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

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The critical behavior of self-assembled rigid rods on a square lattice was recently reinvestigated by Almarza *et al*. [Phys. Rev. E **82**, 061117 (2010)]. Based on the Binder cumulants and the value of the critical exponent of the correlation length, the authors found that the isotropic-nematic phase transition occurring in the system is in the two-dimensional Ising universality class. This conclusion contrasts with that of a previous study [López *et al*., Phys. Rev. E **80**, 040105(R) (2009)] which indicates that the transition at intermediate density belongs to the $q = 1$ Potts universality class. Almarza *et al*. attributed the discrepancy to the use of the density as the control parameter by López *et al*. The present work shows that this suggestion is not sufficient, and that the discrepancy arises solely from the use of different statistical ensembles. Finally, the necessity of making corrections to the scaling functions in the canonical ensemble is discussed.

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The isotropic-nematic (IN) phase transition in a model of self-assembled rigid rods (SARRs) on a square lattice was considered for the first time by Tavares *et al*. [1]. Using a theoretical approach and Monte Carlo (MC) simulation, the existence of a continuous phase transition was pointed out. However, the universality class of the transition was not studied and the ordering of SARRs was assumed to be that of monodisperse rigid rods (RRs), which was found to be the two-dimensional (2D) Ising class [2].

The criticality of the SARRs model in the square lattice was investigated in Ref. [3] by means of canonical MC simulation and finite-size scaling theory. The existence of a continuous phase transition was confirmed. In addition, the determination of the critical exponents along with the behavior of the Binder cumulant (g_4) for different system sizes revealed that the universality class of the IN transition, at intermediate density, changes from 2D Ising-type for monodisperse RRs without self-assembly to $q = 1$ Potts-type (random percolation) for polydisperse SARRs.

Recently, a multicanonical MC method based on a Wang-Landau sampling scheme was used by Almarza *et al*. [4] to reinvestigate the critical behavior of the model studied in Refs. [1,3]. Employing the crossing point of the Binder cumulants (g_4^*) and the value of the critical exponent of the correlation length (ν), it was observed that the criticality of the SARRs model is in the 2D Ising class, as in models of monodisperse RRs. This finding is in sharp contrast to that reported in [3], and the authors have given a possible explanation for this discrepancy [4] (μ denotes the chemical potential): "In the analysis of López *et al*., the use of the density as the control parameter leads to a value of the g_4 crossing that differs substantially from that of the 2D Ising universality class. We have shown that using μ as the control parameter leads to a more robust scaling of g_4 and to a much better overall Ising scaling."

The purpose of this Comment is to show that the above explanation is insufficient, and to point out and discuss the source of the discrepancy between our results and that obtained by Almarza *et al*. As in Ref. [4], the distinction between the two universality classes is based on the determination of both the value of g_4^* and the value of ν, which are clearly different for the two universality classes under discussion.

Then, in order to analyze the explanation given by Almarza *et al*., a series of MC simulations have been conducted in the canonical ensemble. The procedure was similar to that used in [3], but this time maintaining as constant the surface coverage (at $\theta = 0.525$, critical density obtained in [3]) and varying the temperature of the system (the natural control parameter in the canonical ensemble).

The fourth-order Binder cumulant was computed as a function of the temperature for different lattice sizes ($L \times L$), at $\theta = 0.525$ (see Fig. 1). The values obtained for the critical temperature and the intersection point of the cumulants were $T_c = 0.25$ and $g_4^* = 0.639$, respectively. The same fixed value of the cumulants was reported in [3], which is consistent with the $q = 1$ Potts universality class (ordinary percolation). As was mentioned in [3], a value of $g_4^* \approx 0.638$ was obtained by Vink for 2D site percolation [5]. Vink's result was recently reproduced by the authors via Monte Carlo simulation [6].

Once T_c was calculated, the scaling behavior was tested by plotting g_4 versus $\epsilon L^{1/\nu}$ (where ϵ is the normalized scaling variable $\epsilon \equiv T/T_c - 1$) and looking for data collapsing. Using the exact value of the critical exponent of the correlation length for ordinary percolation, $\nu = 4/3$, an excellent scaling collapse was obtained, as shown in Fig. 1.

As mentioned above, the use of the density as the basic variable in our previous study [3] led us to calculate values of the critical exponents and the crossing point of the cumulants that differ from those obtained by Almarza *et al*. [4]. In Ref. [4], the authors indicated that the difference in the values of ν can be understood by introducing a correction ($\ln L$) when using θ as the scaling variable. However, the behavior of the curves in Fig. 1, where the control parameter now is the temperature, provides convincing evidence that the value of

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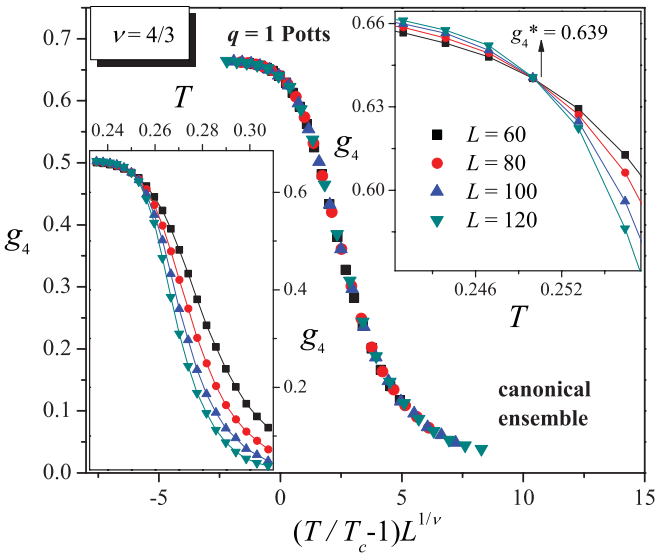

FIG. 1. (Color online) Data collapsing of the cumulant, g_4 vs $\epsilon L^{1/\nu}$. Upper-right inset: Curves of $g_4(T)$ vs T for lattices of different sizes. From their intersections one obtains g_4^*. In the lower-left inset, the data are plotted over a wider range of densities.

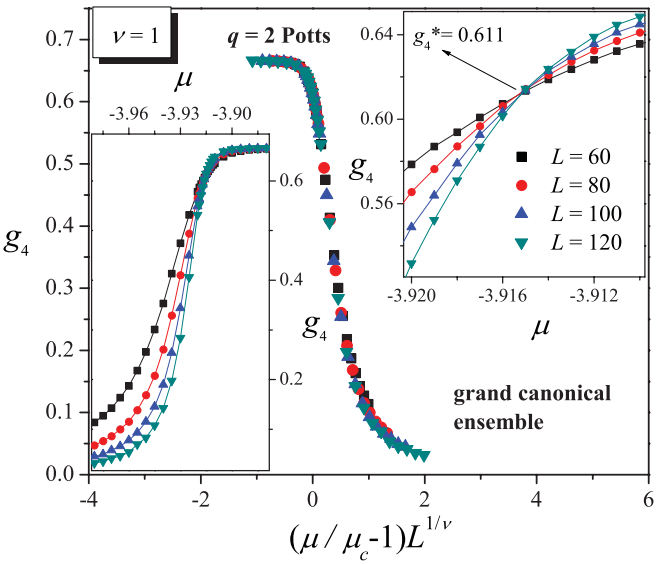

FIG. 2. (Color online) Data collapsing of the cumulant, g_4 vs $\epsilon L^{1/\nu}$. Upper-right inset: Curves of $g_4(\mu)$ vs μ for lattices of different sizes. From their intersections one obtains g_4^*. In the lower-left inset, the data are plotted over a wider range of densities.

g_4^* and the scaling obtained using $\nu = 4/3$ are not due to "the use of the density as the control parameter," as claimed in Ref. [4]. This immediately suggests that the discrepancy between the results of [3] and [4] arises from the use of different ensembles. To test this new statement and, at the same time, to check the data presented by Almarza *et al.*, MC simulations in the grand canonical ensemble were carried out using an adsorption-desorption algorithm. It is important to note that the algorithm used here is different from that used by Almarza *et al.*

In the grand canonical ensemble, the critical behavior was studied at the same point of the phase diagram, fixing the temperature at $T = 0.25$ and varying the chemical potential μ. The Binder cumulants versus μ are shown in Fig. 2. The intersection point converges to a fixed point, allowing an accurate estimation of the fixed value of the cumulants, $g_4^* = 0.611$. This value is consistent with the extremely precise transfer-matrix calculation of $g_4^* = 0.610\,690\,1(5)$ [7] for the 2D Ising model. On the other hand, very good collapse was obtained with $\nu = 1$ in the scaling plot of g_4 (Fig. 2), thus corroborating the data of Almarza *et al.*

The results presented above confirm that the discrepancy under study arises solely from the use of different statistical ensembles. This behavior, which appears to be a violation of the principle of ensemble equivalence, has been discussed many times in the literature, usually related to systems subject to constraint (such as the constraint of fixed density that is imposed in canonical ensemble studies).

In this sense, Fisher [8] (i) showed that, for systems with thermodynamic constraints, critical exponents characterizing scaling behavior at continuous phase transitions may deviate significantly from their ideal theoretical counterparts (without constraint) due to the effects of such constraints; and (ii) established elegant relations between the exponents of the ideal and constrained systems. In this scheme, known in the literature as the "standard Fisher renormalization scheme," the critical exponents in the constrained system are renormalized if the specific-heat exponent for the ideal system α is positive, or remain the same when α is negative or zero.

The case presented here, where the system without constraint belongs to the two-dimensional Ising universality class, shows that a generalization of the Fisher renormalization is necessary in certain circumstances where $\alpha = 0$ (Dohm [9] has also discussed this possibility for cases where $\alpha < 0$).

In summary, several conclusions can be drawn from the present Comment: (i) The discrepancy between the results in [3] and [4] arises solely from the use of different statistical ensembles. In this sense, even though it might be more appropriate (or convenient) to use the grand canonical ensemble to study a system such as the one described here, the consistency of the results obtained in the canonical ensemble warrants an explanation that has not yet been given. (ii) The system under study represents an interesting case where the use of different statistical ensembles leads to different and well-established universality classes. (iii) Since most of the studies on the critical behavior of self-assembled systems have been carried out in the canonical ensemble, they should be revisited. (iv) Fisher renormalization arguments predict that the values of the critical exponents should remain unchanged since the specific-heat exponent α for the present model is zero. However, our simulations disagree with this prediction. The development of a modified (or alternative) renormalization scheme, as was done in Refs. [9,10], could help to solve this problem. Obviously, this task is beyond the scope of this Comment.

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