Letter | Editors' Suggestion

Athermal tricriticality

Mauro Sellitto*

Dipartimento di Ingegneria, Università degli Studi della Campania "Luigi Vanvitelli", Via Roma 29, 81031 Aversa, Italy

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I construct a two dimensional monodisperse lattice gas model with selective geometric constraints featuring a fluid-solid continuous phase transition on the square lattice and a dimerized ground state with fourfold degeneracy. Finite-size scaling analysis confirms that the lattice gas belongs to the universality class of two-dimensional four-state Potts model, and since its thermodynamics is governed by entropy alone, this provides possibly the simplest statistical mechanical realization of an athermal tricritical point.

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Entropy is often considered as a synonym of disorder and yet it can play a very constructive role in systems dominated by steric effects, where it has a paramount importance in shaping the key intermolecular forces underpinning biological complexity [1,2]. A question that naturally arises is to what extent the variety of critical behaviors we observe in nature can be driven by purely entropic forces alone. Interest for such a question has both a fundamental theoretical aspect, related to the paradoxical nature of entropy-driven ordering [3], and an experimental one, relevant to the issue of entropy engineering in soft material science and technology [4].

Among the different kinds of critical phenomena, the tricritical behavior is one of the most fascinating [5]. A tricritical point (TCP) can be defined as the locus in the space of thermodynamic variables (temperature, chemical potential, pressure, etc.) at which a first-order transition line smoothly joins a line of critical points [6], and it has been found to occur in physical systems as different as He^3-He^4 mixtures [7], metamagnets, multicomponent fluid systems, polymer solutions (where it is known as Θ point) [8], superconductors [9], liquid crystals [10], and quantum cromodynamics [11], to mention only a few. Compared to the ordinary Ising critical point, the TCP is rather peculiar as the Ginzburg criterion implies that the upper critical spatial dimension above which the order parameter fluctuations become irrelevant is three (instead of four, as in the Ising case), and therefore the predictions of Landau theory basically lead to correct values for tricritical exponents in three dimensions, apart from logarithmic corrections [12]. Furthermore, Coulomb-gas techniques [13,14] and conformal invariance [15–17] in two spatial dimensions allow for the exact derivation of critical exponents.

While interacting hard squares [18–20] and hard square binary mixtures [21] are known to provide a simple istance of athermal tricritical behavior in two spatial dimensions, it is very unclear whether a TCP can be effectively realized in a single component (monodisperse) lattice gas endowed with solely excluded volume interactions. The problem is by no means obvious because a TCP generally requires the tuning of at least two thermodynamic variables. These can be temperature and chemical potential, as in the Blume-Emery-Griffiths model, for example, or temperature and number of states, as in the s-state Potts model. In this paper I show that this problem can be tackled and solved rather straightforwardly.

The starting point is an idea that was originally put forward by Biroli-Mézard (BM) for modeling glassy systems [22], according to which every particle in a dense liquid is geometrically constrained to have ℓ or fewer occupied nearest neighbors on a lattice with coordination number c, where $0 < \ell < c$. For a suitable ternary mixture made up of particles with different types of geometric constraints one observes in fact that crystallization in three spatial dimensions is inhibited due to the clash of the different crystallization motifs associated with each value of ℓ, which leads to characteristic glassy features such as dynamic heterogeneity and slow relaxation [23]. However, if one tries to go beyond the original goal of the BM idea, to encompass static and dynamic behaviors that are not necessarily glassy, one finds somewhat disappointingly the substantial lack of fundamental critical phenomena as opposed, e.g., to the s-state Potts model [24] or to hard-core lattice gases with an extended range of excluded volume interactions [25–31]. In fact, while it is true that for $\ell = 0$ there exists a continuous phase transition in the Ising universality class [32,33], when $\ell = 2$, 3, the phase ordering is discontinuous, possibly very weak, for a monodisperse system on the square lattice [34,35]. (For $\ell = 1$, instead, the clash of symmetries between the dimer and checkerboard closest packing configurations hinders the very occurrence of a phase transition, but without genuine glassines, as the residual ground-state entropy is subextensive [36]).

To obviate this situation I extend the BM idea by restricting the set of possible particle configurations allowed *a priori* by the geometric constraint to a suitable chosen subset. Moreover, an extra vacancy constraint is included, as already done in [37]. We shall see that this extension is sufficiently versatile to guarantee a range of critical behaviors, including those displayed by the s-state Potts model, but which have here a purely entropic origin, as there is no finite-energy interaction between particles.

To be specific, I shall focus here on the peculiar case of tricritical behavior and consider a lattice gas in which (i) every

*Contact author: mauro.sellitto@unicampania.it

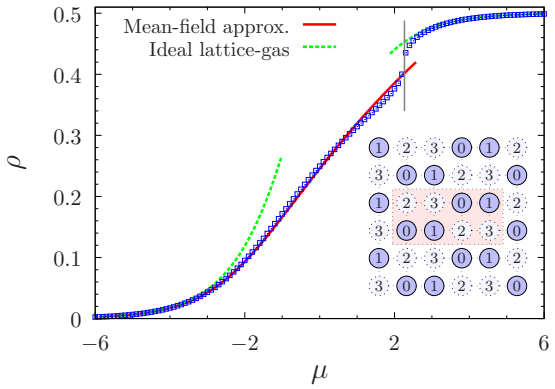

FIG. 1. Particle density ρ vs chemical potential μ in a grand-canonical Monte Carlo simulation of the BMS model on a square lattice of side $L = 48$ (square symbols). The full line represents the mean-field approximation Eq. (2), while the dashed curves correspond to the ideal noninteracting lattice gas equations, respectively, at low density, $1/\rho = 1 + \mathrm{e}^{-\mu}$, and near the close packing density $\rho_{\max} = 1/2$, where $\rho_{\max}/\rho = 1 + \mathrm{e}^{-\mu}$. The vertical segment indicates the phase transition point, which is located at $\mu_c = 2.2675$. Inset: Ground state of the BMS model studied in the paper. Lattice sites are represented by circles: filled (empty) circles denote particles (vacancies). For the sites labeling shown here, the density of sublattices is $\rho_0 = \rho_1 = 1/4$, and $\rho_2 = \rho_3 = 0$. The central shaded portions is the unit cell. The ground state has fourfold degeneracy.

particle has at most one occupied nearest neighbor that is located either to the left or to the right of the particle, and (ii) every vacancy has at least one empty nearest neighbor. Note that the selective nature of the particle geometric constraint (i) forbids the formation of particle pairs in the vertical direction, lifting the eightfold degeneracy the dimer ground state would have in the absence of selection [37]. In the following, I shall also refer to lattice gas with the above selective geometric constraints as to the BMS model, where S stands for selective.

Figure 1 shows grand-canonical Monte Carlo (MC) data (for simulation details, see [34]) of the average particle density ρ vs chemical potential μ for the BMS model on a square lattice of side $L = 48$. Comparison of numerical data with the equation of state of the noninteracting lattice gas, $1/\rho = 1 + \exp(-\mu)$, suggests that the excluded volume effect caused by the geometrical constraints sets in at $\rho \simeq 0.06$, see Fig. 1. Above that density one can give a crude quantitative description of the excluded volume effect within a mean-field approximation in which multipoint particle-density correlations are completely factorized. One writes the chemical potential as

$$\mu = \ln \frac{P_{\mathrm{out}}}{P_{\mathrm{in}}}, \tag{1}$$

where P_{in} and P_{out} are the probability of particle insertion and removal, respectively, due to the coupling between the lattice gas and the reservoir. While the removal probability is simply $P_{\mathrm{out}} = \rho$, to express the insertion probability, one has to take into account only particle configurations allowed by the geometric constraints, which can be expanded according to the binomial formula [36] which leads to

$$\exp(-\mu) = (1-\rho)^{13}(1+2\rho+3\rho^2)^3(\rho^{-1}+6-\rho). \tag{2}$$

Remarkably enough, Eq. (2) is able to capture the entire fluid phase up to density near the transition point.

On approaching the critical point, the geometrical constraints induce a complex effective interaction leading to the formation of particle dimers and vacancy dimers that mutually repel each other. This is accompanied by an entropy-driven transition toward an ordered phase characterized by a dimerized ground state with close packing density $\rho_{\max} = 1/2$, in which the two constraints (i) and (ii) are both saturated, that is, every particle of the system has exactly one occupied nearest neighbor (located either to the left or to the right of the particle) and every vacancy has exactly one empty nearest neighbor, see the inset of Fig. 1. In the dimerized phase near $\rho_{\max}$, defects are isolated and can be considered as an ideal gas of noninteracting excitations described by the equation $\rho_{\max}/\rho = 1 + \exp(-\mu)$. Figure 1 shows that this approximation works rather well except when the system approaches the critical point.

The ground-state structure has fourfold degeneracy and naturally leads to a decomposition of the lattice in four sublattices $\mathcal{L}_\alpha$, with $\alpha = 0, \ldots, 3$, each one having sublattice density ρ_α. Accordingly, the relevant order parameter is

$$q = \frac{1}{\rho_{\max}} \sum_{\alpha=0}^{3} \sum_{\beta>\alpha}^{3} \langle |\rho_\alpha - \rho_\beta| \rangle, \tag{3}$$

where $\langle \cdots \rangle$ is the ensemble average.

To locate more precisely the critical point and identify the universality class of the phase transition it is useful to study the finite-size scaling properties of the order parameter q, the order parameter susceptibility $\chi = L^2(\langle q^2 \rangle - \langle q \rangle^2)$, and the Binder ratio U [38], that is conveniently defined here as

$$U(\mu, L) = \frac{\langle q^4 \rangle}{\langle q^2 \rangle^2} - 1. \tag{4}$$

The quantities U, q, and χ show how the critical behavior emerges from finite systems in the limit of increasingly large system size. They were evaluated throughout the critical region by means of the histogram reweighting technique [39], using time series of long MC runs, tipically 10^8 MC sweeps, and results averaged over ten realizations of the random noise. Since the fourfold degeneracy of the ground state suggests the presence of a TCP in the universality class of two-dimensional four-state Potts model, it is natural to look directly at the theoretically predicted values of critical exponents: $\nu = 2/3$, $\beta = 1/12$, and $\gamma = 7/6$ [13–17]. From the scale invariance of the system near the critical point, it follows that U, q, and χ asymptotically behave as

$$U(\mu, L) = \mathcal{U}[(\mu_c - \mu)L^{1/\nu}], \tag{5}$$

$$q(\mu, L) = L^{-\beta/\nu}\mathcal{Q}[(\mu - \mu_c)L^{1/\nu}], \tag{6}$$

$$\chi(\mu, L) = L^{\gamma/\nu}\mathcal{X}[(\mu - \mu_c)L^{1/\nu}], \tag{7}$$

where $\mathcal{U}$, $\mathcal{Q}$, and $\mathcal{X}$ are scaling funtions and ν, β, and γ are the related critical exponents. Equation (5) implies that the critical chemical potential μ_c can be estimated by looking at the crossing point of $U(\mu, L)$ for different L. Figure 2 shows $U(\mu, L)$ curves on a semilog scale for L in the range [84, 144]. The intersection of the different curves allows to

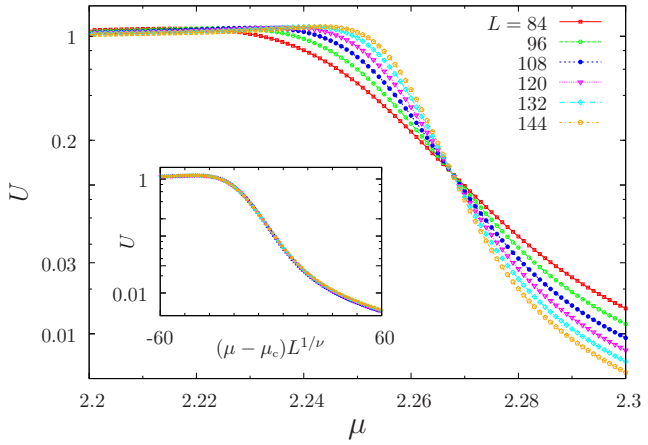

FIG. 2. Binder ratio U vs chemical potential μ in the BMS model on a square lattice of side L. The crossing point is approaximately located at $\mu_c = 2.2675(1)$. Inset: Binder ratio vs scaled distance to the critical point with $\nu = 2/3$. Rescaled data are limited to the four largest sizes.

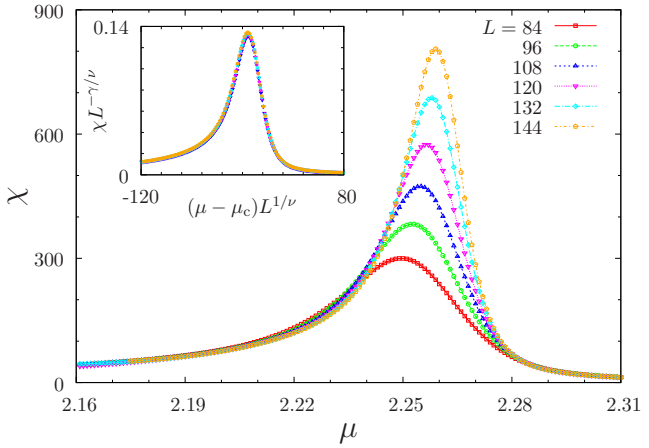

FIG. 4. Finite-size scaling properties of susceptibility χ vs chemical potential μ in the BMS model on a square lattice of side L. Rescaled data in the inset. The values of critical point and critical exponents are $\mu_c = 2.2675$, $\nu = 2/3$, and $\gamma = 7/6$. Rescaled data are limited to the four largest sizes.

locate the critical point at $\mu_c = 2.2675(1)$. The data collapse of the Binder ratio against the scaled distance to the critical point for various system sizes, see the inset of Fig. 2, is very good in the entire region around the critical point when the value of the correlation lenght exponent is set to $\nu = 2/3$.

Figures 3 and 4 show data for q and χ in the critical region and their rescaling in the inset of each figure, respectively, using the previously estimated value of the critical chemical potential $\mu_c = 2.2675$, and the exact value of tricritical exponents $\beta = 1/12$, $\gamma = 7/6$, and $\nu = 2/3$. Also in these cases the data collapse is quite successful and lend substantial support to the presence of a TCP, as expected from the ground state fourfold degeneracy. Similar finite-size scaling is also observed for the compressibility, which is proportional to density fluctuations and directly related, via the static fluctuation dissipation theorem, to the derivative or ρ with respect to μ, and therefore to the singular behavior of $\rho(\mu)$ curve near the

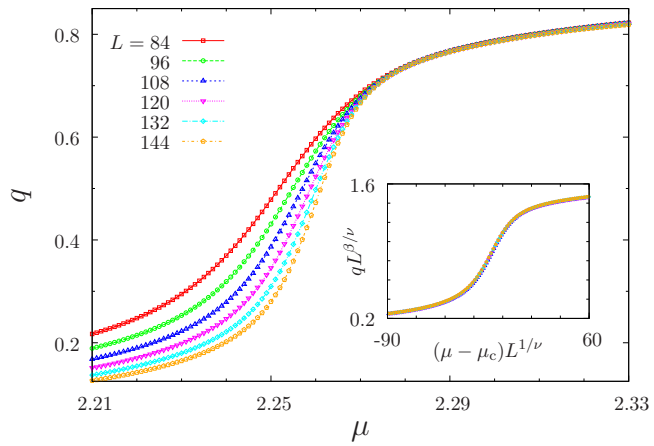

FIG. 3. Finite-size scaling properties of order parameter q vs chemical potential μ in the BMS model on a square lattice of side L. Rescaled data in the inset. The values of critical point and critical exponents are $\mu_c = 2.2675$, $\nu = 2/3$, and $\beta = 1/12$. Rescaled data are limited to the four largest sizes.

transition point. One can therefore conclude rather convincingly that the BMS lattice gas belongs to the universality class of the four-state Potts model.

To summarize, I have introduced a family of lattice gases defined by selective geometric constraints on the values of the site occupation variables. The idea of selective geometric constraints generalizes that of Biroli and Mézard formulated in the context of glassy systems and is motivated by the aim of including a range of critical phenomena. I have studied a specific instance to show that a TCP point can be effectively realized in a monodisperse lattice gas endowed with only excluded volume interactions on the square lattice. Numerical results suggest that the phase ordering transition of the BMS lattice gas belongs to the universality class of four-state Potts model, as expected from the fourfold degeneracy of the dimer ground-state. Interestingly, the fluid phase is excellently described by a simple mean-field approximation that neglects particle correlations up to chemical potentials very near to the transition point. That the TCP investigated here requires only tuning one thermodynamic variable, the chemical potential, should not be surprising. In fact, the situation is very similar to the s-state Potts model, in which the TCP is attained by tuning the temperature and the number of states s of the spin variable. The role of the latter discrete variable is played here by the two thresholds set by the particle and vacancy constraints. However, while in the Potts model the approach to TCP is ruled by the usual energy-entropy tradeoff, here it is controlled solely by entropy. Thus, the BMS lattice gas represents possibly the simplest athermal realization of the two dimensional universality class of tricritical behavior.

One can arguably anticipate that the dimer lattice gas with nearest neighbor exclusion studied by Dickman [40] will also exhibit a similar TCP when endowed with a selective constraint on the dimers orientation. The difference is that in the BMS lattice gas the dimer structure emerges spontaneously as the density increases while in the Dickman lattice gas it is given *a priori* in the model definition.

To see how the TCP found in the BMS model arises from the merging of critical and coexistence lines it is necessary to introduce a suitable extra parameter that can be changed continuously. In analogy to what has been done for the hard square lattice gas [18–20], one could add diagonal particle interactions or, alternatively, consider mixtures of particles with different types of constraints [21]. In the former case, one has to tune the particle interaction from attractive to repulsive, while in the latter it is the mixture composition that has to be varied. It would be interesting to investigate in detail the phase behavior of these models.

Since the particle constraint (i) provides a coarse grained description of T-shaped molecules on a square lattice [34], for a possible experimental realization of the athermal TCP, one should look at adsorbed monolayers of complex fluids formed by T-shaped molecules that can be oriented in a preferential direction (say, $\vdash$ and $\dashv$, or, equivalently, $\top$ and $\perp$) via an external field. From a more theoretical perspective it would be interesting to explore the exact solvability conditions of the BMS lattice gas and its possible relation with other statistical mechanical models [41], as well as the finite-size corrections to the leading power-law scaling behavior, which in the four-state Potts model are known to have a complicated logarithmic dependence [42–44].

The idea of selective geometric constraint is flexible enough to reproduce other types of critical behaviors by changing the two parameters ℓ and m (corresponding to the maximum number ℓ of occupied nearest neighbors a particle can have, and the minimum number m of empty nearest neighbors a vacancy must have), and the subset of permissible configurations. In this respect, it is worth to mention that if $\ell = 2$, $m = 0$, and the selection rule allows every particle on a square lattice to have only two occupied nearest neighbors located in the SE and NW (or, equivalently, SW and NE) directions, then the ground state has a threefold degeneracy that leads to another realization the three-state Potts universality class [45]. The variety of possible static and dynamic behaviors encompassed by more general lattice gases with selective geometric constraints remains, however, largely unexplored. In particular, it is currently unknown whether they can lead to the formation of genuine monodisperse lattice glass states, a wide open problem which has so far resisted most strenuous efforts.

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Data availability. The data that support the findings of this article are not publicly available. The data are available from the author upon reasonable request.

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