Reply to Comment on Effect of polydispersity on the ordering transition of adsorbed self-assembled rigid rods

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We comment on the nature of the ordering transition of a model of equilibrium polydisperse rigid rods, on the square lattice, which is reported by López et al. to exhibit random percolation criticality in the canonical ensemble, in sharp contrast to (i) our results of Ising criticality for the same model in the grand canonical ensemble [Phys. Rev. E **82**, 061117 (2010)] and (ii) the absence of exponent(s) renormalization for constrained systems with logarithmic specific heat anomalies predicted on very general grounds by Fisher [M.E. Fisher, Phys. Rev. **176**, 257 (1968)].

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Extensive Grand Canonical Monte Carlo simulations, for a model of adsorbed self-assembled rigid rods (SARR) on the square lattice, indicate that the polydisperse rods undergo a continuous transition in the two-dimensional (2D) Ising class, in line with models of monodisperse rods [1, 2]. This finding is in sharp contrast to a previous result, based on Canonical Monte Carlo simulations, where equilibrium polydispersity was claimed to change the nature of criticality, from Ising to random percolation [3].

In the preceding comment López et al. elaborate on this claim to conclude that the criticality of the SARR model on the square lattice depends both on polydispersity and on the statistical ensemble. This surprising result is based on simulations and normal finite-size scaling analysis of the SARR model in the canonical and grand canonical ensembles. The conclusion was that the SARR model exhibits random percolation criticality ($q = 1$ Potts) when the system is in the canonical ensemble, while the criticality is Ising-like ($q = 2$ Potts) when the system is in the grand canonical ensemble. This is at odds with very general arguments by Fisher [4] on the absence of exponent renormalization in constrained (e.g. fixed density) systems with logarithmic specific heat anomalies, as well as with the results of a detailed simulation study of Fisher scaling of the 2D Ising magnetic lattice-gas, by Ferreira and Prodanescu [5]. Fisher has also shown that although the universality class of constrained systems, with specific heat anomalies, is that of the unconstrained ones there are logarithmic corrections to the scaling functions, which may affect the scaling behaviour of reasonably sized systems as shown by Ferreira and Prodanescu [5].

The existence of two universality classes for the SARR model, claimed by López et al., is based on the calculation of (i) the fourth-order Binder cumulant of the order parameter, δ, $g_4 = 1- < \delta^4 > /(3 < \delta^2 >^2)$ at the transition, g_4^c, and (ii) the value of the correlation length exponent ν, obtained by normal scaling data collapse of the cumulants, for different system sizes. Both the values of g_4^c and ν, reported by López et al. for the SARR model, in the canonical and grand canonical ensembles, are different.

In the canonical simulations of the preceding comment López et al. kept the surface coverage constant and varied the temperature of the system, rather than fixing the temperature and varying the coverage [3]. As discussed below the logarithmic corrections to the normal finite-size scaling analysis, arising from the constant density constraint apply in both cases. In other words, Fisher logarithmic corrections [4, 6] as well as the simpler logarithmic correction suggested by us [1] apply due to the constant density constraint (which is also one of the control parameters in the canonical ensemble). We stress that although Fisher renormalization predicts that the critical exponents are unchanged in constrained systems with logarithmic specific heat anomalies, as in the SARR model on the square lattice, it does predict finite-size logarithmic corrections to the scaling functions, which if neglected will lead to effective exponents that may differ significantly from the true asymptotic exponents of the unconstrained system.

A very careful analysis of the criticality of the Ising magnetic lattice gas on the square lattice, in the canonical ensemble, was carried out by Ferreira and Prodanescu [5] and illustrates in detail how the effective exponents depend on the scaling analysis of the constrained system. The authors point out that the values of g_4 at the intersection of the Binder cumulants for different system sizes decrease (slowly) as the system size increases and their best estimate for the cumulant at criticality is reported to be significantly larger than the corresponding 2D Ising value. Using normal scaling ν was found to differ from 2D Ising but when Fisher scaling was taken into account ν was found to approach the 2D Ising value [5]. The authors also estimated γ/ν and obtained excellent agreement with 2D Ising when using Fisher scaling by contrast to the value obtained from normal scaling. The results for the 2D magnetic Ising gas show clearly that when Fisher scaling is taken into account, the effective exponents are closer to the values observed in the unconstrained system, as expected on theoretical grounds [4, 5]. The authors stress that Fisher scaling is not a correction to normal scaling but a scaling which deviates from normal logarithmically, rendering the numerical investigation of the criticality of these systems a very challenging problem.

Finite-size-scaling theory asserts that on the critical line $T_c(\mu)$, $g_4(L)$ adopts a non-trivial value, g_4^c independent of the system size L. For a given set of boundary conditions, this value of g_4^c is the same for systems in the same universality class. In addition, the dependence of g_4 on the coupling parameter(s), K, in the critical region scales as[7]: $(\partial g_4/\partial K) \propto L^{1/\nu}$. This is what we referred to above as normal scaling. Using normal scaling, López et al. obtained results for the constrained SARR model, consistent with $\nu = 3/4$. They also report that the crossing of g_4 occurs at $g_4^c \simeq 0.638$, which is claimed to be the value corresponding to the $q = 1$ Potts universality class (random percolation).

The use of normal scaling for the constrained SARR model, leading to López et al. conclusion of percolation critical behavior, has to be questioned. Previously [1], we proposed a simple argument that accounts for the effective value of $\nu = 4/3$ reported by Lopez et al. [3] for the constrained SARR model. We indicated that, for large systems, there is an additional $L/\ln L$ term in the scaling of the density derivatives compared to field derivatives. In the range of sizes investigated by [3] $L/\ln L$ is fitted by: $L/\ln L \simeq aL^{1/\nu'}$, with $\nu' \simeq 1.291$, close to $\nu = 4/3$ of the $q = 1$ Potts model [1]. This logarithmic correction arises from the density constraint and has been discussed in much more detail by Fisher [4] and was investigated numerically by Ferreira and Prodanescu [5]. We note that the simple $L/\ln L$ correction [1] is in line with Fisher scaling for large systems (see equations (14) and (16) of [5]). Therefore, in what follows we focus on the difference between the values of g_4^c reported by López et al., for constrained and unconstrained SARR models.

Lopez et al., discard the possibility of Ising criticality of the constrained SARR model based on the value of g_4^c, which differs from that of the unconstrained model: $g_4^{Ising} \simeq 0.611$. The results of [5] indicate that such an assumption is far from justified. In normal scaling, appropriate for unconstrained models, finite-size scaling[8, 9] considers the singular part of the appropriate thermodynamic potential in terms of the thermodynamic fields: temperature, T; chemical potential, μ; external fields. The corresponding intensive conjugate variables: energy per unit volume, density, ρ; magnetization are the natural variables of the constrained models, where Fisher scaling applies [4, 5]. The SARR model on the square lattice may be described as a symmetric binary mixture, where a species corresponds to a given orientation. The relevant thermodynamic fields are then T and μ. Within this Grand Canonical description of the SARR model (completed by taking the volume as the extensive variable that defines the system size), normal scaling theory applies. Of course, one can invesigate the criticality of the model in other ensembles but then the appropriate scaling theory must be used [5, 10].

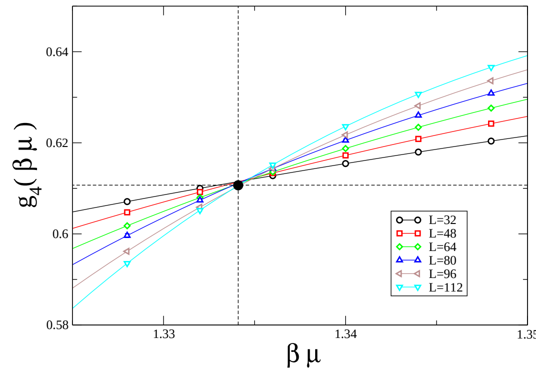

FIG. 1: Results for the Binder cumulant of the hard square lattice model in the grand canonical ensemble for different system sizes (See the legends). The filled circle marks the critical chemical potential of the HSL model and the corresponding value of g_4^c for the 2D-Ising universality class (for unconstrained systems) with periodic boundary conditions.

In order to check the effect of the density constraint on g_4^c in systems where $(\partial\rho/\partial\mu)_T$ diverges at the critical point we consider the behavior of the hard square lattice (HSL) model [11]. The HSL is an athermal model (an occupied site excludes occupation of its nearest neighbor sites) defined on the square lattice and exhibits a continuous order-disorder transition: at high densities particles occupy preferentially one of the two sublattices. The order parameter is defined as: $\delta = |N_1 - N_2|/L^2$, where N_i is the number of occupied sites in sublattice i, and L^2 is the number of lattice sites. The transition of the HSL model is in the 2D Ising class and both the chemical potential and the density at the critical point are known with high accuracy[11].

We simulated the transition of the HSL model using a multicanonical sampling procedure [1, 12–14] that allows results in the canonical and grand canonical ensembles to be obtained simultaneously. In figures 1 and 2 we illustrate the results for $g_4(\beta\mu)$ and $g_4(\rho)$, in the grand canonical (unconstrained) and canonical (constrained) ensembles respectively. We find that the results in the grand canonical ensemble are fully consistent with the expected

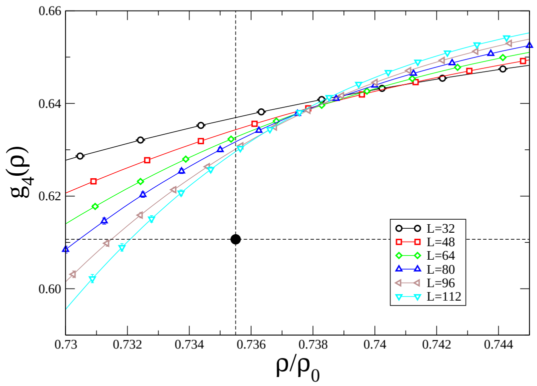

FIG. 2: Results for the Binder cumulant of the hard square lattice model in the canonical ensemble. The filled circle marks the critical density of the HSL model and the corresponding value of g_4^c for the 2D-Ising universality class (unconstrained systems) with periodic boundary conditions. ρ_0 is the density at maximum lattice occupancy.

2D Ising behavior. The curves $g_4(\beta\mu)$ for different system sizes cross (within error bars) at the the expected value $(\beta\mu_c, g_4^{Ising})$. However, in the canonical ensemble, the crossings occurs at a density slightly larger than ρ_c, (this could be a finite-size effect), while the crossing of g_4 decreases slowly as the lattice size increases, in line with the results reported for the Ising lattice gas model [5]. More importantly, the results suggest that the universal value of g_4^c for the constrained system may differ from the 2D Ising value for the unconstrained system, g_4^{Ising}. Incidentally, the crossings of g_4 in the canonical ensemble, occur at values close to the value reported by López et al. as the universal value of the cumulant for the $q = 1$ Potts criticality.

We conclude that the dependence of the universality class of the SARR model on the statistical ensemble, reported by López et al., is very likely the result of inadequate use of normal scaling to investigate the critical properties of the constrained (constant density) system. A full analysis following the lead of Ferreira and Prodanescu [5] seems to be called for but it is clearly outside the scope of this Reply.

Acknowledgments

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