Finite-Size Scaling Approach for Critical Wetting: Rationalization in Terms of a Bulk Transition with an Order Parameter Exponent Equal to Zero

Ezequiel V. Albano[1,2] and Kurt Binder[2]

[1]Instituto de Física de Líquidos y Sistemas Biológicos, CCT-CONICET La Plata, UNLP, Calle 59, No. 789 (1900) La Plata, Argentina
[2]Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, D-55099 Mainz, Germany

(Received 24 April 2012; published 16 July 2012)

Clarification of critical wetting with short-range forces by simulations has been hampered by the lack of accurate methods to locate where the transition occurs. We solve this problem by developing an anisotropic finite-size scaling approach and show that then the wetting transition is a "bulk" critical phenomenon with order parameter exponent equal to zero. For the Ising model in two dimensions, known exact results are straightforwardly reproduced. In three dimensions, it is shown that previous estimates for the location of the transition need revision, but the conclusions about a slow crossover away from mean-field behavior remain unaltered.

DOI: 10.1103/PhysRevLett.109.036101 PACS numbers: 68.08.Bc, 05.10.Ln, 05.70.Np

Introduction.—When phase coexistence, e.g., as saturated vapor coexisting with liquid, is possible for a system exposed to a wall, the latter can be either partially or completely wet [1–3]. In the former case, a liquid droplet would meet the wall under a nonzero contact angle θ; in the latter case $\theta = 0$, the wall is coated by a macroscopically thick liquid layer, avoiding direct contact between vapor and wall. Similar phenomena are ubiquitous in condensed matter, e.g., for unmixed phases of fluid or solid mixtures, isotropic-nematic coexistence of liquid crystals, etc. [1–3]. Varying control parameters, e.g., the temperature T, the system may undergo a transition from partial to complete wetting, where $\theta \to 0$; this transition can be of 1st or 2nd order. The latter case is interpreted as a continuous unbinding of a fluctuating interface from the wall. For short-range forces between the particles and the wall, the theory of critical wetting has given rise to a long-standing controversy [4–12]. Computer simulations of suitable models should be a tool to clarify this controversy, but it turns out that this approach has also suffered from severe problems in this case. In the following, we briefly recall these issues.

One needs to describe the critical singularity of the surface excess free energy f_s, which in a notation inspired by standard bulk critical phenomena, is written as [1–3]

$$f_s^{(\mathrm{sing})}/k_BT = |t|^{2-\alpha_s}\tilde{F}_s(H|t|^{-\Delta_s}), \quad t = 1 - T/T_w, \quad H \to 0, \tag{1}$$

where $k_B \equiv 1$ is Boltzmann's constant, T_w is the wetting critical temperature, and H is the field conjugate to the bulk order parameter (magnetic field for an Ising magnet, chemical potential difference for a fluid, etc.). The scaling function $\tilde{F}_s$ need not be specified here. The critical exponents α_s and Δ_s can be related to the exponent $\nu_\parallel$ of the correlation length $\xi_\parallel$ ($\xi_\parallel \propto t^{-\nu_\parallel}$) of interfacial fluctuations in the direction (s) parallel to the wall: $2 - \alpha_s = (d-1)\nu_\parallel$, and $\Delta_s = (\nu_\parallel/2)(d + 1 - \eta_\parallel) = (\nu_\parallel/2)(d+1)$, $d = 2(3)$ being the dimensionality. Note that capillary wave descriptions of the fluctuating interface imply that the exponent $\eta_\parallel$ describing the decay of interfacial correlations at $t = 0$ vanishes [2]. From Eq. (1) one readily obtains the singular behavior of surface excess order parameter [13], $m_s = -(\partial f_s/\partial H)_T$ and susceptibility, $\chi_s = -(\partial^2 f_s/\partial H^2)_T$, namely, $m_s = |t|^{\beta_s}$, $\beta_s = \nu_\parallel(d-3)/2$, and $\chi_s = |t|^{-\gamma_s}$, $\gamma_s = 2\nu_\parallel$.

For $d = 2$, the exact solution [14,15] verifies this description, yielding $\nu_\parallel = 2$ (and hence $\Delta_s = 3$, $\beta_s = -1$, $\gamma_s = 4$). One can also derive the correlation length describing interfacial fluctuations in the transverse direction, $\xi_\perp \propto |t|^{-\nu_\perp}$, with $\nu_\perp = 1$. For $d = 3$, an exact solution is lacking, of course. Mean field theory yields [1,2] $\nu_\parallel = 1$, $\Delta_s = 2$, $\gamma_s = 2$, and $\beta_s = 0$ (i.e., logarithmic divergence, the same holds for $\xi_\perp$, i.e., $\nu_\perp = 0$).

Consideration of fluctuations around mean field theory, however, shows that $d = 3$ is a marginal case [4–6,9,10]. Renormalization group treatments relied on the interface Hamiltonian [4–6,9,10] $\mathcal{H} = \int d\vec{\rho}[\frac{\sigma}{2}(\nabla\ell)^2 + V(\ell)]$, with $\vec{\rho} = (x, y)$ the coordinates parallel to the wall, $\ell(\vec{\rho})$ the local distance of the interface from the wall, σ the interfacial stiffness, and $V(\ell)$ a short-ranged wall potential. The prediction resulted that critical exponents are nonuniversal and differ markedly from mean field theory. For the $d = 3$ Ising model, the relation $\nu_\parallel = (\sqrt{2} - \sqrt{\omega})^{-2}$ leads to $\nu_\parallel \approx 3.7$, since the value of the nonuniversal parameter ω is close to $\omega \approx 0.8$ [16] throughout the regime of interest, being $\omega = k_BT/4\pi\sigma\xi_b^2$, where ξ_b is the bulk correlation range. These results have been called into question from two sides: (i) Monte Carlo simulations of wetting for the Ising model failed to see clear deviations from mean field theory [7]; (ii) theoretical arguments convincingly proved that the starting point of the theory is too simplified, since one needs to describe the wall-interface interaction by a nonlocal Hamiltonian [11,12,17,18]. Despite recent simulation evidence [19] for this assertion, deviations from the mean field exponents should occur which have not been seen.

One basic problem for simulations of critical wetting is, however, that the existing work [7,8] could not study the close vicinity of the transition, simply because the latter could not be located with significant accuracy. While for bulk critical phenomena finite-size scaling [20–22] provides a framework for the accurate estimation of critical properties [23], a similar approach for wetting phenomena has been lacking; it is the purpose of the present Letter to fill this gap.

Finite-size scaling approach.—Equation (1) is less suitable as a basis for finite-size scaling than its bulk counterpart: separating f_s from the bulk requires a semi-infinite system, while simulations require systems with finite linear dimensions L, M (perpendicular and parallel to the surface). To cope with this problem, we choose two equivalent but "antisymmetric" walls: in an Ising context, a surface magnetic field $-|H_1|$ acts at the layer $n = 1$, and $H_L = |H_1|$ acts at the layer $n = L$ (we choose the lattice spacing as length unit). Capillary condensationlike effects then are avoided, and phase coexistence still occurs for $H = 0$ [24]. Second, when linear dimensions L, M are varied, ratios $L/\xi_\perp$, $M/\xi_\parallel$ need to change in the same way (cf. Fig. 1). This means that a generalized aspect ratio $L/M^{\nu_\perp/\nu_\parallel} = C^*$, or equivalently $L^{\nu_\parallel/\nu_\perp}/M = C$, needs to be kept constant [25,26], since at criticality the coarse-grained configurations of the system (cf. Fig. 1) are self-similar on all length scales.

We then observe that for partial wetting the interface is bound to either the layer $n = 1$ or to the layer $n = L$, with equal probability. Thus, in the limit $L \to \infty$ for constant C

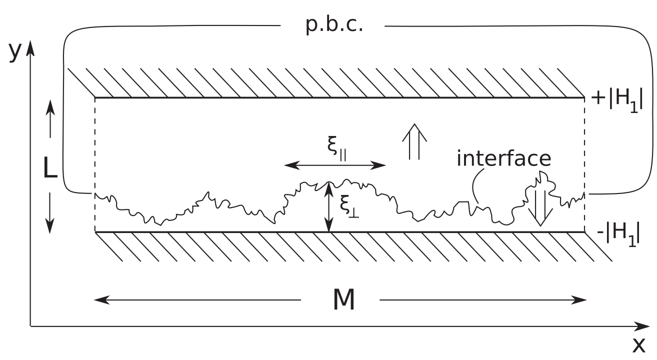

FIG. 1. Schematic description of the system geometry (for $d = 2$ dimensions) and a state slightly below the wetting transition temperature, such that both $\xi_\parallel$ and $\xi_\perp$ are much larger than the lattice spacing, and the coarse-grained interface between domains of different orientation is assumed to be bound to the lower wall (double arrows indicate the orientation of the magnetization). The choice of linear dimensions L, M, the location of the competitive surface fields H_1, and of the periodic boundary conditions (p.b.c.) are indicated.

the bulk order parameter $\langle|m|\rangle$ clearly is nonzero, namely the spontaneous magnetization m_b in the bulk, for an Ising model. In the wet state, the interface is unbound from either wall, it fluctuates around the midpoint position; hence $\langle|m|\rangle \to 0$ for $L \to \infty$. Consequently, we simply take the total magnetization per spin (m) of our system as order parameter density for the wetting transition. We make the standard scaling ansatz [26] for the probability distribution $[P_{LM}(m)]$, then

$$P_{LM}(m) = \xi_\parallel^{\beta/\nu_\parallel}\tilde{P}(C, M/\xi_\parallel, m\xi_\parallel^{\beta/\nu_\parallel}), \quad m \to 0, \qquad \xi_\parallel \to \infty, \tag{2}$$

where β is the order parameter exponent. Since the scaling functions $\tilde{P}$, $\tilde{m}$, and $\tilde{\chi}$ need not be specified, from Eq. (2) we get

$$\langle|m|\rangle = \int_{-1}^{+1} dm|m|P_{LM}(m) = \xi_\parallel^{-\beta/\nu_\parallel}\tilde{m}(C, M/\xi_\parallel), \tag{3}$$

and the susceptibility becomes [23]

$$\begin{aligned} T\chi' &= LM^{d-1}(\langle m^2\rangle - \langle|m|\rangle^2) \\ &= M^{d-1+\nu_\perp/\nu_\parallel - 2\beta/\nu_\parallel}\tilde{\chi}(C, M/\xi_\parallel). \end{aligned} \tag{4}$$

The relation $T\chi' = M^{\gamma/\nu_\parallel}\tilde{\chi}(C, M/\xi_\parallel)$ then just implies the standard hyperscaling for anisotropic criticality [26], $\gamma + 2\beta = (d-1)\nu_\parallel + \nu_\perp$. On the other hand, the singular behavior of χ' in the thermodynamic limit (taken at fixed C) must be compatible with the singularity caused by the surface excess susceptibility χ_s, as derived above

$$\chi' = \chi_s/L \propto M^{-\nu_\perp/\nu_\parallel}\xi_\parallel^{2-\eta_\parallel} \propto M_{(t=0)}^{2-\eta_\parallel-\nu_\perp/\nu_\parallel}. \tag{5}$$

Now, using the above result, [2] $\eta_\parallel = 0$ and equating the powers of M in Eqs. (4) and (5), we find $d - 3 - 2\beta/\nu_\parallel = -2\nu_\perp/\nu_\parallel$, which implies $\beta = 0$ both in $d = 2$ and $d = 3$ (remember $\nu_\perp/\nu_\parallel = 1/2$ in $d = 2$ but $\nu_\perp = 0$ in $d = 3$). Of course, this result could have been guessed since $\langle|m|\rangle = m_b$ for $T < T_w$ while $\langle|m|\rangle = 0$ for $T > T_w$, in the considered limit $L \to \infty$ at fixed C. Second-order transitions with an exponent $\beta = 0$ are rather unusual; for a recent example see Jaubert *et al.* [27]. Another consequence of $\beta = 0$ is that the susceptibility maximum $T\chi_{\max} \propto M^{d-1+\nu_\perp/\nu_\parallel}$ [Eq. (4)]. The result $\beta = 0$ also implies that the wetting transition can be located both in $d = 2$ and $d = 3$ by finding intersections of the curves of any moments ($\langle|m|^k\rangle$, $k = 1, 2, \ldots$) vs T (or H_1, respectively) for different L, but keeping C fixed.

Numerical tests.—Figure 2(a) plots $\langle|m|\rangle$ vs T for the $d = 2$ Ising model and three choices of L for $L^2/M = 9/8$, while Fig. 2(b) replots the data in scaled form. Data for other moments as well as the cumulant $U = 1 - \langle m^4\rangle/(\langle m^2\rangle^2)$ scale similarly well [28], and the intersection points are in full agreement with the exact value $k_BT_w/J = 1.6111$ ($H_1 = 0.70$) [14].

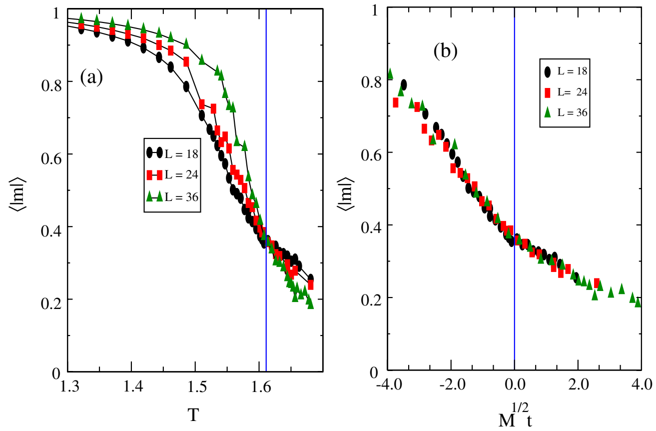

FIG. 2 (color online). (a) Plot of $\langle|m|\rangle$ vs T for $L = 18$, 24 and 36, as indicated, obtained at fixed $L^2/M = 9/8$, and $H_1/J = 0.70$. The vertical line indicates the location of the exactly known [14] wetting transition. Curves connecting points are drawn as guides to the eye only. (b) Scaling plot of $\langle|m|\rangle$ vs $t\sqrt{M}$, using the data of part (a). The vertical line highlights the transition point ($t = 0$). Note that no adjustable parameter occurs there whatsoever.

Figure 3 refers to the $d = 3$ Ising model, using H_1/J as a control parameter at fixed $T/J = 4.0$. A reasonably well-defined intersection occurs for both $\langle|m|\rangle$ [cf. Fig. 3(c)] and the cumulant [cf. Fig. 3(a)] for $H_{1w}/J = 0.585 \pm 0.015$, clearly exceeding the value $H_{1w}/J = 0.55 \pm 0.01$ suggested earlier [7]. In this case, the intersections of $\langle|m|\rangle$ show more systematic scatter. The cumulants can be scaled, at least roughly, with the mean-field value $\nu_\parallel^{\mathrm{MF}} = 1$ [cf. Fig. 3(b)], confirming the earlier conclusion [7] that critical wetting with short-range forces is mean-field-like, at least if one does not approach the transition too closely. In fact, the data for $\langle|m|\rangle$ [Fig. 3(d)] already indicate crossover towards a different critical behavior since $\langle|m|\rangle$ cannot be scaled with $\nu_\parallel^{\mathrm{MF}} = 1$, but rather a (rough) scaling is possible with an effective exponent $\nu_\parallel^{\mathrm{eff}} = 2$.

Figure 4 analyzes the susceptibility both in $d = 2$ and in $d = 3$: indeed, the predictions $\chi_{\max} \propto M^{3/2}$ ($d = 2$) and M^2 ($d = 3$), that hold independently of the value of $\nu_\parallel$ and the estimate for the location of the transition, are nicely verified. The predictions for the position of the maximum, $T_w - T_{\max} \propto M^{-1/\nu_\parallel}$ ($\nu_\parallel = 2, d = 2$) or $H_{1w} - H_{1\max} \propto M^{-1/\nu_\parallel}$ ($= M^{-1}$ in the mean field regime) also are compatible with the data. An interesting limit occurs when $L/\sqrt{M}$ (in $d = 2$) or $L/\ln M$ (in $d = 3$) tends to zero: then a crossover to the interface localization transition occurs, which simply is a transition belonging to the universality class of the $(d - 1)$ Ising model (it is properly defined taking M to infinity keeping L finite [24,29,30]. Note that for large L it has a mean field character, apart from a very narrow regime around the critical point [30]). Although for L tending to infinity the location of this transition converges to the wetting transition, its (mean field) exponents are not at all related to critical wetting [30].

So far, by determining the intersection points of the moments of the order parameter and the cumulant, we

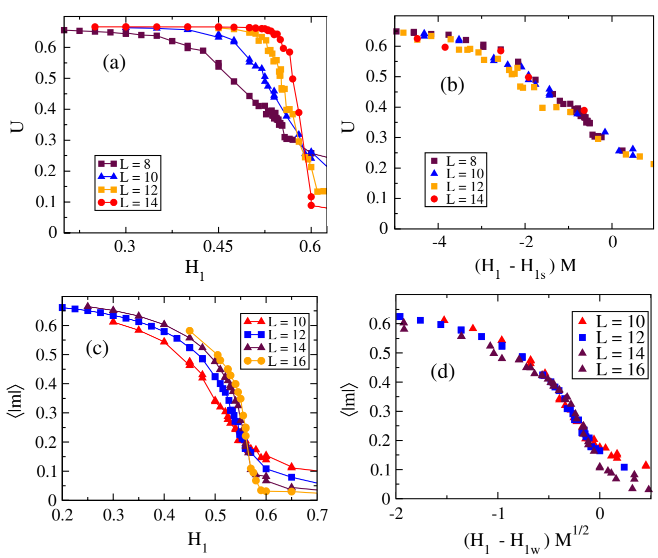

FIG. 3 (color online). (a) and (c) show plots of the cumulant $U = 1 - \langle m^4\rangle/(3\langle m^2\rangle^2)$ and $\langle|m|\rangle$ vs H_1/J, respectively. Data obtained for a fixed value of $C^* = L/\ln M = 2.8854$ and different lattice sizes, as indicated. (b) and (d) show scaling plot of U and $\langle|m|\rangle$ vs $(H_1 - H_{1w})M^{1/\nu_\parallel}$, obtained by using $H_{1w}/J = 0.585$, $\nu_\parallel = 1$ (b) and $\nu_\parallel = 2$ (d), respectively. If we assign the exponents in the reverse way in (b) and (d), the scatter in the data points is distinctly larger.

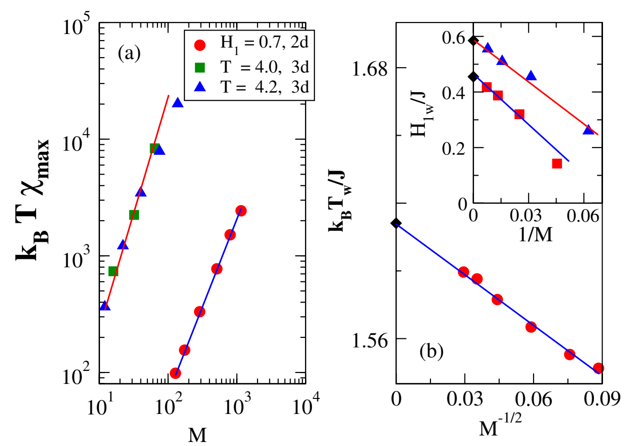

FIG. 4 (color online). (a) Log-log plot of $k_BT\chi'_{\max}$ vs M for both $d = 2$ at $H_1/J = 0.70$, $L^2/M = 9/8$, and $d = 3$ at both $k_BT/J = 4.0$, $L/\ln M = 2.8854$ and $k_BT/J = 4.2$, $L/\ln M = 3.246$. The slopes $\gamma/\nu_\parallel = 3/2 (d = 2)$ and $2 (d = 3)$ are indicated. (b) Plot of the location of the susceptibility maxima k_BT_w/J vs $M^{-1/\nu_\parallel}$ ($\nu_\parallel = 2$, $d = 2$) and H_{1w}/J vs. M^{-1} ($\nu_\parallel = 1$, $d = 3$, inset). In the inset we used the same symbols as in (a) for data taken at different temperatures. In all cases the (black) diamonds show the location of the extrapolated values, namely $k_BT/J = 1.6111$ ($H_{1w}/J = 0.70$, $d = 2$), $H_{1w}/J = 0.585$ ($k_BT/J = 4.0$, $d = 3$), and $H_{1w}/J = 0.455$ ($k_BT/J = 4.2$, $d = 3$). Error bars are not exceeding the size of the symbols.

TABLE I. Summary of critical wetting points of the $d = 3$ confined Ising magnet. The error bars merely reflect the scattering of the intersection points of the moments of the order parameter and the cumulants.

T	2.857	3.8	4.0	4.2	4.35
H_{1w}	0.905(15)	0.667(20)	0.585(15)	0.455(15)	0.275(10)

have evaluated the critical points for the wetting transition in $d = 3$ listed in Table I. In this way, we can address an additional problem of great interest, namely the wetting behavior of the Ising model near bulk criticality. In fact, for a second-order wetting transition one has that

$$H_{1w} \propto (T_{cb} - T)^{\Delta_1}, \tag{6}$$

where Δ_1 is a surface critical exponent [31]. In mean-field theory, supposed to be exact for $d \geq 4$, one has $\Delta_1 = 1/2$. On the other hand, in $d = 2$ the exact solution [14,15] implies $\Delta_1 = 1/2$, in full agreement with our numerical data [28] (not shown here for the sake of space). But, in $d = 3$ the exponent is only know approximately from numerical data, e.g., $\Delta_1 \simeq 0.45(3)$ [8]. Furthermore, by using a scaling relationship between Δ_1 and the critical exponent of the magnetization of the layer in contact to the wall, i.e., $m_1 \propto t^{\beta_1}$ [31], one obtains $\Delta_1 \simeq 0.48(3)$, by using both the numerical result $\beta_1 \simeq 0.78$ [32] and a field-theoretical calculation $\beta_1 \simeq 0.8$ [31]. Our results (cf. Table I) suggest a somewhat larger effective exponent $\Delta_1^{\mathrm{eff}} \simeq 0.60(5)$, but presumably one needs to obtain data closer to T_{cb} for a realiable estimate.

Concluding remarks.—The framework of finite-size scaling, that is a very powerful tool [22,23] for the study of bulk critical phenomena, has been extended to critical wetting. In $d = 2$, it works straightforwardly for the Ising model, and can yield useful results also for other models (e.g., the Blume-Capel model [28]). In $d = 3$, we find previous estimates [8] for the location of the wetting transition to be rather inaccurate, but we confirm the mean-field like critical behavior (except for a very narrow region around the wetting transition, which will require much larger linear dimensions than were accessible in our study). We expect that the present approach will allow a new look on this long-standing problem, including also further experimental work [3,33].

One of us (E. V. A.) received support from the Schwerpunkt für Rechnergestützte Forschungsmethoden in den Naturwissenschaften (SRFN), Mainz (Germany); CONICET and UNLP (Argentina). One of us (K. B.) is indebted to P. Bryk for stimulating discussions.

[1] D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986), p. 45.
[2] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12, p. 1.
[3] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley, Rev. Mod. Phys. **81**, 739 (2009).
[4] E. Brézin, B. I. Halperin, and S. Leibler, Phys. Rev. Lett. **50**, 1387 (1983).
[5] R. Lipowsky, D. M. Kroll, and R. K. P. Zia, Phys. Rev. B **27**, 4499 (1983).
[6] D. S. Fisher and D. A. Huse, Phys. Rev. B **32**, 247 (1985).
[7] K. Binder, D. P. Landau, and D. M. Kroll, Phys. Rev. Lett. **56**, 2272 (1986); K. Binder and D. P. Landau, Phys. Rev. B **37**, 1745 (1988).
[8] K. Binder, D. P. Landau, and S. Wansleben, Phys. Rev. B **40**, 6971 (1989).
[9] T. Halpin-Healey and E. Brezin, J. Phys. (Paris) **48**, 757 (1987); Phys. Rev. Lett. **58**, 1220 (1987).
[10] R. Lipowsky and M. E. Fisher, Phys. Rev. B **36**, 2126 (1987); Phys. Rev. Lett. **57**, 2411 (1986).
[11] A. O. Parry and C. J. Boulter, Phys. Rev. E **53**, 6577 (1996).
[12] A. O. Parry, J. M. Romero-Enrique, and A. Lazarides, Phys. Rev. Lett. **93**, 086104 (2004).
[13] K. Binder and P. C. Hohenberg, Phys. Rev. B **6**, 3461 (1972); **9**, 2194 (1974).
[14] D. B. Abraham, Phys. Rev. Lett. **44**, 1165 (1980).
[15] D. B. Abraham, in *Phase Transition and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1986), Vol. 10, p. 1.
[16] M. E. Fisher and A. J. Jin, Phys. Rev. Lett. **69**, 792 (1992).
[17] A. O. Parry, C. Rascón, N. R. Bernardino, and J. M. Romero-Enrique, J. Phys. Condens. Matter **18**, 6433 (2006); **19**, 416105 (2007).
[18] A. O. Parry, C. Rascón, N. R. Bernardino, and J. M. Romero-Enrique, Phys. Rev. Lett. **100**, 136105 (2008).
[19] L. Pang, D. P. Landau, and K. Binder, Phys. Rev. Lett. **106**, 236102 (2011).
[20] M. E. Fisher, in *Critical Phenomena*, edited by M. S. Green (Academic, New York, 1971), p. 3.
[21] K. Binder, Phys. Rev. Lett. **47**, 693 (1981).
[22] *Finite Size Scaling and Numerical Simulation of Statistical Systems*, edited by V. Privman (World Scientific, Singapore, 1990).
[23] K. Binder, Rep. Prog. Phys. **60**, 487 (1997).
[24] K. Binder, D. P. Landau, and A. M. Ferrenberg, Phys. Rev. Lett. **74**, 298 (1995); Phys. Rev. E **51**, 2823 (1995).
[25] S. M. Bhattacharjee and J. F. Nagle, Phys. Rev. A **31**, 3199 (1985).
[26] K. Binder and J. S. Wang, J. Stat. Phys. **55**, 87 (1989).
[27] L. D. C. Jaubert, J. T. Chalker, P. C. W. Holdsworth, and R. Moessner, Phys. Rev. Lett. **105**, 087201 (2010).
[28] E. V. Albano and K. Binder, Phys. Rev. E **85**, 061601 (2012).
[29] A. O. Parry and R. Evans, Phys. Rev. Lett. **64**, 439 (1990).
[30] K. Binder, R. Evans, D. P. Landau, and A. M. Ferrenberg, Phys. Rev. E **53**, 5023 (1996).
[31] H. W. Diehl, Int. J. Mod. Phys. B **11**, 3503 (1997).
[32] D. P. Landau and K. Binder, Phys. Rev. B **41**, 4633 (1990).
[33] Y. Hennequin, D. G. A. L. Aarts, J. O. Indekeu, H. N. W. Lekkerkerker, and D. Bonn, Phys. Rev. Lett. **100**, 178305 (2008).