Nature of the Prewetting Critical Point

D. Nicolaides and R. Evans

H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, United Kingdom

(Received 26 April 1989)

In a Monte Carlo simulation of a three-dimensional lattice-gas model of the adsorption of a liquid film on a substrate, we have observed the thick-film–thin-film (prewetting) transition, located the prewetting critical point, and determined its nature via finite-size scaling. We find this critical point to be two-dimensional Ising type, confirming the conjecture that surface phase transitions out of bulk coexistence should belong to this universality class.

PACS numbers: 68.45.Gd, 05.70.Jk, 64.60.Fr

Gas adsorption at an inert substrate can result in a variety of surface phase transitions, one of which is prewetting. This is a transition from a thin to a thick adsorbed liquid layer induced, for example, by increasing μ, the chemical potential of the gas, towards its value at bulk saturation $\mu_{\rm sat}(T)$ at a fixed temperature T above the wetting temperature T_W. The line of first-order prewetting transitions $\mu_{\rm pw}(T)$ $[<\mu_{\rm sat}(T)]$ extends from the point of the (first-order) wetting transition $(T_W,\mu_{\rm sat})$ to the prewetting critical point $(T_{\rm pwc},\mu_{\rm pwc})$, where the distinction between thin and thick films disappears. Prewetting was investigated first by Cahn[1] and Ebner and Saam[2] in mean-field density-functional treatments of continuum fluids. Subsequently Ebner[3] and Sen and Ebner[4] observed prewetting in Monte Carlo (MC) simulations of a lattice-gas model of a fluid at an adsorbing wall.[5] Very recently prewetting was found in MC simulations[6] of a Lennard-Jones model of fluid argon at a structureless substrate. In none of these simulations was the critical point located accurately, nor was there any attempt to determine the nature of the criticality. It has been conjectured[7] that prewetting criticality should be equivalent to that of the pure surface transition which, it is argued,[8] should display standard $(d-1)$-dimensional Ising-type criticality when the bulk system is a d-dimensional system. Indeed, it is conjectured[9] that *all* surface phase transitions out of bulk coexistence should exhibit two-dimensional Ising critical exponents. The order parameter, which is the difference between the coverage in each adsorbed phase, is a scalar $(n=1)$ and the correlation length $\xi_\parallel$ can only diverge in two dimensions (parallel to the substrate) since, out of coexistence, the adsorbed phases are of finite thickness. In an earlier study[10] we succeeded in locating the prewetting line and its critical point in MC simulations of a lattice gas confined between two adsorbing walls. The purpose of this Letter is to elucidate, via a finite-size scaling analysis, the nature of prewetting criticality in the lattice-gas model of adsorption, and thereby ascertain the validity of the above conjectures.

The model we have investigated is essentially the same as that described in Ref. 10. It consists of a simple cubic, nearest-neighbor (Ising) lattice gas bounded by a wall that exerts a potential $V_j \equiv V_s(ja)$ on a particle in the jth layer from the wall. The form of the wall potential is chosen to model Lennard-Jones 12-6 interactions between atoms in the fluid and those constituting the wall:

$$V_s(z)=\frac{R\epsilon\pi}{45}\left\{9\left(\frac{a}{z}\right)^{10}+\frac{a^9}{(z+0.72a)^9}-45\left(\frac{a}{z}\right)^4-\frac{15a^3}{(z+0.61a)^3}\right\}, \tag{1}$$

where a is the lattice spacing, ϵ (>0) is the strength of the nearest-neighbor bond, and R is a constant fixed at the value[4,10] of 0.31. In the previous simulations[10] we were concerned with the effects of confinement on phase transitions so we studied lattices confined between two identical parallel adsorbing walls for various wall separations. Here we deliberately avoid the phenomenon of capillary condensation, which can preclude the observation of prewetting between *stable* phases,[10] by keeping only a single wall and matching the bulk gas at a distance of 32 layers by means of a contact potential: $V_{32}=V_s(32a)+\epsilon\rho_b$. The bulk gas occupancy (density) ρ_b was determined self-consistently from the density profile; the latter is constant beyond 7 or 8 layers, except for the thick film close to $T_W\sim 0.5T_c$, with bulk critical temperature $T_c=1.1279\epsilon/k_B$.

First-order prewetting transitions were determined using thermodynamic integrations[10] to determine the grand potential of the thin and thick films; these coexist when the grand potentials are equal. An example of coexisting films is shown in Fig. 1 for a temperature which is about $\frac{3}{4}$ of the way along the prewetting line. Both films are certainly three dimensional in character. The thin film shows substantial occupancy of the second and third layers, while the thick film extends as far as the sixth layer. As the temperature is increased the profiles of the coexisting films become closer. However, as emphasized in Ref. 10, it is not feasible to locate the critical point accurately by searching for the disappear-

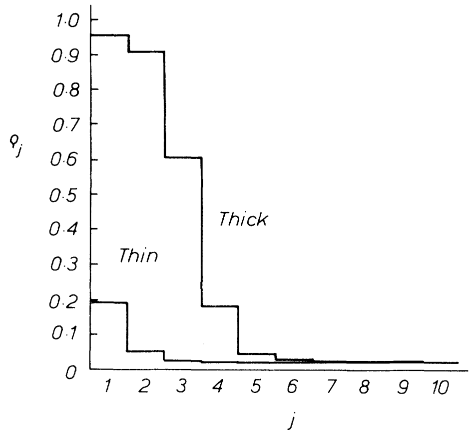

FIG. 1. Average occupancy (density) profiles ρ_j of coexisting thin and thick films at a point on the prewetting line: $T/T_c = 0.64$ and $(\mu_{sat} - \mu)/(\mu_{sat} - \mu_{pwc}) = 0.88$). j denotes the layer number. $L = 64$.

ance of the order parameter or for the absence of hysteresis in the adsorption isotherms. Rather we adopted finite-size scaling techniques of the type used in a recent study[11] of criticality in strictly two-dimensional lattice models.

The probability density of the coarse-grained order parameter, $P(M_L)$, contains universal information,[12] over and above that associated with critical exponents, and this function can be regarded as the hallmark of a universality class.[11] In the case of prewetting we take M_L to be the difference between the mean number of occupied sites in the thick and thin films, and choose the coarse-graining length to be L, where L^2 is the wall area, equal to the number of sites in a layer. (We recall that correlations can only diverge parallel to the wall since the film remains of finite thickness at criticality.)

The scaling form for $P(M_L)$ is

$$P(M_L) = b_0 L^{\beta/\nu} \tilde{P}(b_0 L^{\beta/\nu} M_L, L^{\lambda_1}\mu_1, L^{\lambda_2}\mu_2, L^{\lambda_3}\mu_3), \qquad (2)$$

with $\lambda_1 = 1/\nu$, $\lambda_2 = d^* - \beta/\nu$, $\lambda_3 = -\omega$, $\mu_1 = a_1\Delta t + a_2\Delta\mu$, and $\mu_2 = b_1\Delta t + b_2\Delta\mu$. Here β and ν are the usual critical exponents, Δt and $\Delta\mu$ are the deviations in temperature and chemical potential from their values at the prewetting critical point, d^* is the effective dimensionality, and the a_i and b_i are nonuniversal constants. The second and third arguments of $\tilde{P}$ are the two relevant scaling fields at the critical point, while the last term represents the leading correction to scaling; μ_3 is the leading irrelevant scaling field. If the arguments are all small then (2) can be expanded as

$$P(M_L) = b_0 L^{\beta/\nu}\{P_0^*(\tilde{M}_L) + \mu_1 L^{\lambda_1} P_1^*(\tilde{M}_L) + \mu_2 L^{\lambda_2} P_2^*(\tilde{M}_L) + \mu_3 L^{\lambda_3} P_3^*(\tilde{M}_L) + \cdots\}, \qquad (3)$$

where the scaled order parameter $\tilde{M}_L = b_0 L^{\beta/\nu} M_L$.

The functions P_i^*, as well as the exponents λ_i and β/ν, are specific to a universality class.[11] We have determined P_0^*, β/ν, and the $\{\lambda_i\}$ $(i = 1,2,3)$ by performing χ^2 fits to the moments $M_L^{(n)} \equiv \langle M_L^n \rangle$ of the distribution (3) for 23 different combinations of L, Δt, and $\Delta\mu$, in a manner similar to that in Ref. 11. The results are presented in Table I and in Fig. 2.

TABLE I. Critical exponents governing the scaling of the moments of the adsorption difference probability density at the prewetting critical point. The numbers in brackets are the error estimates.

Exponent	Estimate from χ^2 fit	$d = 2$ Ising result
β/ν	0.124 (5)	$\frac{1}{8}$
$\lambda_1 = 1/\nu$	1.098 (99)	1
$\lambda_2 = d^* - \beta/\nu = d^*\delta/(1+\delta)$	1.770 (26)	$\frac{15}{8}$
$-\lambda_3 = \omega$	1.201 (374)	$\frac{4}{3}$

The MC simulations measured $P(M_L)$ using walls with $L = 8$, 16, 32, and 64 and represent some 3000 central-processing-unit hours on the Active Memory Technology DAP 510. The algorithm used was a parallel version of the Metropolis algorithm but we have now implemented a cluster algorithm[13] for this inhomogeneous system which should reduce the critical slowing down that occurs with increasing L, thereby shortening run times. A typical data point for the $L = 64$ system consisted of 8 bins of 100000 time steps each, with a measurement every 20 time steps, discarding 2000 time steps between each bin and for equilibration.

The first entry in Table I, β/ν, was determined from a χ^2 fit to the ratio of moments $R_L \equiv M_L^{(4)}/M_L^{(2)}$ which, according to (2), behaves as

$$R_L = r_0 L^{-2\beta/\nu}(1 + r_1\mu_1 L^{1/\nu} + r_3 L^{-\omega} + \cdots). \qquad (4)$$

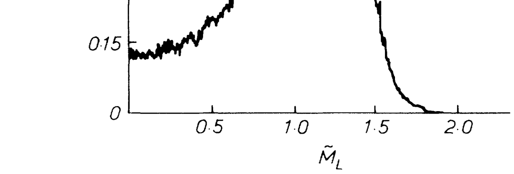

FIG. 2. The fixed-point distribution of the scaled adsorption difference $\tilde{M}_L$ at the prewetting critical point. The argument is scaled so that the function has unit variance and the function is symmetric about $M_L = 0$. $L = 64$.

Note that the term involving the scaling field μ_2 does not contribute to the even moments, as the function P_2^* is an odd function of its argument. The χ^2 analysis now provides estimates of the parameters r_i, μ_1, β/ν, $1/\nu$, and ω which best fit the measured R_L with the form (4). We have also fitted the combination of even moments $G_L \equiv [3(M_L^{(2)})^2 - M_L^{(4)}]/2(M_L^{(2)})^2$ and the odd moments $M_L^{(1)}$ and $M_L^{(3)}$, the last two allowing estimates of λ_2. The entries in Table I represent the average estimate of each exponent obtained from the various fits; in all cases the estimates agreed to within error. Our fitting procedure also provides an estimate of the location of the prewetting critical point, where the two relevant scaling fields μ_1 and μ_2 vanish. We estimate $T_{\rm pwc}/T_c = 0.703$ and $(\mu_{\rm sat} - \mu_{\rm pwc})/k_B T_c = 0.0238$.[14]

The χ^2 analysis indicated that the $L=8$ wall was not sufficiently large for corrections to scaling [the last term on the right-hand side of (4)] to be negligible. Thus $L=8$ data were not included in the fitting. We were not able to determine whether the leading correction to scaling assumed its predicted two-dimensional Ising value[11] with $\omega = \frac{4}{3}$, or whether the correction was of the form $1/L$, as might be expected from a simple balancing of surface and volume terms.

Our best estimate of the fixed-point distribution $P_0^*(\tilde{M}_L)$ comes from a simulation with $L=64$ at $(T_{\rm pwc}, \mu_{\rm pwc})$, as determined by the χ^2 analysis of the moments. This is plotted in Fig. 2, with the nonuniversal amplitude b_0 chosen so that $P_0^*(\tilde{M}_L)$ has unit variance. As $P_0^*(\tilde{M}_L)$ depends on the boundary conditions of the coarse-graining block, which in our case are three-dimensional anisotropic, we do not expect this function to be identical to the $P_0^*(\tilde{M}_L)$ measured in Ref. 11 for strictly two-dimensional scalar spin systems. Nevertheless, our present results do exhibit two features in common with the earlier ones: a small value at $\tilde{M}_L = 0$ and steep tails—both indicative of low-dimensional criticality. The tails of $P_0^*(\tilde{M}_L)$ should decay as $\exp(-|\tilde{M}_L|^{1+\delta})$.[15] Fitting the measured function to this form for $|\tilde{M}_L| > 1.50$ gives $\delta = 14.87 \pm 0.74$, with a χ^2 of 46.2 for 39 degrees of freedom. This estimate should be compared with the exact two-dimensional Ising value $\delta = 15$.

Our results show that the prewetting critical point, corresponding to the disappearance of the adsorption difference between thin and thick adsorbed layers, of the lattice-gas model of a fluid at a substrate, exhibits two-dimensional Ising universality. We believe that this constitutes the first confirmation by simulation of earlier conjectures[7-9] on the nature of prewetting criticality. By choosing a substrate potential V_s of moderate strength[4,10] we have avoided the occurrence of a sequence of discrete layering transitions associated with strongly attractive substrates. As we ensure that $T_W > T_R$, the roughening temperature of the lattice, our result should be directly applicable to prewetting in continuum fluids, where the liquid-gas interface is always rough. Layering transitions, where the coverage jumps from a value corresponding to n layers to that corresponding to $n+1$ layers, should exhibit the same type of criticality as prewetting.[9,16] MC simulations have found a sequence of layering transitions in lattice-gas models[3,17] but critical exponents were not determined. Our present result, taken with the experimental results based on heat-capacity measurements for the liquid-gas transition in submonolayer methane on graphite: $\beta = 0.127 \pm 0.02$[18] and for the monolayer-bilayer transition in C_2D_4 on graphite: β between 0.08 and 0.17[19] would also seem to confirm the two-dimensional Ising conjecture for layering.[20]

We are grateful to A. D. Bruce for helpful correspondence and to A. O. Parry for suggesting the argument of Ref. 15. This research was supported by the Science and Engineering Research Council of the U.K., whose Computational Science Initiative provided a grant for the purchase of the Active Memory Technology DAP 510.

[1]J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[2]C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).

[3]C. Ebner, Phys. Rev. A **23**, 1925 (1981).

[4]A. K. Sen and C. Ebner, Phys. Rev. B **33**, 5076 (1986).

[5]K. Binder and D. P. Landau, Phys. Rev. B **37**, 1745 (1988) found a prewetting transition for an Ising model with a short-ranged (contact) wall field h_1.

[6]J. Finn and P. A. Monson, Phys. Rev. A **39**, 6402 (1989).

[7]H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982).

[8]A. J. Bray and M. A. Moore, J. Phys. A **10**, 1927 (1977), and references therein. The pure surface transition corresponds to the point where the prewetting critical line meets the symmetry axis $h = h_1 = 0$ at a temperature above the bulk critical temperature. $h \equiv \mu - \mu_{\rm sat}$ is the bulk field and h_1 is the wall field. Although such a transition is not expected for pure fluids at substrates, since it requires an enhancement of the surface coupling, Ref. 7 makes clear the relationship with other prewetting transitions.

[9]M. P. Nightingale, W. F. Saam, and M. Schick, Phys. Rev. B **30**, 3830 (1984).

[10]D. Nicolaides and R. Evans, Phys. Rev. B **39**, 9336 (1989).

[11]D. Nicolaides and A. D. Bruce, J. Phys. A **21**, 233 (1988).

[12]A. D. Bruce, J. Phys. C **14**, 3667 (1981); K. Binder, Z. Phys. B **43**, 119 (1981). For a recent review, see K. Binder, Ferroelectrics **73**, 43 (1987).

[13]F. Niedermayer, Phys. Rev. Lett. **61**, 2026 (1988).

[14]Our present estimate differs somewhat from that obtained earlier from inspection of the peaks in the susceptibility—see Fig. 6(b) of Ref. 10. Note $\mu_{\rm sat} = -3\epsilon$ for the simple cubic lattice.

[15]The exact result for the large-M_L limit of the probability distribution function of the $d=2$ Ising model has this form at its bulk critical point; B. M. McCoy and T. T. Wu, *The Two Dimensional Ising Model* (Harvard Univ. Press, Cambridge, 1973). A scaling argument for the singular part of the free energy F_S suggests that the same form should be valid for pre-

wetting criticality. We suppose $F_S \approx \xi_{\parallel}^{-(d-1)}$ with (transverse) correlation length $\xi_{\parallel} \approx M_L^{-\nu/\beta}\Lambda(\Delta t/M_L^{1/\beta})$, where Λ is a scaling function. Then we have $P_L(M_L) \approx \exp(-F_S/k_B T) \approx \exp(-c\,|M_L|^{(d-1)\nu/\beta})$. Critical exponent relationships imply $(d-1)\nu/\beta = (2-\alpha)/\beta = \delta + 1$, for $\xi_{\parallel}$ diverging in $d-1$ dimensions, i.e., $d^* = d-1$.

[16]D. A. Huse, Phys. Rev. B **30**, 1371 (1984).

[17]I. M. Kim and D. P. Landau, Surf. Sci. **110**, 415 (1981).

[18]H. K. Kim and M. H. W. Chan, Phys. Rev. Lett. **53**, 170 (1984).

[19]Q. M. Zhang, Y. P. Feng, H. K. Kim, and M. H. W. Chan, Phys. Rev. Lett. **57**, 1456 (1986).

[20]There is still no convincing experimental evidence for a prewetting transition.