Equilibrium crystal shapes in the Potts model

R. P. Bikker, G. T. Barkema, and H. van Beijeren
Institute for Theoretical Physics, Utrecht University, P.O. Box 80.195, TD Utrecht, The Netherlands
(Received 17 November 2000; published 26 June 2001)

The three-dimensional q-state Potts model, forced into coexistence by fixing the density of one state, is studied for $q=2$, 3, 4, and 6. As a function of temperature and number of states, we studied the resulting equilibrium droplet shapes. A theoretical discussion is given of the interface properties at large values of q. We found a roughening transition for each of the numbers of states we studied, at temperatures that decrease with increasing q, but increase when measured as a fraction of the melting temperature. We also found equilibrium shapes closely approaching a sphere near the melting point, even though the three-dimensional Potts model with three or more states does not have a phase transition with a diverging length scale at the melting point.

DOI: 10.1103/PhysRevE.64.016125 PACS number(s): 05.50.+q, 68.05.−n, 68.35.Md, 75.10.Hk

I. INTRODUCTION

If a binary mixture of fixed composition is brought into a coexistence state it will phase-separate into two pure phases, separated by an interface with a shape that minimizes the free energy of the system [1]. The phase with the smaller volume will typically organize itself into a compact shape, known as the equilibrium shape. If the surface tension (excess free energy per unit interface area) is isotropic, this equilibrium shape will be a sphere. If either of the coexisting phases is crystalline, the anisotropic surface tension will lead to an aspheric equilibrium crystal shape (ECS). The ECS and the orientation dependence of the surface tension are intimately related. Once the surface tension is known for all orientations, the so-called Wulff construction [2,3] allows the generation of the ECS. The reverse is also possible, i.e., determining the surface tension as a function of orientation from the ECS; this is a procedure followed in this manuscript.

The ECS has been the subject of experimental studies [4–11]. One striking feature the ECS may show is a roughening transition: the disappearance of facets (macroscopically flat surfaces) under rising temperature. In practice equilibrium shapes are rarely seen and they are hard to produce experimentally, but this does not mean they are without practical importance. For example, the presence or absence of facets in the ECS influences growth properties, such as the speed of growth and the growth mode, even though growth shapes may differ strongly from the ECS. In general, the determination of the orientation dependence of the surface tension is a tough problem. Experimentally it is very difficult to measure, mainly due to equilibration problems. Numerical studies suffer from the same equilibration problems, and in the most common simulation techniques each surface orientation requires a separate simulation. Theoretical results only have been obtained for simplified models like the body-centered solid-on-solid (BCSOS) model [12].

The prototypical model in which such properties are studied numerically, is the conserved-order-parameter Ising model with nearest-neighbor interactions, in which the total magnetization is kept constant. In the two-dimensional Ising model, the ECS is a square at zero temperature, but at any finite temperature the ECS loses all flat faces. It gradually changes into a circle when the temperature is approaching the critical temperature. The behavior is richer in the three-dimensional Ising model. At zero temperature, the ECS is a cube. At finite temperatures below the roughening temperature T_R, the ECS still has macroscopically flat faces but the corners as well as the edges are rounded. Above the roughening temperature, the ECS does no longer feature macroscopically flat faces. If the temperature is increased from the roughening temperature to the critical temperature, the ECS gradually approaches a sphere.

An extension of the Ising model is the Potts model, defined by the Hamiltonian

$$H=-J\sum_{\langle i,j\rangle}\delta(\sigma_i,\sigma_j), \tag{1}$$

in which J is the coupling constant, δ denotes the Kronecker delta function, and the summation runs over all pairs of nearest-neighbor sites, each having a spin with value $\sigma=1,\ldots,q$. Note that the two-state Potts model is equivalent to the Ising model. The topic of this manuscript is to study how the ECS and related properties such as the roughening temperature behave with increasing number of states. Like in two dimensions the model undergoes a phase transition at a temperature we will refer to as the melting temperature T_m. Below this temperature the model has q different phases, each of which is dominated by one of the q possible spin values, whereas for temperatures above T_m there is only a single phase in which on average all of the spin values are present in equal amounts. It is known that for $q\geqslant 3$ the melting transition is of first order [13], in contrast to the two-state (Ising) case where the transition is continuous. It is therefore not clear *a priori* whether there is a roughening transition when $q\geqslant 3$, nor in how far the ECS should approach a sphere when T approaches T_R. Furthermore, one should expect the surface tension to approach a nonzero limit as the melting temperature is approached from below, whereas for continuous transitions it vanishes in this limit.

The manuscript is organized as follows. First, in Sec. II we outline the numerical procedure to efficiently determine the ECS and show the resulting shapes for all numbers of states for which accurate numerical estimates of the melting temperature have been reported: $q=2$ (Ising), 3, 4, and 6. In

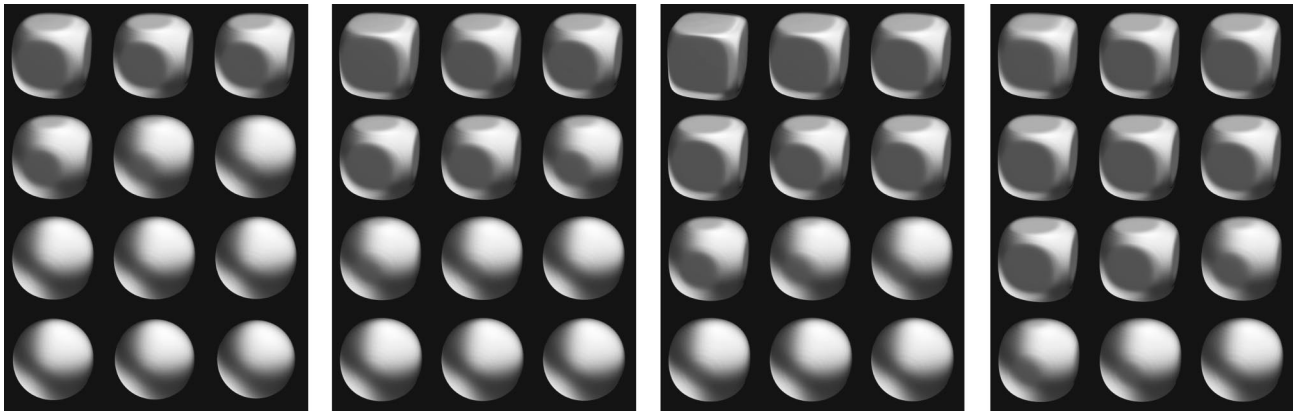

FIG. 1. Symmetrized equilibrium cluster shapes. From left to right, the boxes show the shapes for the 2-, 3-, 4-, and 6-state Potts model, successively. Within each box, again from left to right, the temperature increases from 0.25 T_m to 0.80 T_m, in increments of 0.05 T_m.

Sec. III we present some theoretical considerations on the behavior of the model for large values of q. Section IV covers the measurements on the location of the roughening transition. In Sec. V we present the orientation-dependent surface tension as extracted from the data on the ECS. We conclude with a discussion of the results and an outlook to further research.

II. OBTAINING THE ECS

Equilibrium shapes can be determined numerically for the q-states Potts model by forcing it into coexistence. This may be achieved by enforcing a constraint on the spin densities. The richest behavior is observed in case the maximum of $q-1$ constraints are enforced, but mostly the resulting configurations are still determined by the orientation dependence of the surface tension, and can thus be obtained indirectly from numerical simulations with a single constraint enforced.

The constraint enforced in our simulations is the conservation of the density of state 1, while the densities of all other states are allowed to fluctuate freely. To implement this, we combined a density-conserving cluster algorithm, described in a recent article [14], with Glauber dynamics [1], constrained to never flip spins into or out of state 1. We chose the ratio of cluster updates and Glauber updates per site to be unity (i.e., a comparable amount of computational effort was spent to each). The run-times of the simulations varied between 400 000 and 800 000 Monte Carlo updates per site and we typically allowed the system to thermalize for 60 000 to 100 000 time steps. The lateral system size was 50 sites in all lattice directions, with periodic boundary conditions, and the fraction of conserved spins was typically 0.25. In order to directly obtain the ECS we repeatedly took ''snapshots'' of the evolving system, each time centering the cluster around the origin. Taking the autocorrelation time into account, we typically obtained 2000 independent equilibrium snapshots from one simulation. At the end we calculated the time-averaged density profile of the conserved component. Our results for the ECS were obtained from the 50% isodensity surface in this time-averaged density profile.

In Fig. 1, we show the equilibrium crystal shapes for several temperatures, for the case of $q=2$ (Ising), 3, 4, and 6 states, respectively. These shapes are obtained from the 50% isodensity surface in the density profile, after full symmetrization, i.e., after we averaged over all 48 possible invariant mirror images of the cube.

The simulation temperatures are chosen as fractions of the estimates for the melting temperatures reported in Refs. [15–17]; these values are given in Table I.

III. BEHAVIOR FOR LARGE q

For large values of q the thermal evolution of the ECS can be understood from the following arguments. First of all notice that at low temperatures the q phases of the q-state Potts model without conservation laws will be very close to the zero temperature phases in which all spins on the lattice have equal value. In d dimensions the free energy per site f of these states therefore satisfies

$$f(T_{low}) \approx -dJ. \tag{2}$$

The high-temperature phase is completely dominated by the entropy resulting from the q different occupation options for each site, with a resulting entropy per site of $k_B \ln q$ and free energy

$$f(T_{high}) \approx -k_B T \ln q. \tag{3}$$

The melting temperature is obtained to a good approximation by equating these two expressions, with the result

$$\beta_m J \approx \frac{1}{d} \ln q \tag{4}$$

for large q, with $\beta = 1/(k_B T)$. Note that for $d=2$ this is in agreement with the exact result [17] $\beta_m J = \ln(1+\sqrt{q})$. For large q one sees that $J \gg k_B T$ for temperatures below T_m. Therefore local excitations, typically consisting of single overturned spins, will be extremely rare in the low-temperature phases, as they require an energy far exceeding the gain in free energy due to the entropy increase. Similarly,

TABLE I. Inverse transition temperature, ratio of the roughening and transition temperatures, and inverse roughening temperature of the q-states Potts model. The references in the first column point to the sources we used for the data on the transition temperatures. For comparison we added the critical interaction parameter $\beta J_m = \ln(1+\sqrt{q})$ for the two-dimensional Potts model in the last column.

q	βJ_R	βJ_m	T_R/T_m	$\beta J_m(2D)$
2 [15]	0.84(2)	0.443309(2)	0.53(3)	0.8813
3 [16]	0.86(2)	0.5505(1)	0.64(3)	1.0051
4 [17]	0.89(2)	0.631(2)	0.71(3)	1.0986
6 [17]	0.93(2)	0.751(2)	0.81(3)	1.2382

the tendency to form clusters of equal spin in the high-temperature phase is very weak, as the resulting gain of energy by far does not compensate for the resulting loss of entropic free energy. As a result the melting transition for high q will become very sharp.

Now we can also estimate the orientation dependence of the surface tension. In good approximation, an interface of (001)-orientation (or symmetrically equivalent) is just a flat interface between two pure states, with a free energy of J (one broken bond) per unit area. Similarly, by counting broken bonds, one finds that an interface of $kl1$-orientation (here k and l are not necessarily integers) has an energy per unit area of $(1+k+l)/\sqrt{1+k^2+l^2}$. For nonzero temperature there is an additional contribution from the entropy of the steps required to form such an interface. For not too large values of k and l this may be obtained by multiplying the step density needed to create a surface of orientation $kl1$ with the meandering entropy of such a step. The resulting expression is

$$f(T)=\frac{(1+k+l)J-k_BT\ln[(k+l)^{k+l}/(k^k l^l)]}{\sqrt{1+k^2+l^2}}. \qquad (5)$$

This result is independent of the value of q, especially it also holds for the Ising model. Excitations creating spins not belonging to the two phases that coexist at the interface are so rare that they may be neglected completely. For k/l or $l/k \ll \exp(-\beta J)$ the entropy becomes dominated by thermal step fluctuations, but this concerns an extremely small range of orientations only (However, it does set the distance between facet edges). Blöte and Hilhorst [18] give expressions for the free energy from which the low-temperature ECS may be obtained for all orientations.

The unimportance of all but the two coexisting phases implies that for large q the (001)-facets do not roughen, as T_m is well below the roughening temperature of these facets in the Ising model (see Sec. IV). The equilibrium shape then remains nearly cubic for all temperatures up to T_m.

IV. LOCATION OF THE ROUGHENING TRANSITION

Roughening transitions of crystal surfaces are characterized by the disappearance of macroscopically flat regions, or facets, in the ECS. Facets existing at low temperatures often disappear when the temperature increases, at a characteristic temperature known as the roughening temperature T_R of the specific-facet orientation. At this temperature the inverse radius of curvature $(R_c)^{-1}$ of the crystal surface at the center of the facet jumps from zero (when a facet is present) to a nonzero value. Using renormalization-group calculations, Jayaprakash *et al.* [19] (see also van Beijeren and Nolden [12]) showed that the size of this jump satisfies the universal relationship

$$R_c=\frac{z_0 kT_R\pi}{2\gamma_0}, \qquad (6)$$

where z_0 is the distance from the tangent plane at the facet to the center of mass of the crystal and γ_0 is the surface tension of the 001-facet at $T=T_R$. The latter is not known exactly for any of the q-state Potts models in three dimensions. An approximation consisting of the ground-state value plus the first correction term in a low-temperature expansion is

$$\gamma_0=\beta J-2e^{-4\beta J}. \qquad (7)$$

It will turn out that this approximation suffices for our goal: even for the smallest q values the contribution of the correction term at $T=T_R$ is already smaller than the estimated systematic error in the curvature measurements.

If the center of mass of the ECS is placed at the origin, the centers of the facets that are present below the roughening temperature are located on the principal axes. To estimate the location of the roughening transition, we first measure the curvature at the six points where the ECS (obtained as in the previous section) cuts a principal axis, in the two principal directions tangential to the surface. The curvature was obtained by fitting a quadratic function $y=y_0-\frac{1}{2}y_1x^2$; the fitted result for y_1/y_0 is the normalized inverse radius of curvature. Since we use a nonzero fitting range, the slope of the curve cannot become infinite and consequently we do not observe a jump in curvature; in fact we find quite smooth dependence of curvature on temperature, as a result of finite size, round-off and fluctuation effects. However, we made sure that our procedure to estimate T_R is not very sensitive to this. Notably, our estimate of the roughening temperature for the Ising model is close to previous estimates: Adler [20], reported $T_R/T_m=0.55\pm0.02$, Mon *et al.* [21] reported $T_R/T_m=0.54\pm0.02$, and Holzer and Wortis [22] reported $T_R/T_m=0.545\pm0.004$.

The resulting measurements of the normalized inverse curvature are plotted in Fig. 2. The error bars indicate the statistical error; additional simulations for some points indicate that the systematic errors arising from the effects of thermalization, cluster shape deformations, long lived thermal excitations, etc., are larger. In the same plot, the curves described by Eq. (6) are also plotted. The intersection points of these two curves are estimates of the location of the roughening transition. The resulting values for the roughening temperature can be found in Table I; the error indications are our estimates of the statistical and systematic errors combined.

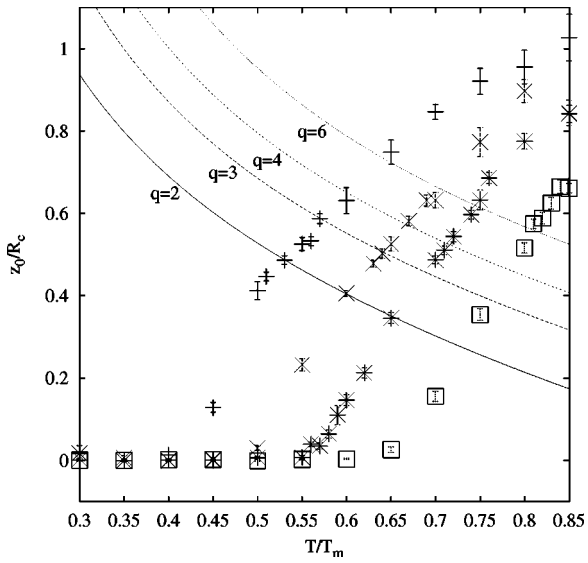

FIG. 2. Normalized inverse curvature for the Potts model with $q=2$ (pluses), 3 (crosses), 4 (stars), and 6 states (squares). The intersection points of the lines, described by Eq. (6), and the data points are estimates for the roughening temperature T_R.

In the previous section we noted that for large q there is no roughening transition. Obviously, $q=6$ is not large enough to observe this, but the increase of T_R/T_m is very clear. It would be interesting to know the largest q value for which a stable roughening transition does exist. The values of βJ_R quoted in Table I combined with the estimate of T_m of Eq. (4) suggest a value between 20 and 40. With the present method this would make simulations very slow, and it would also require an accurate measurement of the melting temperatures, since no literature values exist.

V. ORIENTATION DEPENDENCE OF THE SURFACE TENSION

In general, the surface tension γ can be written as $\gamma=\gamma_0\gamma(\hat{n})$, where γ_0 is the surface tension of an interface oriented in the (001), or symmetrically equivalent direction [12]. In experiments with Pb crystals in equilibrium with their vapor, Heyraud and Métois used the inverse Wulff construction (see Ref. [12]) to obtain the angular part of the surface tension $\gamma(\hat{n})$ as a function of orientation $\hat{n}$ and the same method has been employed by Surnev *et al.* [10]. Here we use it to obtain the orientation dependence of the surface tension for each ECS as obtained in Sec. II.

The surface tension $\gamma(\hat{n})$ is proportional to the distance from the center of the cluster to the tangent plane perpendicular to $\hat{n}$, touching the isosurface in the point $\vec{X}$. If the ECS is scaled such that the distance to the surface from the center of the shape along the lattice axes is unity, then

$$\gamma(\hat{n})=\max_I \hat{n}\cdot\vec{X}, \tag{8}$$

where $\vec{X}$ is an element of the scaled isosurface I. Thus, for every direction $\hat{n}$, we have to find the point $\vec{X}$ in the isosurface, for which the number $\hat{n}\cdot\vec{X}$ is maximal. This procedure works in both two and three dimensions.

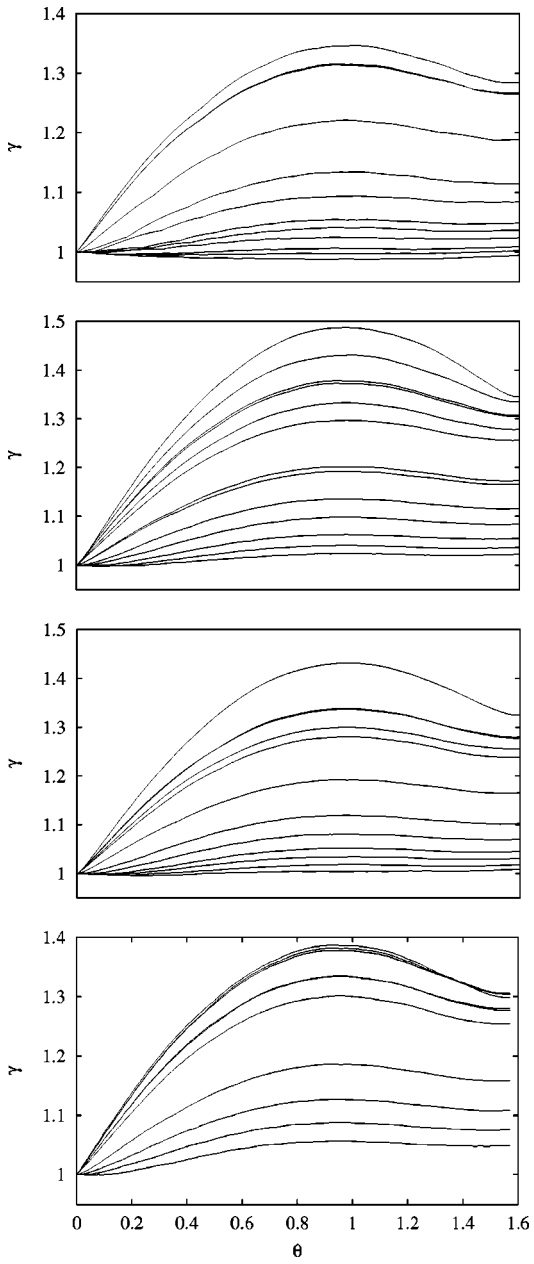

FIG. 3. Angular part of the surface tension $\gamma(\hat{n})$ as a function of orientation $\hat{n}$, measured along the arc that connects the 001 (at $\Theta=0$), 111 (at $\Theta=0.955$), and 110 directions (at $\Theta=\pi/2$, where θ is the azimuthal angle). From top to bottom the plots show the 2, 3, 4, and 6 states results. In each plot, from the uppermost curve downwards, the temperature ranges from 0.25 T_m to 0.80 T_m, in increments of 0.05 T_m.

Using ECS's obtained from fully symmetrized density profiles, we measured $\gamma(\hat{n})$ along the arc in the 11k zone, which connects the (100), (111), and (110) directions. Figure 3 shows the results.

These figures show that the angular dependence of the surface tension becomes nearly constant at increasing temperature, for all numbers of states q considered here. Thus,

for $q \leqslant 6$ the ECS approaches a sphere. For the Ising model ($q=2$) this was to be expected, since this model undergoes a continuous phase transition at the melting point. On the other hand, it is also clear that aspheric deviations become larger with increasing q. As we saw in Sec. III the ECS becomes nearly cubic for large q. Obviously, $q=6$ still should be considered a small q value in this context.

If the ECS is not faceted, the angular part of the surface tension will approach the point $\Theta=0$ with zero slope. If, however, the ECS has (001) facets, the approach to the point $\Theta=0$ will occur with a nonzero slope, resulting in a cusp in the slope along the arc through this point [12]. Looking for the temperature where these cusps first appear is an alternative way to measure the roughening temperature. We found this to be less accurate than the procedure described in Sec. IV. The results were, however, consistent.

VI. DISCUSSION AND FUTURE RESEARCH

We studied the Potts model with $q=2$, 3, 4, and 6 states, forced into coexistence by fixing the density of one state. The resulting ECS was studied as a function of temperature and number of states.

We found that the roughening transition, which is well known for the Ising model (equivalent to the two-states Potts model), persists for higher numbers of states, at least up to six states. The temperature T_R, at which this roughening transition occurs, measured as a fraction of the melting temperature, tends to increase with increasing number of states.

In the future, we want to study the more general and richer behavior of the ECS in case more than one quantity is conserved. For instance, in the three-state Potts model close to its melting point, with the constraint $\rho_1 \geqslant \rho_2 \geqslant \rho_3$, the ECS resembles the shape of two soap bubbles with a common interface; this changes under variations of temperature and the ratio ρ_2/ρ_3.

We also want to look at equilibrium shapes in constrained geometries, like fluids between parallel plates, or systems with grain boundaries.

Finally we are investigating the behavior for larger q values with the aid of different Monte Carlo techniques.

[1] M.E.J. Newman and G.T. Barkema, *Monte Carlo Methods in Statistical Physics* (Oxford University Press, Oxford, 1999).
[2] G. Wulff, Z. Kristallogr. Mineral. **43**, 449 (1901).
[3] C. Rottman and M. Wortis, Phys. Rep. **103**, 59 (1984).
[4] J.C. Heyraud and J.J. Métois, Surf. Sci. **128**, 334 (1983).
[5] J.J. Métois and J.C. Heyraud, Surf. Sci. **180**, 647 (1987).
[6] J.M. Bermond, J.J. Métois, J.C. Heyraud, and F. Floret, Surf. Sci. **416**, 430 (1998).
[7] A. Pavlovska, K. Faulian, and E. Bauer, Surf. Sci. **221**, 233 (1989).
[8] A. Pavlovska, D. Dobrev, and E. Bauer, Surf. Sci. **286**, 176 (1993); **314**, 341 (1994).
[9] S. Surnev, P. Coenen, B. Voigtländer, H.P. Bonzel, and P. Wynblatt, Phys. Rev. B **56**, 12 131 (1997).
[10] S. Surnev, K. Arenhold, P. Coenen, B. Voigtländer, and H.P. Bonzel, J. Vac. Sci. Technol. A **16**, 1059 (1998).
[11] K. Arenhold, S. Surnev, H.P. Bonzel, and P. Wynblatt, Surf. Sci. **4242**, 271 (1999).
[12] H. van Beijeren and I. Nolden, in *Structure and Dynamics of Surfaces II (Topics in Current Physics 43)*, edited by W. Schommers and P. von Blanckenhagen (Springer-Verlag, Berlin, 1987).
[13] G.T. Barkema and J. de Boer, Phys. Rev. A **44**, 8000 (1991).
[14] R.P. Bikker and G.T. Barkema, Phys. Rev. E **62**, 5830 (2000).
[15] H.W.J. Blöte, E.J. Luijten, and J.R. Heringa, J. Phys. A **28**, 6289 (1995).
[16] J. Machta, Y.S. Choi, A. Lucke, T. Schweizer, and L.M. Chayes, Phys. Rev. E **54**, 1332 (1996).
[17] F.Y. Wu, Rev. Mod. Phys. **54**, 235 (1982).
[18] H.W.J. Blöte and H.J. Hilhorst, J. Phys. A **15**, L631 (1982).
[19] C. Jayaprakash, W.F. Saam, and S. Teitel, Phys. Rev. Lett. **50**, 2017 (1983).
[20] J. Adler, Phys. Rev. B **36**, 2473 (1987).
[21] K.K. Mon, S. Wansleben, D.P. Landau, and K. Binder, Phys. Rev. Lett. **60**, 708 (1988); Phys. Rev. B **39**, 7089 (1989).
[22] M. Holzer and M. Wortis, Phys. Rev. B **40**, 11 044 (1989).