

Prewetting at a fluid-solid interface via Monte Carlo simulation

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An isobaric-isothermal Monte Carlo simulation method has been used to investigate the approach to wetting in a 12-6/9-3 potential model of fluid Ar and solid CO₂. We have studied adsorption from the subcritical vapor at pressures up to saturation along isotherms at several temperatures. At each state the density profile and the adsorption excess were determined. At the lowest temperatures studied, the adsorption isotherms and density profiles exhibit behavior consistent with partial wetting at coexistence, in that the adsorption remains finite all the way up to coexistence. Over an intermediate range of temperatures we have found behavior consistent with the existence of a prewetting line, a locus of first-order phase transitions from thin- to thick-film adsorption. The adsorption excess increases discontinuously at pressures below saturation as thick liquidlike films form. These liquid films grow in thickness until the saturation pressure is reached and the adsorption excess diverges. At a still higher range of temperatures, behavior consistent with complete wetting at saturation is observed but with a continuous growth in the film thickness as the pressure is increased toward saturation. In contrast with earlier work on the same model system using the grand ensemble Monte Carlo method, our observations are in qualitative agreement with the predictions of density-functional and related theories of wetting phenomena. We discuss possible reasons for the failure to observe such phenomena in previous simulation work.

I. INTRODUCTION

A fluid at bulk phase coexistence adsorbed upon a substrate can undergo a surface phase transition from partial to complete wetting of the substrate. Recent theories of adsorption predict that when this wetting transition is first order, a locus of first-order surface phase transitions extends away from the bulk-fluid coexistence curve. This locus, the prewetting line, was first predicted independently by Cahn¹ and Saam and Ebner.^{2,3} Although first-order wetting transitions have been found for numerous systems, the prewetting line has not been detected in experiments, and until now has not been found in computer simulations of continuous systems. In this paper we present results of a computer simulation study of a model fluid-solid interface in which we find behavior consistent with the existence of a first-order wetting transition, and, in addition, it has been possible to locate a prewetting line.

Theoretical understanding of wetting transitions has developed considerably since the work of Cahn¹ and Saam and Ebner.³ Several extensive reviews of these theories exist in the literature,⁴ and here we will review only some theoretical predictions which pertain to prewetting. The wetting transition, by Cahn's argument, should occur at any three-phase interface in which one phase is far from critical and the other two phases are sufficiently near critical. The theory presented by Cahn¹ predicts a first-order wetting transition accompanied by a prewetting line. Cahn's original analysis applies to arbitrary phases and to mixtures as well as pure components. However, in this discussion we will consider only the transition of a pure fluid in contact with an inert, planar solid.

The prewetting line begins at a wetting temperature

T_w on the vapor side of the coexistence line of the bulk fluid, leaves the coexistence line, and ends at a surface critical temperature T_{sc} (Fig. 1). In terms of adsorption isotherms, the prewetting phenomenon should manifest itself as follows.¹ At temperature $T < T_w$, adsorption beginning with a thin film increases continuously as the pressure is increased to the saturation pressure P_0 . At P_0 the bulk vapor condenses completely, and the adsorption becomes infinite. On an adsorption versus pressure diagram (Fig. 2), the adsorption isotherm reaches P_0 with a

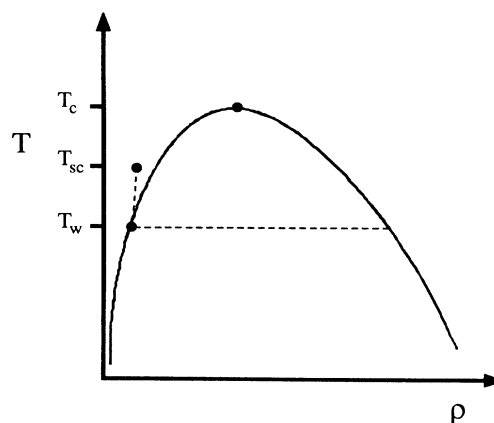


FIG. 1. A typical fluid phase coexistence curve of a pure substance, with first-order surface phase transitions as predicted by Cahn (Ref. 1) shown as dashed lines. The horizontal dashed line denotes the transition from partial to complete wetting at coexistence for $T = T_w$. The prewetting line extending from T_w to T_{sc} denotes transitions from thin to thick adsorbed films.

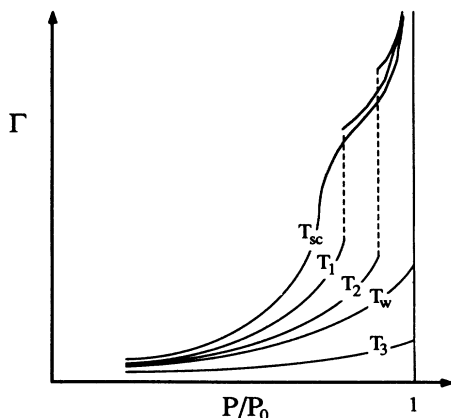


FIG. 2. Schematic diagram of adsorption isotherms near a first-order wetting transition. $T_{sc} > T_1 > T_2 > T_w > T_3$. Dashed lines connect adsorption values of coexisting thin and thick films at presetting transitions (for T_1 and T_2).

finite slope. At $T_w < T < T_{sc}$, the thin film grows as the pressure is increased until a transition pressure $P' < P_0$ is reached. At P' , a thin film is in equilibrium with a thick, liquidlike film of finite thickness. At higher pressures approaching P_0 , this first-order transition is followed by continuous growth of the thick film which becomes essentially infinite in thickness at P_0 . The adsorption isotherm reaches P' with a finite slope, jumps discontinuously to a higher value at P' , then continuously increases until it diverges to infinity at P_0 . The coexisting thin and thick films have their most pronounced difference at T_w , where the thick film is infinitely thick. At higher temperatures, the difference in adsorption along the prewetting line becomes less, until at T_{sc} the two films become indistinguishable from one another. At $T > T_{sc}$, the thin film grows continuously into a thick film with increasing pressure and eventually becomes infinite in thickness at P_0 . The adsorption isotherm increases continuously until it diverges at P_0 .

Cahn's original phase diagram has been modified somewhat following the work of several others. It has been shown⁵ that the prewetting line is tangent to the coexistence curve at T_w . Numerical calculations for several model systems find that the prewetting line probably lies very close to the coexistence curve.⁶⁻⁸ Also, while T_{sc} may theoretically lie above the bulk-fluid critical temperature T_c (via "surface-enhanced transitions"⁹), T_{sc} for most model systems lies well below T_c .^{7,8}

The 12-6/9-3 model of the Ar/CO₂ system has been the choice of many theoretical studies of wetting.^{2,3,6-8,10-12} The density-functional calculations of Saam and Ebner^{2,3} corroborate Cahn's interpretation of prewetting phenomena. The density profiles obtained from their theory for the Ar/CO₂ system showed the thin- to thick-film transition between T_w and T_{sc} , thin films only below T_w , and the continuous growth of films above T_{sc} . Later density-functional theories have not qualitatively changed these conclusions. At this point it is worth noting that grand ensemble Monte Carlo

(GEMC) simulations were carried out by Lane *et al.*¹³ which contradicted the findings of Saam and Ebner. The Monte Carlo density profiles did not exhibit thick-film growth of any kind at the same temperatures and densities as the density-functional calculations. Possible reasons for this will be discussed in Sec. IV of this paper.

The wetting transition is not always first order; second-order wetting transitions have been predicted for several systems. The relative strengths and ranges of the interparticle and wall-particle potentials seem to play the most important role in determining the order of the transition.^{5,7,14} Weaker wall-particle interactions tend to favor second-order transitions. The global surface phase diagrams of Pandit, Schick, and Wortis¹⁴ depict the relationship between temperature, chemical potential, and the relative strengths of the interparticle and wall-particle interactions with regard to wetting phenomena. Second-order wetting transitions do not have prewetting lines associated with them.¹⁵ Film growth is always continuous as the pressure is increased; below T_w adsorption isotherms reach P_0 with finite slope, and above T_w adsorption isotherms diverge to infinity. However, in virtually all theoretical studies of the Ar-CO₂ system, the wetting transition is predicted to be first order.^{2,3,6-8,10-12}

Our own interest in this problem began during the testing of a new isobaric simulation method for studying adsorption equilibrium.¹⁶ We found¹⁷ that thick adsorbed films could exist at pressures below saturation for the model considered by Lane *et al.*,¹³ in marked contrast with their results. We have since made a more extensive study of this system, and this paper reports the results. The density profiles obtained from our simulations exhibit the remarkable thin- to thick-film transitions associated with prewetting, similar to those predicted by density-functional theory.^{2,3,11} By performing simulations of adsorption from the subcritical vapor in the approach to saturation we have been able to estimate the location of the prewetting line. The results are in qualitative agreement with the predictions of density-functional and related theories of wetting transitions. We have also carried out some GEMC simulations of the same system. We again find evidence for prewetting, but as we have found in our earlier work,¹⁶ the results show substantially larger fluctuations than the isobaric ensemble results in the multilayer regime.

II. SIMULATION METHOD

The general features of the isobaric-isothermal ensemble Monte Carlo (NPTMC) method used in this work are described elsewhere.¹⁶ In this section we discuss the details of the NPTMC method peculiar to this study, the model system used, and important aspects of the simulations themselves.

The Monte Carlo cell consisted of a parallelepiped closed at each end of the long (z) axis by a rhombus with a side of nine molecular diameters. Periodic boundaries existed at the four remaining faces of the cell. The intermolecular forces in the system were modeled with a truncated Lennard-Jones 12-6 potential

$$u(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], & 0 \leq r \leq R_c \\ 0 & r > R_c \end{cases}, \quad (1)$$

with parameters for argon $\epsilon/k = 119.8$ K and $\sigma = 3.40$ Å, where k is the Boltzmann constant. The dimensionless quantities used in this paper are $T^* = kT/\epsilon$, $p^* = p\sigma^3/\epsilon$, and $\rho^* = \rho\sigma^3$. The truncation radius R_c was set to 2.5σ , and no corrections were made during or after simulations for this truncation.

The fluid-solid interaction at one wall was specified as a Lennard-Jones 9-3 potential:

$$w(z) = \frac{2\pi}{3} \rho_w \sigma_w^3 \epsilon_w \left[\frac{2}{15} \left(\frac{\sigma_w}{z} \right)^9 - \left(\frac{\sigma_w}{z} \right)^3 \right]. \quad (2)$$

Parameters correspond to the model Ar-CO₂ system; $\sigma_w = 3.727$ Å, $\epsilon_w/k = 153$ K, and $\rho_w \sigma_w^3 = 0.988$. This potential was not truncated. The potentials used in this work are the same as those used by Saam and Ebner^{2,3} and Lane *et al.*¹³ and several others, except for the truncation in the interparticle potential. A hard wall was used at the other end of the Monte Carlo cell so that any capillary condensation effects could be avoided.^{18,19} This choice of wall, rather than having two 9-3 walls,¹⁷ also resulted in larger volume fluctuations for a given cell length (an effectively longer system was simulated) and substantially reduced the computation time required for a given set of statistics when the adsorption was high.

An accurate knowledge of where the coexistence curve of the bulk fluid lies is crucial to this study because of the proximity of the prewetting line to the coexistence curve. The truncation to the Lennard-Jones potential has a large effect on the coexistence curve of the fluid. Corrections for the truncation were made to the equation of state of Nicolas *et al.*²⁰ for the full Lennard-Jones potential via

$$p_{\text{tr}}^*(T, \rho) = p_{\text{LJ}}^*(T, \rho) + \frac{8}{3} \pi \rho^* R_c^{*3}, \quad (3)$$

where p_{tr}^* is the pressure of the model fluid, p_{LJ}^* is the pressure of the full Lennard-Jones fluid obtained from the Nicolas equation of state, and $R_c^* = R_c/\sigma$. The correction term accounts for both the absence of the long tail and the contribution to the virial pressure arising from the discontinuity in the potential at R_c .²¹ The critical point resulting from this equation of state is located at approximately $T_c^* = 1.23$ and $\rho_c^* = 0.32$, which may be compared to the critical point from the Nicolas *et al.* equation of state, $T_c^* = 1.35$ and $\rho_c^* = 0.35$. The coexistence curve as a whole is shifted to lower temperatures, and the effect of the truncation upon the vapor pressure is large. For example, the vapor pressure of the full Lennard-Jones fluid from the Nicolas *et al.* equation of state at $T^* = 0.88$ is $P_0^* = 0.0095$. The vapor pressure obtained from the corrected equation is $P_0^* = 0.0157$.

The correction to the Nicolas *et al.* equation of state was checked by simulating coexisting states of the truncated Lennard-Jones fluid at $T^* = 0.88$, using the recently developed Gibbs ensemble Monte Carlo simulation method²² for a system with 500 particles and results averaged over 10^7 configurations. The coexistence pressure

obtained via this simulation method is $P_0^* = 0.017 \pm 0.002$, in excellent agreement with the pressure obtained from the corrected empirical equation of state. Finite system size effects should also have some effect upon the location of the coexistence curve, but we do not believe these to be significant.

Simulations were usually started from the final configurations of earlier simulations at lower pressure. When no such configuration was available, the particles were uniformly distributed in a rectangular lattice as an initial configuration. 500 particles were used in almost all calculations. This number is large enough so that if the system condensed, a wall separation (L) of approximately 15σ would be maintained. A cell length of this size ensures, for the range of conditions simulated in this paper, that the fluid in the middle of such a system would essentially be the bulk liquid at the given temperature and pressure. When vapor is present the Monte Carlo cell length can become quite large, even when thick adsorbed films exist. In general, for undersaturated vapor states $L > 150\sigma$. For some state points far from the coexistence and prewetting lines, it was possible to use fewer particles to save on computation time. A pass in our NPTMC calculations¹⁶ consists of (1) N attempted small scale translations, (2) one attempted volume displacement, and (3) N attempted random translations, where N is the number of particles in the system. In these calculations, the maximum size parameter for small scale transitions was set to $\sim 0.25\sigma$, which gave a translational acceptance ratio of 0.20 or higher in the adsorbate. Similarly, the volume displacement parameter was chosen to produce an acceptance ratio of ~ 0.25 for volume shifts. The size of this parameter depended largely upon the state point simulated. Random translations were used to assist in sampling the bulk-fluid region and the large-density gradient between the adsorbate and the bulk fluid. These translations reassign the coordinates of particles to sets chosen at random from anywhere in the system.

Density profiles $\rho(z)$ were recorded for each state point, and the adsorption was calculated via

$$\Gamma = \int_0^\infty [\rho(z) - \rho_b] dz, \quad (4)$$

where ρ_b is the density of the bulk fluid. ρ_b was that given by the five-term virial equation of state for the Lennard-Jones fluid²³ with corrections made for the truncated potential. For all state points simulated, this density was found to agree well with the simulated bulk density.

The length of equilibration used in these calculations is important. During simulations of states far from transitions to prewetting and condensation, we generally discarded the first 1000 passes as equilibration. This number of equilibration passes was found to be insufficient near these transitions, where equilibrations of 5000 to 10000 passes were used. Control charts of adsorption were used to follow the progress of the simulations and to determine the length of equilibration required. Data collection followed equilibration for at least 5000 passes. Simulations at state points near prewetting and condensation transitions exhibited large fluctuations in adsorption, and were run for longer times to improve the accuracy of

the calculated adsorption excess.

Grand ensemble Monte Carlo (GEMC) simulations following the method of Rowley *et al.*²⁴ were also run for comparison with the NPTMC results. The system was the same as that described earlier. A wall separation of 50σ was used; because of the single hard wall, capillary condensation effects were avoided. Comparison was made with NPTMC calculations by relating the chemical potential to the pressure through the five-term virial equation of state,²³ and bulk densities obtained from the two simulation methods at the same state points were in excellent agreement.

III. RESULTS

NPTMC calculations were carried out in the Ar-CO₂ system for several temperatures between $T^*=0.83$ and 1.0, and for pressures up to saturation. As the pressure was increased toward saturation, three different types of behavior in the growth of the films were noted, corresponding to three ranges of temperature. Representative temperatures of $T^*=0.83$, 0.88, and 1.0 are used in the following paragraphs to discuss these types of behavior.

At $T^*=0.83$, the thin film grows continuously until the saturation pressure is reached (Fig. 3). For all pressures below P_0 the thin-film profiles remain far from the profile of the saturated liquid. The adsorption versus pressure isotherm (Fig. 4) reaches P_0 with a finite slope, indicating partial wetting.

At $T^*=0.88$, the thin film again grows continuously, but jumps suddenly to a thick film at $P^*=0.0145$ before P_0 is reached (Fig. 5). As the pressure is increased further, the thick film grows in thickness rapidly, and tends to diverge at P_0 . The jump in adsorption (Fig. 6) is

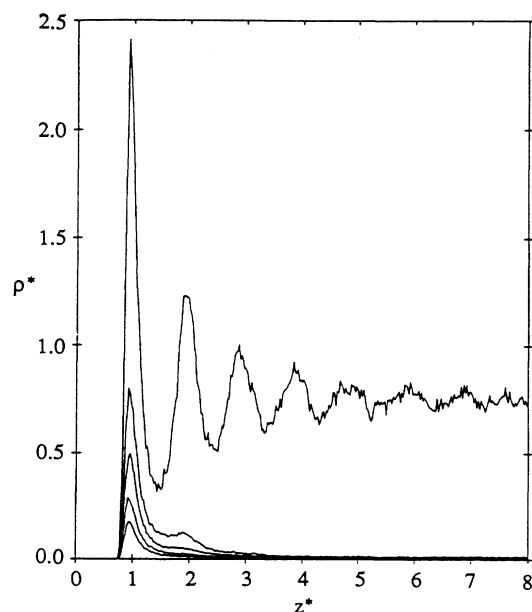


FIG. 3. Density profiles obtained from NPTMC simulations of the model Ar-CO₂ interface at $T^*=0.83$. Profiles are for pressures of $P^*=0.004$, 0.006, 0.008, 0.010; the liquid profile is for $P^*=0.0105$. $z^*=z/\sigma$.

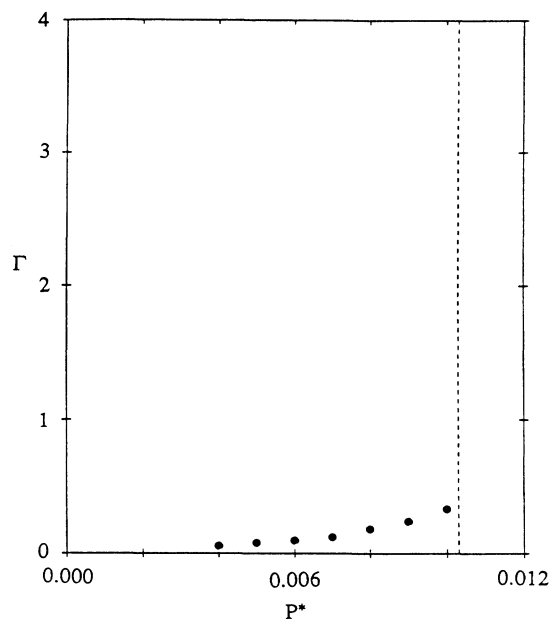


FIG. 4. Adsorption isotherm for the model Ar-CO₂ system at $T^*=0.83$. The apparently finite slope of the isotherm at $P_0^*=0.0103$ (dashed line) indicates partial wetting. Equation (3) predicts $P_0^*=0.0103$. The adsorption isotherm does not readily yield a value for P_0^* .

reproducible and apparently discontinuous, which suggests the crossing of the prewetting line. The first peak in the density profile jumps to a value corresponding to that of a liquid in contact with the wall. At higher pressures, much of the density profile near the wall becomes indistinguishable from the saturated liquid density profile. At

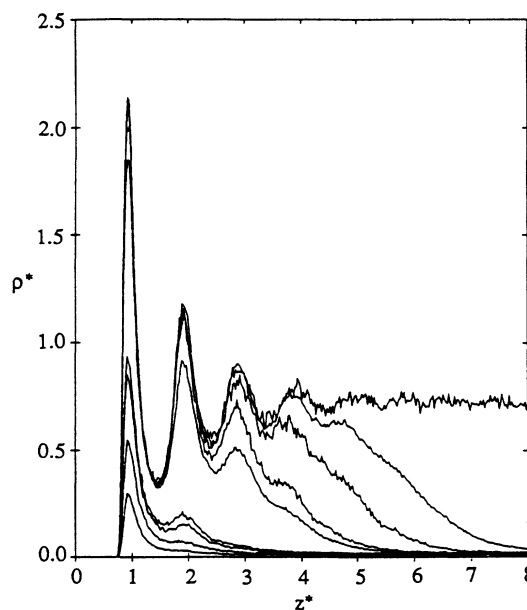


FIG. 5. Density profiles obtained from NPTMC simulations of the model Ar-CO₂ interface at $T^*=0.88$. Profiles are for pressures of $P^*=0.008$, 0.012, 0.014, 0.0145, 0.01475, 0.015, 0.0155, and 0.016; the liquid profile is for $P^*=0.0165$.

temperatures in this range that are lower than 0.88, the jump occurs nearer to P_0 and the change in adsorption at the discontinuity is larger than at 0.88. Above 0.88, the jump occurs farther from P_0 and the change in adsorption is smaller.

At $T^*=1.0$, the thin film builds to a thick one continuously as the pressure is increased (Fig. 7). The density of the first peak in the profile only gradually increases to that of an adsorbed liquid. Near P_0 , the absorption isotherm (Fig. 8) tends toward infinite adsorption. Our results support a growth in film thickness t governed by the power law

$$t = [\ln(P_0/P)]^{-1/3}, \quad (5)$$

although precise determination of the exponent is difficult.

Extensive NPTMC calculations over entire isotherms were completed for only these three temperatures, and were used to establish upper and lower temperature bounds for the prewetting line. At other temperatures, we concentrated our effort on obtaining the prewetting transition alone. This was accomplished by simulating several state points below and above transition pressures. Because no surface-tension calculations were done, it was necessary to use the jump in adsorption at pressures below saturation and the fluctuations accompanying the jump as signatures of the transition. This method makes an accurate estimate of T_{SC} difficult.

Our estimate of the location of the prewetting line is shown on a T - ρ diagram in Fig. 9. Figure 10 shows the position and the size of the prewetting line relative to the upper portion of the full coexistence curve of the bulk

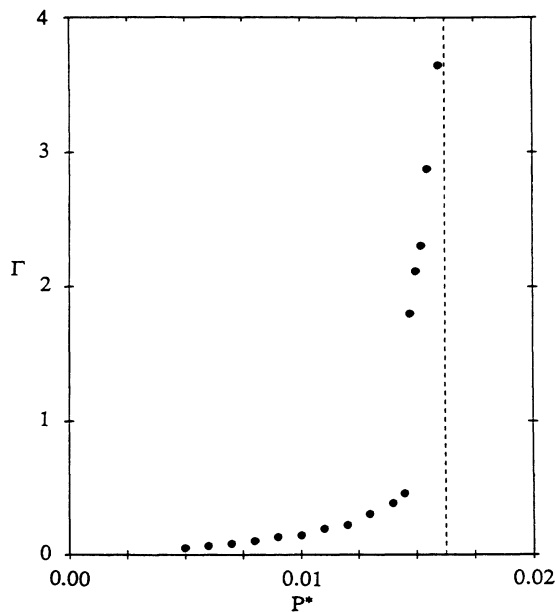


FIG. 6. Adsorption isotherm for the model Ar-CO₂ system at $T^*=0.88$. A large increase in adsorption over a small increase in pressure suggests a prewetting transition near $P^*=0.0145$. Equation (3) predicts $P_0^*=0.0157$; P_0^* suggested by these simulations is 0.0163.

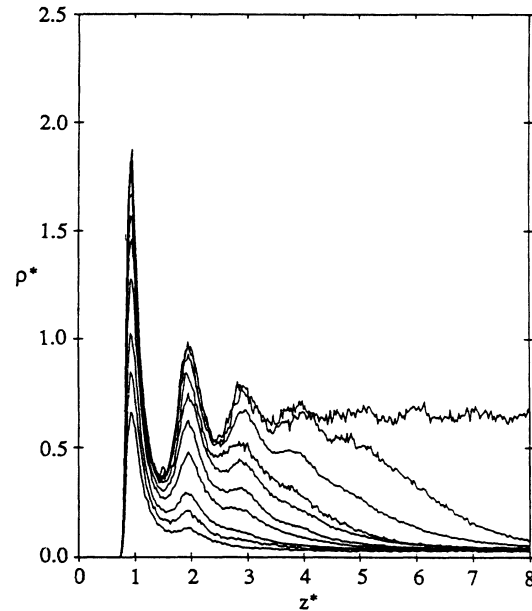


FIG. 7. Density profiles obtained from NPTMC simulations of the model Ar-CO₂ interface at $T^*=1.0$. Profiles are for pressures of $P^*=0.024, 0.028, 0.030, 0.032, 0.033, 0.034, 0.035, 0.036,$ and 0.037 ; the liquid profile is for $P^*=0.038$.

fluid. The characteristics of this line are very similar to those resulting from theoretical calculations for similar systems.⁶⁻⁸ By extrapolating this locus toward the coexistence curve (which the line should meet tangentially), we estimate $T_{SC}^*=0.84\pm 0.01$ for this system. The jump in adsorption associated with prewetting was not seen

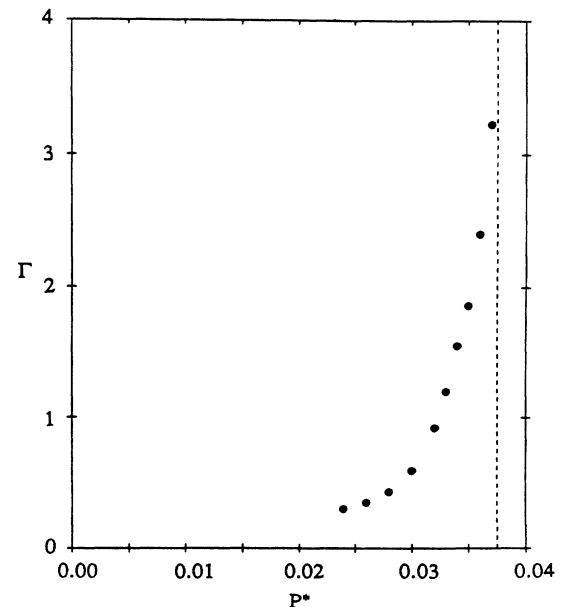


FIG. 8. Adsorption isotherm for the model system at $T^*=1.0$. The continuous increase in adsorption indicates $T > T_{SC}$. Equation (3) predicts $P_0^*=0.0368$; P_0^* suggested by these simulations is 0.0375.

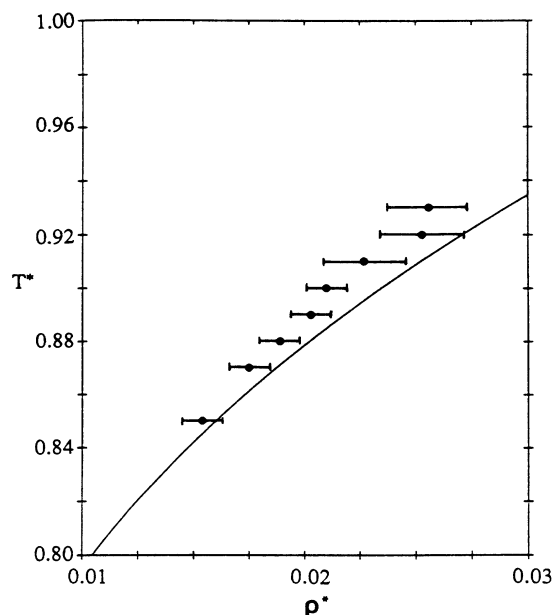


FIG. 9 Points on the prewetting line of the model system from NPTMC simulation. The solid curve is the coexistence curve predicted by Eq. (3).

with any degree of clarity above $T^*=0.93$, and we estimate $T_{SC}^*=0.94\pm 0.02$ for this system. Table I gives a comparison of these results with the predictions from various implementations of density-functional theory. The results of Saam and Ebner² appear to lie closest to our estimates. However, it is difficult to draw definitive conclusions from this comparison since the bulk equation of state in our work is different from those used in the density-functional theories.

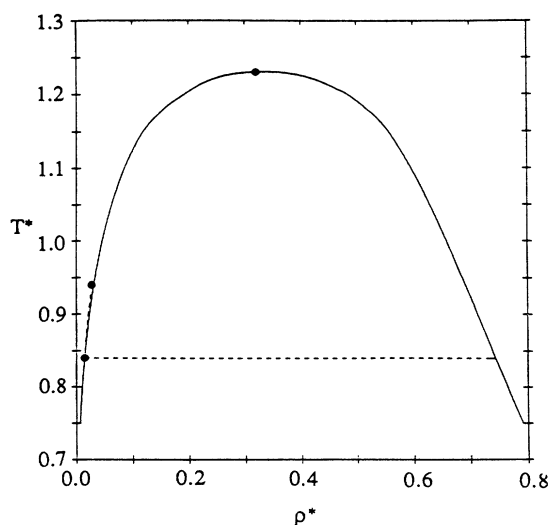


FIG. 10. The prewetting line for the Ar-CO₂ system for simulation (dashed line) and the coexistence curve of fluid Ar as obtained from Eq. (3).

TABLE I. Wetting and surface critical temperatures of the Ar-CO₂ system from various density-functional theory studies, and estimates from simulation.

Source	T_w^*	T_{SC}^*
Ebner and Saam, Ref. 2	0.77	0.92
Evans and Tarazona, Ref. 6	0.957	0.988
Meister and Kroll, Ref. 11	0.90	a
This work	0.84 ± 0.01	0.94 ± 0.02

^aA value for T_{SC} was not reported by Meister and Kroll.

A prewetting transition was also found to occur in the GEMC calculations for this system at $T^*=0.88$, at about the same state point as in the NPTMC calculations. However, very large fluctuations in the adsorption occurred at higher pressure in the GEMC calculations, similar to those found in multilayer adsorption on a model graphite surface.¹⁶

IV. DISCUSSION

To our knowledge, the simulation work presented in this paper represents the first direct, conclusive evidence for the existence of prewetting in a continuum system (prewetting has been seen in lattice gas adsorption with nearest-neighbor interactions²⁵). The results are in qualitative agreement with theoretical predictions.^{2,6,8,12} The wetting transition for this system is first order, because the prewetting line does not exist for second-order wetting transitions.¹⁵ First-order wetting and drying transitions have been seen in molecular-dynamics computer simulations;^{19,26} however, these studies did not pursue the prewetting transition. While both first- and second-order wetting transitions have been observed in nature, no conclusive experimental evidence for prewetting exists, despite intensive searches.²⁷

There are several possible reasons why prewetting, or for that matter thick-film growth, was not seen in earlier computer simulation studies of the present model system using the GEMC method.¹³ Perhaps the most likely reason was an inaccurate knowledge of the coexistence curve of the bulk fluid. The prewetting line and thick-film growth occur for states close to coexistence and accurate data for the coexistence properties would seem to us to be a prerequisite to the observation of these phenomena. Had the GEMC calculations been carried out to chemical potentials nearer to saturation, it is likely the thick-film buildup would have been seen, despite large fluctuations in adsorption. Our own results using the GEMC method support this conclusion. In fact, the existence of thick films in GEMC calculations has already been demonstrated in a number of studies^{24,28} of adsorption on model graphite surfaces.

It can also be misleading to compare directly the density profiles obtained from these computer simulations with profiles obtained at the same state points via density-functional theory. This is because the equations of state of the bulk fluid in the two techniques may differ substan-

tially, giving rise to differences in the coexistence properties. Lane *et al.*¹³ concluded that density-functional theory as implemented by Saam and Ebner^{2,3} was incorrect in predicting surface phase transitions and the growth of thick films. In contrast, we find that density-functional theory does indeed give a qualitatively correct picture of adsorption near bulk-fluid coexistence conditions. Our results fully support the qualitative predictions of wetting phenomena made by Saam and Ebner.^{2,3} While the shapes of the density profiles close to the wall differ significantly from the Saam-Ebner predictions, they are qualitatively similar to those predicted by recent mean-field density-functional theories¹¹ which use non-local approximations for the Helmholtz free energy of the inhomogeneous hard-sphere reference fluid.

The present work has been limited to a study of the density profile and adsorption excess as a function of pressure. More precise location of the wetting transition will require calculations of the surface tension.²⁹ Tarazona and Evans^{6,7,30} analyzed the behavior of the transverse structure factor at the liquid-film-vapor interface. Transverse pairwise correlations diverge faster than the film thickness in the approach to condensation, giving a

more easily recognized signature of the condition. Along the prewetting line, they diverge at T_{SC} while the adsorption remains finite. Both surface-tension and transverse-correlation measurements can be incorporated into computer simulations, although there could be difficulties in obtaining long-range transverse correlations in the liquid-vapor interface due to the periodic boundaries and to fluctuations in film thickness.

These subjects and other aspects of the wetting transition will be investigated in future simulation work. In particular, adsorption from fluid mixtures will be considered. Density-functional theory has been formulated for mixtures³¹ and has made a variety of interesting predictions concerning the wetting of a solid by a binary solution near its consolute point, including the formation of composite wetting films.³²

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