally reported in [17]. Our earlier estimate of T_{w} was obtained by fitting an empirical expression to data, whereas the value used here was determined by modeling the temperature dependence of the difference between bulk and prewetting saturation chemical potentials along the prewetting line with a theoretically based function.
[19] K. Binder, Phys. Rev. A **25**, 1699 (1982).
[20] J. R. Errington, J. Chem. Phys. **118**, 9915 (2003).
[21] G. E. Norman and V. S. Filinov, High Temp. **7**, 216 (1969).
[22] M. Fitzgerald, R. R. Picard, and R. N. Silver, J. Stat. Phys. **98**, 321 (2000).
[23] B. A. Berg and T. Neuhaus, Phys. Rev. Lett. **68**, 9 (1992).
[24] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988).
[25] J. R. Errington, Phys. Rev. E **67**, 012102 (2003).
[26] J. O. Indekeu, Physica (Amsterdam) **183A**, 439 (1992).
[27] E. M. Blokhuis, Physica (Amsterdam) **202A**, 402 (1994).
[28] S. Perković, E. M. Blokhuis, and G. Han, J. Chem. Phys. **102**, 400 (1995).
[29] We use the same scaling values that are used in S. Perković, E. M. Blokhuis, E. Tessler, and B. Widom, J. Chem. Phys. **102**, 7584 (1995).
[30] H. Dobbs, Langmuir **15**, 2586 (1999).
[31] B. Widom and A. S. Clarke, Physica (Amsterdam) **168A**, 149 (1990).
[32] B. Widom, in *Condensed Matter Theories*, edited by L. Blum and F. B. Malik (Plenum, New York, 1993), pp. 589–593.
[33] J. Y. Wang, S. Betelu, and B. M. Law, Phys. Rev. Lett. **83**, 3677 (1999).
[34] J. Y. Wang, S. Betelu, and B. M. Law, Phys. Rev. E **63**, 031601 (2001).
[35] T. Pompe, Phys. Rev. Lett. **89**, 076102 (2002).