PHYSICAL REVIEW E **88**, 030401(R) (2013)

Non-mean-field behavior of critical wetting transition for short-range forces

Paweł Bryk*
Department for the Modeling of Physico-Chemical Processes, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

Kurt Binder
Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, D-55099 Mainz, Germany

(Received 5 June 2013; published 5 September 2013)

Critical wetting transition for short-range forces in three dimensions ($d = 3$) is reinvestigated by means of Monte Carlo simulation. Using an anisotropic finite size scaling approach, as well as approaches that do not rely on finite size scaling, we show that the critical wetting transition shows clear deviation from mean-field behavior. We estimate that the effective critical exponent $\nu_{\parallel}^{\rm eff} = 1.76 \pm 0.08$ for $J/kT = 0.35$ and $\nu_{\parallel}^{\rm eff} = 1.85 \pm 0.07$ for $J/kT = 0.25$. These values are in accord with predictions of Parry *et al.* [Phys. Rev. Lett. **100**, 136105 (2008)]. We also point out that the anisotropic finite size scaling approach in $d = 3$ requires additional modification in order to reach full consistency of simulational results.

DOI: 10.1103/PhysRevE.88.030401 PACS number(s): 68.03.Cd, 68.08.−p, 68.35.Md

Understanding interfacial properties of fluids is important for many applications including adsorption in porous materials [1], nanofluidic devices [2], and design of superhydrophobic surfaces [3]. The common problem pertinent to these research areas is the prediction and control of the wetting properties of surfaces. The introduction of patterns on the nanoscale leads to substantial changes in wettability and creates a host of new effects [4–6]. While the wetting phenomena at planar surfaces is well understood [7], there is one notable exception. Critical wetting has been a long-standing and stubbornly difficult problem to understand.

Renormalization group calculations based on a local interfacial Hamiltonian [8,9] predict that the critical wetting transition for short-range forces is strongly nonuniversal. When temperature T approaches the wetting temperature T_w, the critical exponent characterizing the divergence of the parallel correlation length, $\xi_{\parallel} \sim (T_w - T)^{-\nu_{\parallel}}$, depends on a nonuniversal dimensionless wetting parameter, $\omega = \frac{kT}{4\pi\Sigma\xi^2}$, where k is Boltzmann's constant, Σ is the interfacial stiffness (or surface tension for simple liquids), and ξ is the correlation length in the phase that wets the wall. For the case of the Ising model in three dimensions ($d = 3$) one has $1/2 < \omega < 2$, which leads to

$$\nu_{\parallel}(\omega) = (\sqrt{2} - \sqrt{\omega})^{-2} . \tag{1}$$

Surprisingly, subsequent simulation studies [10–12] showed only minor deviations from mean-field value, $\nu_{\parallel}^{\rm MF} = 1$. In order to reconcile theory and simulation Parry *et al.* [13] proposed a new nonlocal (NL) interface Hamiltonian which removed various intrinsic inconsistencies of previous approaches. Reanalysis of the NL model showed the appearance of another diverging length $\xi_{\rm NL} = \sqrt{l\xi} \propto \sqrt{\ln \xi_{\parallel}}$, which cuts some of the interfacial fluctuations for small film thicknesses l. This in turn leads to a reduction in the effective value of the wetting parameter $\omega_{\rm eff}$, and to an effective exponent $\nu_{\parallel}^{\rm eff}$.

Very recently a new *anisotropic* finite size scaling (AFSS) theory which should be suitable for studying wetting transitions in general was proposed [14,15]. These authors have suggested that the previous [10–12] estimates for the location of the critical wetting transition need a revision, however, the critical exponent has not been determined. In this Rapid Communication we reconsider this approach and show that the critical wetting transition for short-range forces in $d = 3$ shows clear deviations from mean-field theory. We also give evidence that the AFSS theory is problematic in $d = 3$, which was not anticipated before [14,15].

We consider simple-cubic Ising $L \times L \times D$ systems with two free surface layers $L \times L$, and periodic boundary conditions in two remaining directions. The local order parameter of the corresponding phase transition is a pseudospin variable $s_i = \pm 1$ at lattice site i. The Hamiltonian for the system is

$$\mathcal{H} = -J \sum_{\rm bulk} s_i s_j - H \sum_{\rm bulk} s_i - H_1 \sum_{k \in {\rm surf}\,1} s_k - H_D \sum_{k \in {\rm surf}\,D} s_k , \tag{2}$$

where J is the bulk exchange constant and H is the bulk field. Surface fields H_1 and H_D act only on the first and last layer, respectively. In order to avoid effects connected to capillary condensation we select "antisymmetric" walls, i.e., $H_1 = -H_D < 0$. During the course of simulation several quantities were accumulated, including the average absolute value $\langle |m| \rangle$ of the magnetization $m = (L^2 D)^{-1} \sum_i s_i$, susceptibility $\chi' = L^2 D(\langle m^2 \rangle - \langle |m| \rangle^2)/kT$, and the fourth order cumulant $U_4 = 1 - \langle m^4 \rangle / 3\langle m^2 \rangle^2$. When the system is in the partial wetting regime, the interface is bound to the wall $k = 1$ or $k = D$ with equal probability. Consequently, $\langle |m| \rangle$ is nonzero in the thermodynamic limit. On the other hand, for the wet state the interface is unbound from either of the walls and wanders around the middle of the system. Consequently, $\langle |m| \rangle$ is zero for $D \to \infty$. The systems were simulated using a highly efficient multispin coding algorithm [16]. In order to overcome critical slowing down near the critical wetting point we applied a hyperparallel tempering technique [17] and simulated many systems at the same time, and allowed for frequent swaps between them. Statistical effort was at least 5×10^7 spin flips per site.

Within the AFSS approach the thermodynamic limit $D \to \infty$ must be taken in a special way, keeping the generalized aspect ratio $C = D^{\nu_{\parallel}/\nu_{\perp}}/L$ (or, alternatively $C^* = D/L^{\nu_{\perp}/\nu_{\parallel}}$) constant [14,15]. The scaling ansatz for the order parameter

*pawel.bryk@gmail.com

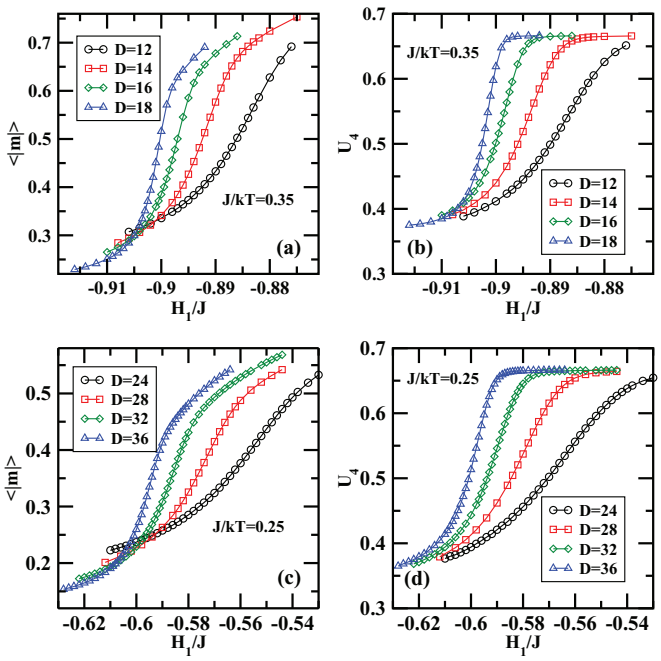

FIG. 1. (Color online) Average absolute magnetization $\langle|m|\rangle$, and cumulants U_4, vs surface field H_1/J. Parts (a) and (b) show the results evaluated at $J/kT = 0.35$ and for the generalized aspect ratio $C^* = 2.8854$, while parts (c) and (d) show the results calculated for $J/kT = 0.25$ and for $C^* = 5.770\,78$. System sizes D are given in the figure.

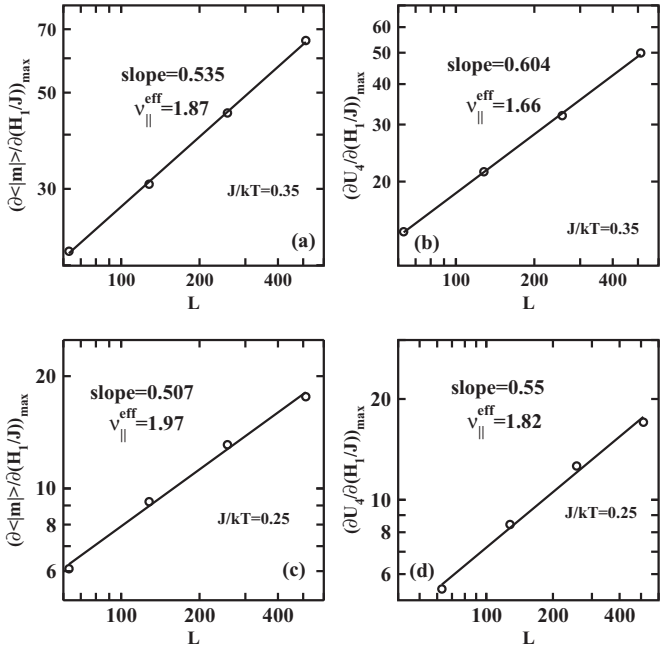

FIG. 2. Estimation of the effective critical exponent $\nu_\parallel^{\rm eff}$ using the AFSS approach. Plots show the maximum slope of the average absolute magnetization $[\partial\langle|m|\rangle/\partial(H_1/J)]_{\rm max}$ and the maximum slope of the cumulant $[\partial U_4/\partial(H_1/J)]_{\rm max}$ vs linear system size L. Parts (a) and (b) denote the results obtained for $J/kT = 0.35$, while parts (c) and (d) are for $J/kT = 0.25$.

probability distribution is given by

$$P_{D,L}(m) = \xi_\parallel^{\beta/\nu_\parallel}\,\tilde{P}(C, L/\xi_\parallel, m\xi_\parallel^{\beta/\nu_\parallel}), \quad m \to 0,\ \ \xi_\parallel \to \infty, \tag{3}$$

where $\tilde{P}$ is a scaling function, whereas β is the order parameter critical exponent. For $d = 3$, $\beta = 0$ while the exponent for the transverse correlation length $\nu_\perp = 0$. Consequently we keep fixed the generalized aspect ratio of the form $C^* = D/\ln(L)$.

Following earlier papers [10–12,14] we keep the temperature constant (which keeps fixed the bulk correlation length) and vary the surface field H_1. The calculations were carried out for two temperatures: $J/kT = 0.35$ with $C^* = 2.8854$, and $J/kT = 0.25$ with $C^* = 5.77078$, and for several lateral system sizes.

Figure 1 shows the plots of the average absolute magnetization and the cumulant vs H_1 calculated for the two temperatures. Unlike the case of $d = 2$, where both $\langle|m|\rangle$ and U_4 exhibit rather well-defined unique intersection points, here the cumulants hardly intersect and the intersections of $\langle|m|\rangle$ have not converged to a unique location either. The nonexistence of intersection points is not as serious a problem, as it looks at first sight. Finite size can cause a shift as well as a rounding of a transition. Both should scale in the same way, should a straightforward application of finite size scaling work. However even then it is possible that the amplitude prefactor for the shift is much larger than the rounding. In such case one would find no intersections for the cumulant.

The large statistical effort together with hyperparallel tempering technique yielded accurate, smooth data allowing for an estimation of the exponent $\nu_\parallel^{\rm eff}$. It has been established [14,15] that $[\partial\langle|m|\rangle/\partial(H_1/J)]_{\rm max} \propto L^{1/\nu_\parallel^{\rm eff}}$, giving a very convenient way of determination of the critical exponent $\nu_\parallel^{\rm eff}$. Likewise, a similar relation holds for cumulants, $[\partial U_4/\partial(H_1/J)]_{\rm max} \propto L^{1/\nu_\parallel^{\rm eff}}$. Figure 2 shows the plots of the maximum slopes of $\langle|m|\rangle$ and U_4 vs L. We find that for both temperatures $\nu_\parallel^{\rm eff}$ is clearly different from the mean-field value $\nu_\parallel^{\rm MF} = 1$, and attains values slightly below 2.

Figure 3(a) shows a log-log plot of the position of maximum susceptibility χ' vs $L^{-1\nu_\parallel^{\rm eff}}$ for $J/kT = 0.25$. We find that the value of the surface field for the wetting transition $H_{1w} = -0.616 \pm 0.002$. Such a very good fit would not be possible if the mean-field value $\nu_\parallel^{\rm MF} = 1$ was used instead. Further consistency checks are displayed in Figs. 3(b) and 3(c). We find a good scaling of the cumulants [cf. Fig. 3(b)] with the estimated value of the effective exponent. Quite surprisingly, the plot of $\langle|m|\rangle$ vs $(H_1 - H_{1w})L^{1/\nu_\parallel^{\rm eff}}$ does *not* collapse [cf. Fig. 3(c)]. Similar results were found for $J/kT = 0.35$ [18]. It seems that there exists additional finite-size effects that should be applied to the ordinate variable $\langle|m|\rangle$. These effects do not exist in $d = 2$. The comparison of the diverging length scales indicates that for $d = 3$ there is still one more divergence, $l_{\rm eq}/\xi_\perp \propto \sqrt{\ln \tau}$ [19], where $l_{\rm eq}$ is the equilibrium film thickness, and τ is the distance from the transition. In contrast, for $d = 2$ this ratio is constant. It is tempting to speculate that the fact that the cumulants *do* collapse is connected with the fact that these additional finite-size effects cancel out, since U_4 is a ratio of moments of magnetization. Unfortunately, at present we do not see a straightforward way of incorporating this effect into the AFSS framework.

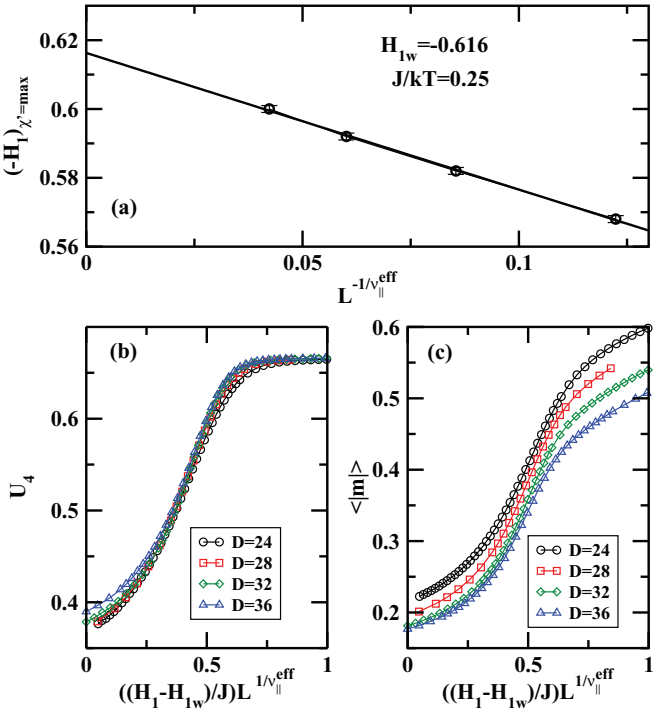

FIG. 3. (Color online) (a) Estimation of the critical surface field for the wetting transition H_{1w}, for $J/kT = 0.25$. The plot shows the log-log plot of the position of the maximum susceptibility χ' vs $L^{-1/\nu_{\parallel}^{\rm eff}}$. The intercept with $L^{-1/\nu_{\parallel}^{\rm eff}} = 0$ yields H_{1w}. (b) Scaling plot of U_4 vs $(H_1 - H_{1w})L^{1/\nu_{\parallel}^{\rm eff}}$ obtained using $H_{1w} = -0.616$ and $\nu_{\parallel}^{\rm eff} = 1.97$. (c) Scaling plot of $\langle|m|\rangle$ vs $(H_1 - H_{1w})L^{1/\nu_{\parallel}^{\rm eff}}$ obtained using $H_{1w} = -0.616$ and $\nu_{\parallel}^{\rm eff} = 1.97$.

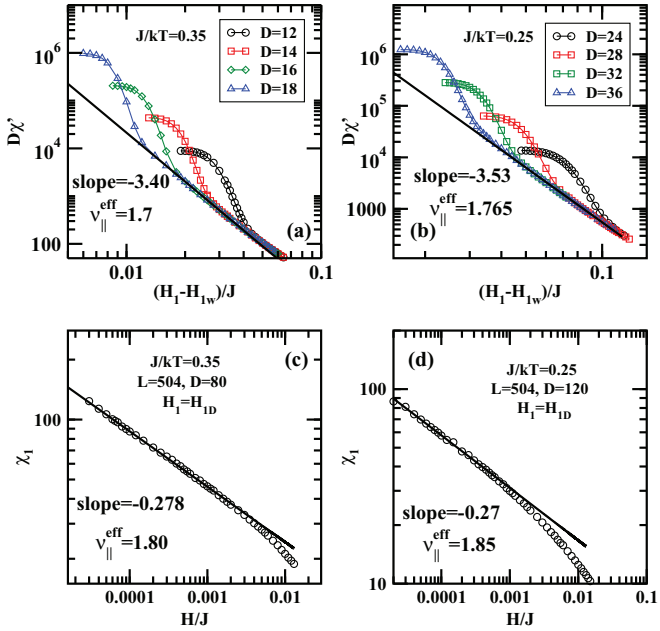

FIG. 4. (Color online) (a), (b) Plots of the mixed surface susceptibility vs $(H_1 - H_{1w})J$. (c), (d) Plots of χ_s vs bulk field H calculated for $H_1 = H_{1w}$. The results were obtained using symmetric system $H_1 = H_D$ and for system sizes given in the figure.

In view of the above it is natural to seek other evidence of the non-mean-field behavior of critical wetting in $d = 3$, which would not resort to the AFSS approach. It has been demonstrated [10,11] that the "surface layer susceptibility" $\chi_s = D\chi' \propto \xi_{\parallel}^2$. It follows, that when plotting χ_s vs $H_1 - H_{1w}$ for several system sizes, the regions unaffected by finite-size effects should exhibit the same slope equal to $2\nu_{\parallel}^{\rm eff}$. This provides additional estimation of the parallel correlation length exponent, independent of finite-size scaling. Figures 4(a) and 4(b) demonstrate that for both temperatures the slope of χ_s in the region free of finite-size effects is a bit less than 4, which is consistent with previous estimates for $\nu_{\parallel}^{\rm eff}$.

As a final check, in Figs. 4(c) and 4(d) we show log-log plots of the surface susceptibility vs. nonzero bulk field H evaluated at the critical surface fields H_{1w}, for the two temperatures in question. The calculations presented here were carried out using the "symmetric" boundary conditions, i.e., $H_1 = H_D$ in order to follow exactly the computational procedure presented in the first simulational studies on critical wetting [10–12]. In such a system wetting films develop independently on both walls. During the simulations we monitor surface layer susceptibility, $\chi_s = \partial m_1/\partial H = L^2 D(\langle m_1 m\rangle - \langle m_1\rangle\langle m\rangle)$. Since $\chi_s \sim H^{-1/2\nu_{\parallel}^{\rm eff}}$ for $H > 0$ at $H_1 = H_{1w}$, the slope gives information about the universality class of the wetting transition [11]. The mean-field behavior would imply a slope of -0.5 and such was the conclusion of the early reports. However, when the calculations are performed for the new estimations of the critical surface fields H_{1w}, we observe clear deviations from mean-field exponents, again consistent with values obtained by different methods. The final values of $\nu_{\parallel}^{\rm eff}$ are obtained by averaging the exponents resulting from four different methods. Putting together all the results we estimate that $\nu_{\parallel}^{\rm eff} = 1.76 \pm 0.08$ for $J/kT = 0.35$ and $\nu_{\parallel}^{\rm eff} = 1.85 \pm 0.07$ for $J/kT = 0.25$. Once the exponents are determined, we are able to calculate the effective wetting parameter. We obtain $\omega_{\rm eff} = 0.44 \pm 0.03$ and 0.46 ± 0.02 for $J/kT = 0.35$ and 0.25, respectively.

Our results indicate that the early conclusions about the mean-field behavior of critical wetting in $d = 3$ can be traced back to the inaccurate estimation of the critical surface field H_{1w}. This is not to say that those simulations were wrong. Simply, using the computing resources available almost 30 years ago it was not possible to arrive at the correct conclusions. It is now clear that sizes like $L = 50$ [10,11] were far too small. The fact that even for the lateral system size $L = 504$ we reach roughly only half of the full nonuniversal value of $\nu_{\parallel} \approx 3.7$ is in accordance with theoretical conjecture of Parry *et al.* [13] about very slow crossover to the asymptotic regime. We estimate that the system sizes required to see in simulations the full nonuniversal behavior of critical wetting must be of the order of tens of thousands of lattice spacings.

In conclusion, we have carried out accurate Monte Carlo simulations of critical wetting transition in $d = 3$. We have found clear deviations from mean-field behavior. We estimate that the effective critical exponent $\nu_{\parallel}^{\rm eff} = 1.71 \pm 0.1$ for $J/kT = 0.35$ and $\nu_{\parallel}^{\rm eff} = 1.76 \pm 0.17$ for $J/kT = 0.25$. Our results clearly support the nonlocal Hamiltonian model [13] and together with Ref. [20] (where related effects due to $\xi_{\rm NL}$ for complete wetting were studied) provide strong evidence

towards the validity of this approach. We have also found that the understanding of finite-size effects on critical wetting in $d = 3$ is still incomplete: Analytical guidance to find the proper extension of the AFSS approach to cope with the weak logarithmic divergence of the perpendicular correlation length remains a future challenge, to reach a full understanding of the simulation results. Thus, a long-standing puzzle may finally be close to its resolution.

P.B. is grateful to W. Rżysko and N. R. Bernandino for many discussions. K.B. thanks E. V. Albano and D. P. Landau for discussions.

[1] L. D. Gelb, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, Rep. Prog. Phys. **62**, 1573 (1999).
[2] L. Bocquet and E. Charlaix, Chem. Soc. Rev. **39**, 1073 (2010).
[3] X.-M. Li, D. Reinhoudt, and M. Crego-Calama, Chem. Soc. Rev. **36**, 1350 (2007).
[4] O. Gang, K. J. Alvine, M. Fukuto, P. S. Pershan, C. T. Black, and B. M. Ocko, Phys. Rev. Lett. **95**, 217801 (2005).
[5] T. Hofmann, M. Tasinkevych, A. Checco, E. Dobisz, S. Dietrich, and B. M. Ocko, Phys. Rev. Lett. **104**, 106102 (2010).
[6] A. O. Parry and C. Rascón, Phys. Rev. Lett. **107**, 206104 (2011).
[7] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Robey, Rev. Mod. Phys. **81**, 739 (2009).
[8] E. Brezin, B. I. Halperin, and S. Leibler, Phys. Rev. Lett. **50**, 1387 (1983).
[9] D. S. Fisher and D. A. Huse, Phys. Rev. B **32**, 247 (1985).
[10] K. Binder, D. P. Landau, and D. M. Kroll, Phys. Rev. Lett. **56**, 2272 (1986).
[11] K. Binder and D. P. Landau, Phys. Rev. B **37**, 1745 (1988).
[12] K. Binder, D. P. Landau, and S. Wansleben, Phys. Rev. B **40**, 6971 (1989).
[13] A. O. Parry, C. Rascon, N. R. Bernardino, and J. M. Romero-Enrique, Phys. Rev. Lett. **100**, 136105 (2008).
[14] E. V. Albano and K. Binder, Phys. Rev. Lett. **109**, 036101 (2012).
[15] E. V. Albano and K. Binder, Phys. Rev. E **85**, 061601 (2012).
[16] S. Wansleben, Comput. Phys. Commun. **43**, 315 (1987).
[17] Q. Yan and J. J. de Pablo, J. Chem. Phys. **111**, 9509 (1999).
[18] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevE.88.030401 for the relevant results at $J/kT = 0.35$.
[19] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12, p. 29.
[20] L. Pang, D. P. Landau, and K. Binder, Phys. Rev. Lett. **106**, 236102 (2011).