Eur. Phys. J. B **11**, 621–627 (1999)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Entropy and multi-particle correlations in two-dimensional lattice gases

M.G. Donato[1,2], S. Prestipino[1], and P.V. Giaquinta[1,2,a]

[1] Istituto Nazionale per la Fisica della Materia (INFM), Unità di Ricerca di Messina, Contrada Papardo, 98166 Messina, Italy
[2] Università degli Studi di Messina, Dipartimento di Fisica, Contrada Papardo, 98166 Messina, Italy

Received 31 December 1998 and Received in final form 8 March 1999

Abstract. We analyse the statistical entropy of two-dimensional lattice-gas models in terms of the contributions which arise from space correlations of increasing order. The "residual multiparticle entropy", defined as the contribution to the excess entropy that is associated with correlations involving more than two particles, is calculated for the Ising and Coulomb lattice gases. The thermodynamic behaviour of the residual multiparticle entropy is then discussed in relation to the phase diagram of the model and the existence of underlying signatures of order-disorder phase transitions is also investigated.

PACS. 64.60.-i General studies of phase transitions – 64.60.Cn Order-disorder transformations; statistical mechanics of model systems – 65.50.+m Thermodynamic properties and entropy

1 Introduction

Recently, the multiparticle correlation expansion of the statistical entropy, as originally set up for closed and open systems by Green [1] and by Nettleton and Green [2] respectively, has been revisited for a variety of continuous, three-dimensional models by Giaquinta and co-workers [3–6]. In particular, these authors focussed on the thermodynamic behaviour of the so-called "residual multiparticle entropy" (RMPE), a quantity which was proposed as an integral "measure" of the amount of spatial order present in a fluid. More specifically, the RMPE yields the resummed contribution to the excess entropy resulting from n-body correlations, with $n > 2$, and is evaluated as the difference between the excess entropy and the "pair entropy", *i.e.*, the contribution associated with pair correlations only. This last quantity usually provides the overwhelming contribution to the excess entropy.

The evidence gathered so far on the RMPE of continuous, simple-fluid systems shows that, at variance with the pair entropy, it has not a definite sign. In fact, it turns out that this quantity is negative at low density (or at high temperature), but becomes positive in close proximity to a phase transition leading to an even partially ordered phase. As yet, a rigorous derivation of this behaviour from first principles has not been given. However, it is not difficult to understand the rapid increase of the RMPE in the transition region – as the transition is approached from the disordered side – as the necessary consequence of the growing importance of multiparticle spatial correlations in the overall entropic balance. To state it in a different way, the increasing number and average size of statistically ordered domains (*i.e.*, fully-correlated regions) results – in a system approaching an ordered phase – into a rapid growth of the RMPE which, eventually, is bound to attain positive values.

Such a picture was originally discussed in relation to the freezing transition of hard spheres and Lennard-Jones particles [3], and then successfully checked also for the condensation of a hard-core Yukawa fluid [4], for the fluid-fluid separation in binary mixtures of hard spheres [5], and for the isotropic-nematic transition undergone by elongated particles (hard spherocylinders) [6].

In this paper, we apply this method to lattice gases in two dimensions (2D), and analyse two models that will serve as representative cases for studying the RMPE in conditions not considered before: the Ising model and the neutral Coulomb gas. In particular, we intend to verify whether features like the discreteness of space, the reduced space dimensionality, the presence of a long-ranged interaction, and the continuous character of a phase transition may affect in a sensitive way the functional behaviour of the RMPE.

The paper is organized as follows: The general expression for the RMPE, appropriate to a lattice gas, is presented in Section 2; this quantity is then evaluated on a square lattice for the Ising model and for a neutral mixture of unit charges in Sections 3 and 4, respectively; Section 5 is finally devoted to concluding remarks.

[a] e-mail: Paolo.Giaquinta@unime.it

2 The entropy expansion

In the following, we consider systems of particles living on a regular lattice with N sites. If multiple site occupancy is forbidden, a configuration of such a system is a list $\{c_i, i = 1, \ldots, N\}$ of occupation numbers. As anticipated in the Introduction, the RMPE is generally defined as:

$$\Delta s \equiv s^{(\mathrm{ex})} - s_2 \,, \tag{1}$$

which is the difference between the excess entropy (*i.e.*, the total entropy after subtracting the ideal-gas entropy evaluated at the same density of the interacting system) and the pair entropy. All such quantities are evaluated per lattice site. The general expression of the pair entropy is [7]:

$$\frac{s_2}{k_\mathrm{B}} = -\frac{1}{2}\rho^2 \sum_{i \neq j} \left[g_{ij} \ln g_{ij} - g_{ij} + 1 \right] , \tag{2}$$

where $\rho = \langle c_i \rangle$ is the density and

$$g_{ij} = \frac{\langle c_i c_j \rangle}{\rho^2} \,, \tag{3}$$

is the pair correlation function. In equation (3), the average is generally taken over a grand-canonical ensemble of systems. Note that in the case of mixtures formed by two or more species, equation (2) is no longer appropriate and must be modified as will be shown in Section 4.

Finally, the total entropy is determined through the integration of the equation of state along a thermodynamic path, while the entropy of an ideal lattice gas reads [7]:

$$\frac{s_\mathrm{id}}{k_\mathrm{B}} = -\rho \ln \rho - (1-\rho) \ln (1-\rho) \,. \tag{4}$$

3 The Ising lattice gas

Since the exact solution provided by Onsager in 1944 [8], the 2D Ising model has been a crucial test for any approximate theory of phase transitions. In this model, each site of a square lattice is associated with a ± 1 spin σ_i with energy

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i \,, \tag{5}$$

where both J and h are positive quantities. The first sum in equation (5) is performed over nearest-neighbour sites only. The Ising model undergoes a continuous phase transition at zero field from a ferromagnetic to a paramagnetic phase at a temperature T_c given by $k_\mathrm{B} T_\mathrm{c}/J = 2\left[\ln\left(1+\sqrt{2}\right)\right]^{-1} \simeq 2.2692$.

Moreover, the Ising Hamiltonian can be rephrased as a model of a fluid [9]. The mapping $\sigma_i = 2c_i - 1$ defines a lattice gas with the same thermodynamic properties of the Ising spin system. In fact, the Ising partition function turns out to be proportional to

$$\Xi = \sum_{\{c\}} \exp \left[\beta\mu \sum_i c_i + \beta\varepsilon \sum_{\langle i,j \rangle} c_i c_j \right] , \tag{6}$$

with $\beta = (k_\mathrm{B} T)^{-1}$, $\varepsilon = 4J$, and $\mu = -8J + 2h$. Equation (6) represents the grand-canonical partition function of the so-called Ising lattice gas, whose critical temperature becomes $k_\mathrm{B} T_\mathrm{c} / (4J) \simeq 0.5673$, whereas the equation of the critical line reads $\mu = -2\varepsilon$. In turn, the density ρ is simply related to the Ising magnetization $M = \langle \sigma_i \rangle$ through $\rho = (1+M)/2$.

We carried out a numerical simulation of the Ising model at zero field to obtain the internal energy and the correlation function $\langle \sigma_i \sigma_j \rangle$, which were then transformed into the lattice-gas energy and pair correlation function g_{ij}, respectively. In particular,

$$g_{ij} = \frac{1 + 2\langle \sigma_i \rangle + \langle \sigma_i \sigma_j \rangle}{1 + 2\langle \sigma_i \rangle + \langle \sigma_i \rangle \langle \sigma_j \rangle} \,. \tag{7}$$

At zero field, $\langle \sigma_i \rangle = 0$ and $g_{ij} = 1 + \langle \sigma_i \sigma_j \rangle$.

We used the Monte Carlo (MC) method and the Metropolis algorithm to study systems made up of 20 or 40 sites on each side of a square lattice. Periodic conditions were applied to the lattice boundary. Thermodynamic averages were calculated along runs of 10^6 MC sweeps (typically, 50 000 sweeps were discarded for equilibration).

In order to calculate the RMPE of the Ising lattice gas along the critical isochore $\rho = 1/2$, we need to evaluate the total entropy and the pair entropy. The former quantity is obtained through thermodynamic integration. We first calculate the Massieu function relative to β, $\tilde{s}(\beta)/k_\mathrm{B} = s(\beta)/k_\mathrm{B} - \beta u(\beta)$ [10]. Upon integrating the internal energy $u(\beta)$ over β, one obtains the total entropy per site as:

$$\frac{s(\beta_2)}{k_\mathrm{B}} = \frac{\tilde{s}(\beta_1)}{k_\mathrm{B}} + \beta_2 u(\beta_2) - \int_{\beta_1}^{\beta_2} u(\beta) \, \mathrm{d}\beta \,. \tag{8}$$

The initial constant $\tilde{s}(\beta_1)$ was evaluated by resorting to the high-temperature series for the Ising partition function as provided by Kramers and Wannier [11]. We took $\beta_1 = 0.1$, and performed the calculation of the entropy up to $\beta_2 = \frac{1}{2.6}$. Moreover, $s_\mathrm{id} = k_\mathrm{B} \ln 2$ (see Eq. (4)).

On the other hand, the pair entropy requires the knowledge of the lattice-gas pair correlation function. From each MC run we extracted five different and statistically independent spin correlation functions in order to calculate, besides the mean value of Δs, also its mean square deviation. We checked the sensitivity of Δs to the cutoff on g_{ij}, *i.e.*, the error that we make if we cut g_{ij} at a given distance $|i-j|$, starting from the largest distance allowed by the minimum-image convention, namely half of the lattice side. In our figures we present always the largest error. The asymptotic behaviour of $\langle \sigma_i \sigma_j \rangle$ was also successfully checked against the exact results given by Mc Coy and Wu [12].

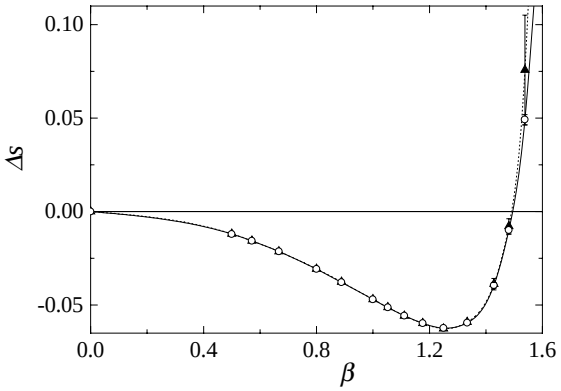

Fig. 1. The residual multiparticle entropy of an Ising lattice gas plotted as a function of β along the critical isochore $\rho = 1/2$. Data for two distinct lattice sizes, $L = 20$ (▲) and $L = 40$ (○), are shown. The lines through the data are spline interpolations. Δs is seen to vanish for $\beta \simeq 1.49$ for both lattice sizes.

Our final result for Δs is shown in Figure 1. We observe that the behaviour of the Ising RMPE, when plotted as a function of β along the critical isochore $\rho = 1/2$, is similar to that exhibited by the hard-sphere RMPE when plotted as a function of the density: there is a negative well at high temperature (low density, in the hard-sphere system), followed by a sharp increase toward positive values which causes Δs to vanish at the inverse temperature $\beta_0 = 1.494$. This value should be compared with that of the inverse critical temperature $\beta_c \simeq 1.7627$. As the lattice size grows from 20×20 to 40×40 sites, the data become more reliable but no appreciable shift is observed in the temperature corresponding to the RMPE zero.

A question can be raised about the larger distance (about 18%) of the RMPE zero from the Ising critical temperature, as compared with that of the same quantity relative to the freezing point of a hard-sphere or Lennard-Jones fluid in three dimensions [3]. In fact, the nature of the two transitions is different and a different structural "mechanism" is manifestly at work in the two cases. In both cases Δs is driven to positive values by the increase in the average size and number of ordered domains. However, in a hard-sphere fluid approaching the solid phase, the RMPE becomes infinite at the random-closest-packing density, which lies well beyond the *first-order* phase-transition point. On the contrary, the divergence of Δs in the disordered Ising lattice gas occurs just at the *second-order* phase-transition point as can be shown on fairly general grounds. In fact, upon assuming an asymptotic behaviour for the pair correlation function in 2D of the type $r^{-\eta} \exp(-r/\xi)$, it is easy to show that the pair entropy behaves like minus $\xi^{2-2\eta}$ near above T_c, resulting into a positive divergence of the RMPE. Therefore, the temperature at which Δs becomes positive can be relatively far from the transition point. As a by-product, one can estimate the quantity $\nu(1-\eta)$ through a fit of the pair entropy in the scaling region close to the critical point. In the Ising case, we find for a 40×40 lattice a value of 0.70 against the exact result of 3/4. We conclude that it is possible to extract fairly accurate (although partial) information on the critical behaviour of the model also from a finite-size-scaling analysis of the pair entropy.

We finally note that inside the ordered phase each term in the entropy expansion is actually infinite. This makes the evaluation of Δs meaningless.

4 The neutral Coulomb gas

4.1 The model

Two-dimensional spin systems with continuous symmetry have no long-range order at any temperature [13], but a quasi-long-range-ordered phase can be defined, below a certain temperature T_c, where the spin correlation function shows an algebraic decay that is typical of critical systems [14]. In fact, a real phase transition occurs at T_c [15]. A prototype of such systems is the XY model, which is isomorphic to the 2D neutral Coulomb gas [16]. Another model, dually related to the XY model, is the discrete Gaussian, solid-on-solid (SOS) model [17]. The phase transition undergone by all these models was named after Kosterlitz and Thouless, who first discussed it in the framework of the XY model, suggesting that the transition was driven by the unbinding at T_c of topological defects called "vortices". Below the critical temperature, such vortices bind together to form pairs with opposite charges. At T_c, the free energy of the system shows an essential singularity only and, for this reason, the Kosterlitz-Thouless (KT) transition is generally referred to as an infinite-order phase transition.

In the 2D neutral Coulomb gas model (NCGM), the low-temperature phase is insulating. The phase transition occurs when dipoles formed by nearest-neighbour particles with opposite charges unbind to form a free-charge, metallic phase. Correspondingly, the inverse dielectric constant jumps from $4T_c$ to zero.

The Hamiltonian of a system of interacting charges on a $L \times L$ lattice reads:

$$\mathcal{H} = \frac{1}{2} \sum_{i \neq j} q_i V(\mathbf{r}_i - \mathbf{r}_j) q_j \,, \tag{9}$$

where the sum is over all pairs of distinct lattice sites and q_i ($i = 1, \ldots, N = L^2$) is an integer-valued charge ($q_i = 0$ means that no charge is present at site i). On a square lattice, the interaction is given by [19]:

$$V(\mathbf{r}) = \frac{\pi}{N} \sum_{(k_x,k_y) \neq (0,0)} \frac{\exp(\mathrm{i}\mathbf{k} \cdot \mathbf{r}) - 1}{2 - \cos k_x - \cos k_y} \,, \tag{10}$$

where $\mathbf{k}$ is a Born-von Karman wave vector:

$$\mathbf{k} = \frac{2\pi m_x}{L} \widehat{\mathbf{x}} + \frac{2\pi m_y}{L} \widehat{\mathbf{y}} \,, \tag{11}$$

with $m_x, m_y = 0, 1, 2, ..., L-1$.

In the NCGM, the neutrality constraint $\sum_i q_i = 0$ must be satisfied. This condition arises naturally

in the framework of the duality transformation of the SOS model into the Coulomb gas [17]. We just mention here that global charge neutrality is crucial for the very existence of thermodynamics for a system of interacting charges [18]. Actually, Lebowitz and Lieb have shown that non-neutral configurations give a negligible contribution to the grand potential. In particular, in the thermodynamic limit, the grand potential of an unconstrained charge system equals that of a neutral system and both are equal to the canonical free energy of a neutral system. Similarly, we expect that globally charged configurations of the 2D Coulomb gas do not contribute to the thermodynamics, which is then ruled by neutral configurations only.

Unless the temperature is extremely high, the occurrence of multiple-charged particles in the NCGM is very rare. Thus, for all practical purposes, unit charges only, $q_i = 0, \pm 1$, play a role. We are thus led to consider in the following a restricted NCGM where unit charges only are present. In the grand-canonical ensemble, the resulting NCGM partition function thus reads:

$$\Xi = 1 + \sum_{n=1}^{N/2} \mathrm{e}^{2\beta\mu n} Z_{n,n} \tag{12}$$

with N even. $Z_{n,n}$ is the canonical partition function of a system of n positive plus n negative unit charges, given by:

$$Z_{n,n} = \sum_{\{q\}} \delta_{\sum_i q_i,0} \delta_{\sum_i q_i^2,2n} \exp\left[-\frac{\beta}{2} \sum_{i\neq j} q_i V\left(\mathbf{r}_i - \mathbf{r}_j\right) q_j\right]. \tag{13}$$

This model is very similar to one studied recently by Lee and Teitel [19]. They considered a neutral Coulomb gas with multiple charges, with a further term in the Hamiltonian given in equation (9) which has the effect of disfavouring strongly the occurrence of multiple charges, while being blind to unit charges. For this reason, we shall refer to the phase diagram of reference [19] as the current NCGM phase diagram. This phase diagram is actually very rich (see Fig. 1 of Ref. [19]). A dipolar fluid is stable at low T and μ; at high temperature, this phase transforms into a liquid metal *via* a KT transition. At low T and for $\mu > \pi/8$, a fully-occupied lattice of "antiferromagnetically ordered" charges becomes stable which, at high temperature, undergoes a KT transition to a metallic state. At still higher temperatures, charges eventually lose their $\pm$ order *via* an Ising transition. Finally, a first-order line at $\mu = \pi/8$ separates the fluid insulator from the "solid" phase.

Besides the existence of as many as four different phases in the NCGM phase diagram, the transition lines themselves are of various nature. In fact, the phase diagram includes a first-order line ending at a tricritical point, an Ising line, and two KT lines. Actually, it is such a variety of behaviour that originally stimulated us to calculate the RMPE for the NCGM, in order to check whether such a quantity is sensitive to the boundaries of the metallic fluid phase, which is by far the most disordered phase of the model.

4.2 Numerical implementation

We sampled the NCGM with a Monte Carlo procedure which, at each step, produces a new neutral configuration where the state of two nearest-neighbour sites is updated. Four different "moves" are allowed:

1) creation of two opposite charges;

2) annihilation of two opposite charges;

3) site exchange of two opposite charges;

4) diffusion of a charge to an empty site.

The acceptance of each move is ruled, as usual, by detailed balance. Because of the long-range character of the Coulomb interaction, the evaluation of the energy change ΔE associated with a trial move is time-consuming. In order to speed up the calculation, we adopted the same procedure used by Lee and Teitel in their MC simulation [19].

We carried out MC runs of about 5×10^6 sweeps in a 12×12 lattice (a preliminary series of 50 000 sweeps was discarded for equilibration). As a check of our code, we first recovered the phase diagram of reference [19].

The following correlation functions were calculated:

$$g_{ij}^{++} = \frac{1}{\rho_+^2} \left\langle c_{i,+} c_{j,+} \right\rangle ; \quad g_{ij}^{--} = \frac{1}{\rho_-^2} \left\langle c_{i,-} c_{j,-} \right\rangle ;$$
$$g_{ij}^{+-} = \frac{1}{\rho_+ \rho_-} \left\langle c_{i,+} c_{j,-} \right\rangle ; \quad g_{ij}^{-+} = \frac{1}{\rho_- \rho_+} \left\langle c_{i,-} c_{j,+} \right\rangle . \tag{14}$$

Here, $c_{i,+} = 1$ only if a positive charge is present at site i, etc.; ρ_+ (ρ_-) is the density of the positive (negative) charges (both are in fact equal, due to neutrality; g^{++} and g^{--}, as well as g^{+-} and g^{-+}, are also equal by symmetry). These correlation functions are needed for estimating the pair entropy (see Eq. (22) below).

We found that the MC sampling becomes rather inefficient in the highly dilute dipolar phase because of the very small acceptance ratio of MC moves. In order to study also this region of the phase diagram, we resorted to a perturbative approximation of the grand-partition function. All the configurations with up to six charges were enumerated on a 12×12 lattice. Within such an approximation, the grand-partition function reads:

$$\Xi \simeq 1 + \mathrm{e}^{2\beta\mu} Z_{1,1} + \mathrm{e}^{4\beta\mu} Z_{2,2} + \mathrm{e}^{6\beta\mu} Z_{3,3} . \tag{15}$$

Once the energy and the density of the NCGM were obtained (either through MC or exact state enumeration) along a thermodynamic path, we calculated the total entropy $s\left(\beta, \beta\mu\right)$ by resorting to thermodynamic integration of the equation of state. The Massieu function relative to β and $\beta\mu$ is:

$$\frac{\tilde{s}\left(\beta, \beta\mu\right)}{k_\mathrm{B}} = \frac{s\left(\beta, \beta\mu\right)}{k_\mathrm{B}} - \beta u\left(\beta, \beta\mu\right) + \beta\mu\, \rho\left(\beta, \beta\mu\right), \tag{16}$$

where $u(\beta,\beta\mu)$ is the energy and $\rho(\beta,\beta\mu)$ is the density. Again, all quantities in equation (16) are evaluated per lattice site. The entropy can be evaluated along a constant-$\beta\mu$ path, as:

$$s\left(\frac{1}{k_{\rm B}T},\beta\mu\right)=\int_0^T u\left(\frac{1}{k_{\rm B}T},\beta\mu\right)\frac{1}{T^2}\,{\rm d}T + \frac{1}{T}u\left(\frac{1}{k_{\rm B}T},\beta\mu\right)-\frac{\mu}{T}\rho\left(\frac{1}{k_{\rm B}T},\beta\mu\right). \quad (17)$$

On the other hand, along a constant-T path the entropy is given by:

$$s\left(\frac{1}{k_{\rm B}T},\beta\mu\right)=\tilde{s}\left(\frac{1}{k_{\rm B}T},0\right)+\frac{1}{T}\int_0^{\mu}\rho\left(\frac{1}{k_{\rm B}T},\beta\mu_1\right){\rm d}\mu_1 + \frac{1}{T}u\left(\frac{1}{k_{\rm B}T},\beta\mu\right)-\frac{\mu}{T}\rho\left(\frac{1}{k_{\rm B}T},\beta\mu\right). \quad (18)$$

In the latter equation, the initial constant $\tilde{s}\left(\frac{1}{k_{\rm B}T},0\right)$ is calculated from the Massieu function along the $\beta\mu=0$ path.

The RMPE is obtained through equation (1) after subtraction from the total entropy of the one-body and two-body terms. As to the former contribution, we recall that the entropy of an ideal, equimolar mixture reads:

$$\frac{s_{\rm id}(\beta\mu)}{k_{\rm B}}=\frac{\ln\Xi_{\rm id}(\beta\mu)}{N}-\beta\mu\,\rho_{\rm id}(\beta\mu), \quad (19)$$

where

$$\Xi_{\rm id}(\beta\mu)=1+\sum_{n=1}^{N/2}{\rm e}^{2\beta\mu n}\frac{N!}{n!\,n!\,(N-2n)!} \quad (20)$$

and

$$\rho_{\rm id}(\beta\mu)=\frac{1}{N}\frac{\partial\ln\Xi_{\rm id}}{\partial\beta\mu}. \quad (21)$$

Finally, the pair entropy can be obtained through a straightforward generalization of the formula given in reference [7] to two-component systems:

$$\frac{s_2}{k_{\rm B}}=-\frac{1}{2}\rho_+^2\sum_{i\neq j}\left[g_{i,j}^{++}\ln g_{i,j}^{++}-g_{i,j}^{++}+1\right] -\frac{1}{2}\rho_-^2\sum_{i\neq j}\left[g_{i,j}^{--}\ln g_{i,j}^{--}-g_{i,j}^{--}+1\right] -\rho_+\rho_-\sum_{i\neq j}\left[g_{i,j}^{+-}\ln g_{i,j}^{+-}-g_{i,j}^{+-}+1\right]. \quad (22)$$

We note that, in principle, the above expression applies to an unconstrained mixture, *i.e.*, to a system where configurations with different numbers of oppositely charged species may also occur. However, as discussed in reference [18], we expect that such configurations make a vanishingly small contribution in the thermodynamic limit.

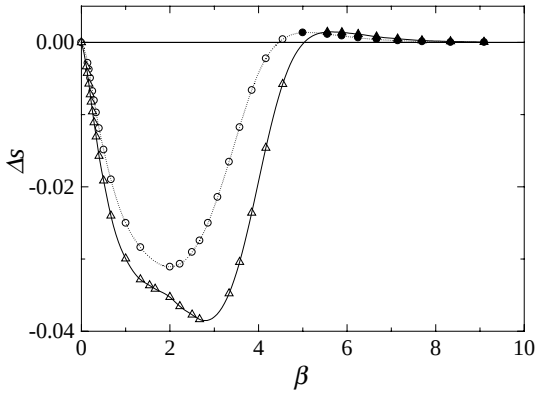

Fig. 2. The residual multiparticle entropy of the neutral Coulomb gas model plotted as a function of β along two paths at constant $\beta\mu$: (○), $\beta\mu=0$; (△), $\beta\mu=0.5$. Solid markers refer to data extracted from the low-density expansion of the partition function, whereas empty markers correspond to MC results. The lines through the data are spline interpolations.

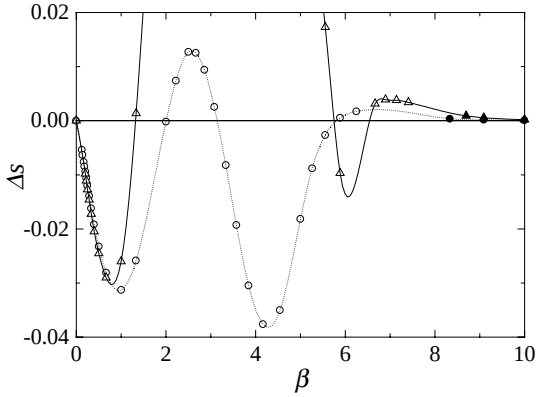

Fig. 3. The residual multiparticle entropy of the neutral Coulomb gas model plotted as a function of β along two paths at constant $\beta\mu$: (○), $\beta\mu=1.2$; (△), $\beta\mu=2$. Solid markers refer to data extracted from the low-density expansion of the partition function, whereas empty markers correspond to MC results. The lines through the data are spline interpolations.

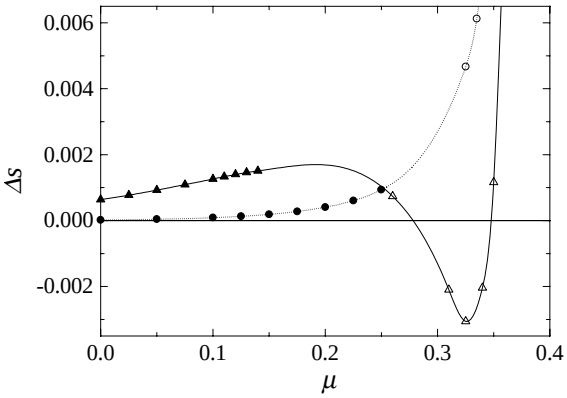

Fig. 4. The residual multiparticle entropy of the neutral Coulomb gas model plotted as a function of μ along two paths at constant T: (○), $T=0.11$; (△), $T=0.16$. Solid markers refer to data extracted from the low-density expansion of the partition function, whereas empty markers correspond to MC results. The lines through the data are spline interpolations.

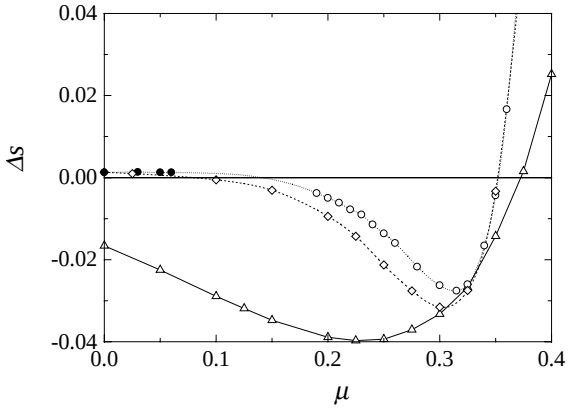

Fig. 5. The residual multiparticle entropy of the neutral Coulomb gas model plotted as a function of μ along three paths at constant T: ($\circ$), $T = 0.19$; ($\diamond$), $T = 0.20$; ($\triangle$), $T = 0.30$. Solid markers refer to data extracted from the low-density expansion of the partition function, whereas empty markers correspond to MC results. The lines through the data are spline interpolations.

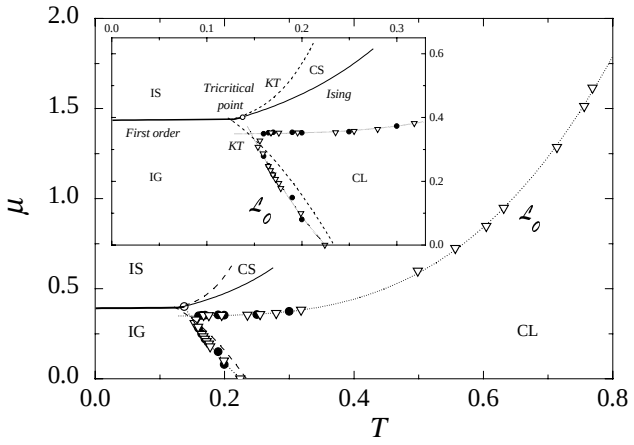

Fig. 6. The phase diagram of the neutral 2D Coulomb lattice gas model on a square lattice [19]. The phases are labelled as follows: insulating gas (IG), insulating solid (IS), conducting liquid (CL), and conducting solid (CS). The inset shows a magnification of the relevant part of the phase diagram. The first-order transition line ends at a tricritical point where the Ising line starts. Dashed lines are Kosterlitz-Thouless (KT) transition lines. $\mathcal{L}_0$ is the locus of points where the residual multiparticle entropy vanishes: ($\triangle$), RMPE zeroes along constant-$\beta\mu$ paths; ($\bullet$), RMPE zeroes along constant-T paths. Dotted lines are traced as a guide to the eye. The picture shows a clear connection between such two "branches" of $\mathcal{L}_0$, associated with the Ising and KT zeroes respectively, and the boundaries of the CL phase. The two dotted lines merge at a point that is close to the tricritical point.

4.3 Results

The behaviour of the RMPE, evaluated along some thermodynamic paths at constant $\beta\mu$, is shown in Figures 2 and 3. For $\beta\mu = 0$, Δs starts negative at high temperatures. As β grows, a minimum appears beyond which Δs first vanishes and then becomes positive. For increasing values of $\beta\mu$, a bump springs up from the bottom of the negative well: this emerging structure eventually generates two new zeroes with a maximum inside which becomes higher and higher with $\beta\mu$.

The evolution of Δs along constant-T paths is shown in Figures 4 and 5. At low temperature, the RMPE is always positive and increases sharply with the chemical potential on approaching the first-order transition line at $\mu \approx 0.4$. When $T \approx 0.16$, a negative well develops inside the RMPE profile which progressively erodes the positive bump for low values of μ. At even higher temperatures, Δs is negative also for very small values of μ.

The (T, μ) states corresponding to a vanishing RMPE (along both types of thermodynamic paths) give rise to a single, continuous locus of points $\mathcal{L}_0$ that is drawn in Figure 6 on top of the phase boundaries of the model. Δs is negative in the high-temperature/low-chemical-potential region of the phase diagram. It is in this region that, according to the entropic picture developed above, structurally disordered states should occur and in fact such a region largely overlaps with the conducting liquid phase.

The threshold associated with the upper, ascending part of $\mathcal{L}_0$ is in clear relation to the Ising transition line: in fact, in this case, the vanishing of Δs anticipates the critical-point divergence (see Figs. 4 and 5), a feature that was already noted in Section 3.2 for the Ising model.

Conversely, the descending part of $\mathcal{L}_0$ runs close to the KT transition line and is therefore associated in a natural way with the loss of dipolar correlations which characterize the insulating-gas phase. The KT transition is weaker than any critical phase transition; moreover, it does not mark the border of a long-range-ordered phase, although a divergent correlation length is still present on the metallic side. Renormalization-group arguments predict a power-law asymptotic decay of the pair correlations in the quasi-long-range-ordered dipolar phase (transition line included) of the kind $r^{-\frac{1}{T\varepsilon(T)}}$ [16], where $\varepsilon(T)$ is the T-dependent dielectric constant. At the transition point, one has $4T_c\varepsilon(T_c) = 1$, while $\varepsilon < \varepsilon(T_c)$ for $T < T_c$. Since large-distance correlations contribute to s_2 approximately as the integral from one to infinity of $r(g(r) - 1)^2$, Δs takes finite values over the whole critical phase as long as $T\varepsilon(T) < 1$ for any $T \leq T_c$. In fact, $T\varepsilon(T) \leq T_c\varepsilon(T_c) = 1/4$; therefore, Δs is well-defined below T_c. On the contrary, the RMPE is expected to diverge like the correlation length (as for Ising) when coming from the high-temperature side of the KT transition. In a finite system, the RMPE singularity at T_c is rounded and shifted. In fact, in our MC simulation we find that Δs turns from negative to positive values near T_c, while remaining small over the entire insulating phase (see Figs. 2 and 3). This behaviour is easily understood since the dipolar fluid, notwithstanding the absence of extended spatial correlations between dipoles, retains more order than the liquid metal. In fact, strong correlations between opposite charges are requested to form dipoles in the insulating phase.

Finally, the RMPE is systematically positive for $T < 0.15$ and $\mu < 0.4$. According to the entropic viewpoint,

this indicates that the system is at least partially ordered in such a region of the phase diagram. Moreover, the rapid increase of Δs that is found as μ approaches 0.4 is reminiscent of the first-order line, in that it records the proximity to a long-range ordered phase.

In closing this Section, we would like to emphasize the non trivial morphology of $\mathcal{L}_0$, the line were Δs vanishes. In fact, the corresponding "Ising" and "KT" loci merge together to form a rounded cusp. Such a feature, which manifestly unveils as the counterpart – in the "fine structure" of the statistical entropy – of the tricritical point, is perhaps the most relevant and surprising finding of the present study.

5 Conclusions

An entropy-based, one-phase method, recently proposed for deciphering hidden signatures of the onset of ordering phenomena in statistical-mechanical models, has been applied to selected 2D lattice-gas systems, specifically the Ising lattice gas and the neutral Coulomb gas. The method rests on the properties of the residual multi-particle entropy (RMPE), a quantity that is found to be negative inside a fully-disordered phase, while becoming positive as soon as spatial correlations build up in relation to the onset of order in the system, *i.e.*, in proximity to phase transition lines.

In the Ising case, the RMPE was calculated along the critical isochore. Its profile is similar to that of the RMPE for a hard-sphere system. However, the Ising RMPE vanishes at a temperature about 18% lower than the critical temperature. This is a consequence of the fact that the RMPE must diverge at the critical point. Therefore, in such cases, the information conveyed by the RMPE is less interesting than for first-order phase transitions as the freezing and phase separation of continuous, three-dimensional multi-component fluids.

Much more interesting is the case of the neutral Coulomb gas. This model describes a binary equimolar mixture with a long-range interaction between particles. The model exhibits a rather complex phase diagram. In particular, the fully-disordered phase is a liquid metal that is separated by an Ising line from a solid metal, and by a Kosterlitz-Thouless (KT) line from a dipolar fluid. Two loci of RMPE zeroes are found in this case, which follow rather accurately the two transition lines. Moreover, these loci merge together, forming a distinct "knee" in the close neighborhood of the tricritical point of the model.

We also found that the RMPE behaviour is strongly affected, in the vicinity of a phase transition, by the nature of the transition itself. While the RMPE blows up along the Ising transition line and remains infinite inside the long-range-ordered phase, Δs is well-defined inside the dipolar phase where it takes a minute positive value owing to the absence of any long-range order. As a result, in a finite system the RMPE vanishes close to the KT transition line.

References

1. H.S. Green, in *The Molecular Theory of Fluids* (North-Holland, Amsterdam, 1952).
2. R.E. Nettleton, M.S. Green, J. Chem. Phys. **29**, 1365 (1958).
3. P. V. Giaquinta, G. Giunta, Physica A **187**, 145 (1992); P V. Giaquinta, G. Giunta, S. Prestipino Giarritta, Phys. Rev. A **45**, 6966 (1992).
4. P.V. Giaquinta, G. Giunta, G. Malescio, Physica A **250**, 91 (1998).
5. F. Saija, P.V. Giaquinta, G. Giunta, S. Prestipino Giarritta, J. Phys.: Cond. Matter **6**, 9853 (1994); *ibidem* **8**, 8137 (1996); F. Saija, G. Pastore, P.V. Giaquinta, J. Phys. Chem. B **102**, 10368 (1998).
6. D. Costa, F. Saija, P.V. Giaquinta, Chem. Phys. Lett. **283**, 86 (1998); *ibidem* **299**, 252 (1999).
7. S. Prestipino, P.V. Giaquinta, J. Stat. Phys. (1999), in press.
8. L. Onsager, Phys. Rev. **65**, 117 (1944).
9. R.J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic Press, London, 1982).
10. H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985).
11. H.A. Kramers, G. H. Wannier, Phys. Rev. **60**, 263 (1941).
12. B.M. Mc Coy, T.T. Wu, *The Two-Dimensional Ising Model* (Harvard University Press, Cambridge, 1973).
13. N.D. Mermin, H. Wagner, Phys. Rev. B **17**, 1333 (1966).
14. For a review, see *e.g.* K.J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988).
15. M. Kosterlitz, D. Thouless, J. Phys. C **6**, 1181 (1973); M. Kosterlitz, *ibidem* **7**, 1046 (1974).
16. For a review, see P. Minnhagen, Rev. Mod. Phys. **59**, 1001 (1987).
17. S T. Chui, J. D. Weeks, Phys. Rev. B **14**, 4978 (1976).
18. J.L. Lebowitz, E. Lieb, Phys. Rev. Lett. **22**, 631 (1969).
19. J.R. Lee, S. Teitel, Phys. Rev. B **46**, 3247 (1992).