

Application of Histogram Reweighting Monte Carlo Method to Network-Forming Two-Dimensional Lattice Gas Model*

by **A. Patrykiewicz, W. Rzyśko and S. Sokołowski**

*Department for the Modelling of Physico-Chemical Processes, Faculty of Chemistry,
MCS University, Lublin 20031, Poland*

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The results of grand canonical Monte Carlo study of two-dimensional lattice gas model of network-forming particles on a triangular lattice are reported. The model takes into account the effects of molecular association, resulting from the orientation-dependent interactions as well as the effects of cooperative interactions, which lead to the weakening of the bond energies. A phase transition between the dilute and the condensed phase is considered. Phase diagrams for different systems are presented and it is shown that the systems studied belong to the universality class of two-dimensional Ising model.

Key words: Monte Carlo method, phase transitions, critical phenomena, network-forming fluids, Ising model, phase diagram

Thermodynamic behavior and structural properties of associating systems are of increasing interest in basic research [1–7]. Also, in many processes of practical and technological importance, the formation of networks resulting from molecular association is of importance. The best known examples of substances that exhibit the association induced network structures are water [8,9] and silica [10,11]. In the super-cooled state, as well as in the solid state, such systems exhibit phase transitions between differently bonded structures [10,12]. Other examples of networking systems are those, which exhibit polyamorphism [13].

Recently, Roberts and Debenedetti [14] have proposed a lattice gas model, which captures several important factors that determine thermodynamic behavior and the internal structure of such network-forming systems. The model has been solved in a three-dimensional space on the bcc lattice within the mean-field approximation and later was also studied by the canonical ensemble Monte Carlo simulation [15]. It has been demonstrated that the presence of strong orientation-dependent interactions leads to the first-order liquid–liquid transition and may induce immiscibility of those different phases over a certain temperature range. A noticeable qualitative agreement between the approximate mean-field solution and the Monte Carlo simulation results has been observed. One of the most interesting results of that study was the demon-

*Dedicated to Prof. Jan Stecki on the occasion of his 70th birthday.

stration that the liquid–liquid equilibrium shows both the upper and the lower critical temperatures under suitable conditions. It has been argued that the presence of the lower critical point is directly connected to entropic contributions to the free energy of the high density condensed phase.

It should be emphasized that other theoretical models of network-forming systems usually assume explicit density dependence of the strength of the molecular interactions [16,17] or allow the molecules in the system to exist in more than one state [18]. The model proposed by Roberts and Debenedetti [14] does not introduce any such explicit relation between the density and the strength of molecular interactions and hence is much more general and more realistic.

In two-dimensions the behavior of network-forming systems should be qualitatively different from the behavior of systems in a three-dimensional space, mostly due to considerably enhanced effects of statistical fluctuations [19]. In particular, one can expect that in two-dimensional space the systems should exhibit considerably reduced tendency to undergo sharp first-order transitions between the condensed phases [20]. It should be stressed that two-dimensional network-forming fluids are also of experimental interest. Here, we can invoke monolayers of adsorbed associating particles as water [21] and organic particles, such as crystal violet [22].

In our recent paper [7] we have presented a two-dimensional modified version of the model presented in [14] and discussed the phase behavior of systems characterized by rather strong association energy and different cooperative effects. It has been argued that the transition between different condensed phases occurs *via* the second-order phase transition. Also, it has been demonstrated that this transition extends from the ground state to a certain temperature T_t , which is considerably lower than the corresponding gas–liquid critical temperature T_c . Below T_t we have found also the first-order transition between a dilute (gas) phase and a condensed phase of the ordered structure. On the other hand, above the temperature T_t only one first-order transition between a gas phase and an amorphous condensed phase occurs and it terminates in the critical point. Sufficiently strong cooperative effects, which lead to the weakening of the association interaction, have been found to introduce important qualitative changes to the topology of phase diagrams. In particular, the transition between a dilute and a condensed phase does not terminate at a critical point but rather ends at a tricritical point, so that at still higher temperatures a continuous transition between the gas and the liquid phase is found.

In this work we present the results of a further study of the model described in [7], and consider systems characterized by a lower strength of the association energy and different contributions due to cooperative effects. Our primary aim is to show that the histogram reweighting Monte Carlo method can be efficiently used to determine critical properties of such network forming systems and to determine the universality class of the model. Besides, we wish to elucidate the effects of orientation-dependent forces on the internal structure of a two-dimensional condensed phase.

The paper is arranged as follows: First we present the model used and discuss briefly its ground state properties. Then, we give a detailed description of the Monte Carlo simulation method used. The results of our calculations are presented and discussed later.

MODEL

We consider a simple two-dimensional hexagonal lattice and assume that each site can be empty or occupied by a single particle. Each particle placed on a site is then assumed to have three equivalent bonding arms, that form the angle 120° one with each other. Orientational degrees of freedom are taken into account by assigning to each particle a set of six Potts-like variables $\sigma_{i,k}$, $k = 1, 2, \dots, 6$. Here we assume that $\sigma_{i,k} = 1$, when k corresponds to any of the bonding arms and equals to zero in the remaining three directions. Since all bonding arms are fully equivalent, the molecule located on site i can take two distinguishable states with respect to the chosen coordination system. Thus, the Potts-like variables $\sigma_{i,k}$ may be equal to $(1, 0, 1, 0, 1, 0)$ or $(0, 1, 0, 1, 0, 1)$, depending on its orientation relative to the surface lattice.

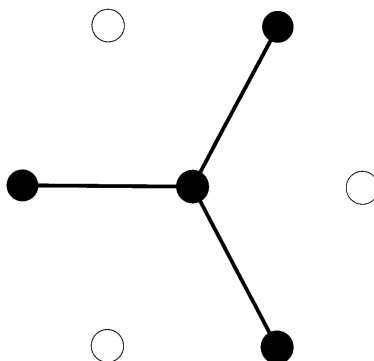


Figure 1. Bonded sites (filled circles) and bond weakening sites (open circles). Each bond weakening sites acts on two adjacent bonds (solid lines).

Two molecules located on a pair of adjacent sites interact one with another with the orientation independent (attractive) energy ε_o and can also form a bond of the energy ε_b , whenever the orientation of their bonding arms is suitable, *i.e.*, when the Potts-like variables of the arms pointing to each other are both equal to 1. The above bond formation mechanism is slightly different than in the three-dimensional model of [14], where Potts variables assumed different values for each arm and the bond could form only when both Potts variables of adjacent molecules were the same. Following the model considered in [14], we also assume that each occupied site, adjacent to both bond-forming molecules, weakens the bond energy by $c\varepsilon_b/2$, where $c \in [0, 1]$, and the factor $1/2$ results from the presence of two such weakening sites (*cf.* Fig. 1). With the above assumptions the potential energy of any specified configuration of the system reads

$$E(\{n_i\}) = -\varepsilon_o \sum_{\langle i,j \rangle} n_i n_j - \varepsilon_b \sum_{\langle i,j \rangle} n_i n_j \delta_{\sigma_{i,m} \sigma_{j,n}} \sum_{k_{ij}=1}^2 \frac{1}{2} (1 - cn_k) \quad (1)$$

where n_i denotes the usual occupation variable, equal to 0 (1) when the site i is empty (occupied), the first two summations are taken over all nearest neighbor pairs of sites, the third sum runs over all bond weakening sites and $\delta_{\sigma_{i,m} \sigma_{j,n}} = 1(0)$, when $\sigma_{i,m} = \sigma_{j,n}$ ($\sigma_{i,m} \neq \sigma_{j,n}$).

In the grand canonical ensemble, the Hamiltonian for the above model is then given by

$$\mathcal{H} = E(\{n_i\}) - \mu \sum_i n_i \quad (2)$$

where μ is the chemical potential and the sum runs over all lattice sites. An analysis of the ground state behavior of (2) showed that the system properties depend strongly on the bonding energy ε_b , as well as on the parameter c . Apart from the trivial dilute (gas) phase, with all $n_i = 0$ at $T = 0$ and with the free energy equal to zero, there can also appear different ordered condensed phases. One possible ordered state corresponds to a fully bonded honeycomb lattice of the density equal to $2/3$, in which a central site of every hexagon of occupied sites is empty. This open honeycomb phase (O) has the free energy (per lattice site) given by

$$\omega_O = -\varepsilon_o - \varepsilon_b - (2/3)\mu \quad (3)$$

Note that ω_O does not depend on c . Other ordered states correspond to a fully occupied lattice. In this situation there are several different structures possible. One obvious case corresponds to the closed honeycomb (C) structure, which is obtained from the open honeycomb structure by filling all central sites by the adsorbate particles. The free energy of this phase is given by

$$\omega_C = -3\varepsilon_o - \varepsilon_b(1 - c) - \mu \quad (4)$$

There are still other ordered states possible, but all of them have a higher free energy than the above mentioned phases and hence are not stable at $T = 0$. The above discussion demonstrates that the ground state of a completely filled lattice is highly degenerated. Both phases, O and C, are degenerated as the empty (in phase O) or occupied but not bonded (in phase C) sites can belong to one of seven different sublattices. Note, that in the case of a completely occupied lattice, all bonds are always fully weakened, independently of the internal structure. Therefore, in the case of $c = 1$ all

possible orientations of the particles are completely equivalent. Thus, the probability that a single particle will form i bonds ($i = 0, 1, 2$ or 3) is given by

$$p_o(i) = \frac{1}{8} \frac{3!}{(3-i)!i!} \quad (5)$$

From the expressions for the free energy of the ordered states O and C (or Z), given by (3) and (4), it follows that at the ground state the open honeycomb structure should be stable only when the reduced strength of the bonding energy $\varepsilon_b^* = \varepsilon_b/\varepsilon_o$ is greater than 1 and when the parameter c is such that

$$c > \frac{3}{2\varepsilon_b^*} - 0.5 \quad (6)$$

In this paper we consider a series of systems characterized by $\varepsilon_b^* = 1.0$ and by different values of c equal to 0 and 1. All the energy-like quantities are expressed in units of ε_o , e.g., $T^* = kT/\varepsilon_o$, $\mu^* = \mu/\varepsilon_o$, etc. For such a choice of the association energy, only one condensed phase can be formed at $T^* = 0$ and it corresponds to a fully occupied lattice.

Computational method: A finite temperature behavior of the above presented model has been studied by a Monte Carlo method in the grand canonical ensemble [23]. The calculations have been carried out for a rhombus simulation cell consisting of $L \times L$ sites with the standard periodic boundary conditions in both directions, using of different size ranging between $L = 36$ and $L = 84$. A typical run consisted of 10^5 – 10^8 Monte Carlo steps (per site) (MCS), depending on the temperature. In each run a similar number of MC steps has been used to equilibrate the system. To ensure that the equilibrium state was reached, we have monitored the behavior of the system energy and density. In order to avoid the effects of strong correlations between subsequently generated states, the averages have been calculated using the configurations generated in the Monte Carlo steps, spaced by a certain number k of omitted Monte Carlo steps. In most cases it has been found sufficient to use the k between 10 and 50. The quantities recorded have been the average energy (per site) u and the density ρ . Since the main purpose of study was to obtain information about the critical behavior of the model, we have performed calculations for systems of different size, in order to use finite size scaling. To characterize the effects of association, the concentrations of differently bonded and nonbonded particles have been also calculated. The histogram reweighting and finite size scaling techniques [24–27] have been used to study the critical behavior of the model. Thus, the two-dimensional histograms $P_L(\rho, u)$ have been calculated for a series of systems of different size L . Then, the joint distribution $P(\rho, u)$ has been constructed. This distribution allows to calculate all the moments required to apply the finite size scaling analysis [24]. Apart from the calculations of the

above mentioned basis quantities (u and ρ), we have also calculated the second moment and the 4th-order cumulant of the order parameter (m) given by

$$U_L = 1 - \frac{\langle m^4 \rangle_L}{3 \langle m^2 \rangle_L^2} \quad (7)$$

where $m = \rho - \langle \rho \rangle_L$. Far above the critical point, the density distribution is a single gaussian, so that $U_L = 0$, while well below T_c , the cumulant reaches also the trivial fixed point $U_L = 2/3$. In the vicinity of critical point cumulants show a strong dependence on the system size. At T_c , however, the cumulants of different size meet at the nontrivial fixed point U^* . The magnitude of U^* depends on the universality class of the transition. The densities at a two-phase coexistence have been determined from either the calculated isotherms, as well as from the block density distribution functions [24].

The coexistence curve has been determined from a “two-state” approximation [28] from the density distribution $\hat{P}(\rho) = \sum_u P(\rho, u)$, which, close to the critical point, exhibits a double peaked structure with a shallow minimum. The precise location of the coexistence has been found by tuning the chemical potential at any given temperature, until the areas under the two peaks of $\hat{P}(\rho)$ have become identical.

RESULTS AND DISCUSSION

We begin with the presentation of typical isotherms for the systems characterized by the parameter $c = 0.0$ (Fig. 2a) and $c = 1.0$ (Fig. 2b) obtained at different temperatures below T_c^{ast} . From the isotherms calculated at different temperatures we have constructed the phase diagrams for both systems (see Fig. 3). One readily notes that the introduction of bond weakening effect ($c = 1.0$) leads to a considerable reduction of the critical temperature and to a lowering of the critical density. Before a detailed discussion of critical properties of the model, which is the primary aim of this work, we consider the differences in the structure of the condensed phase for the systems with $c = 0.0$ and $c = 1.0$. We denote the probability that a given particle has i bonds ($i = 0, 1, 2, 3$) by $p_b(i)$, and the concentration of particles in the state i by $c_b(i) = \rho p_b(i)$. Of course, the following normalizing condition is satisfied

$$\rho = \sum_i c_b(i) \quad (8)$$

Note, that in the case of $c = 1.0$, the presence of bonds is expected to have a small influence on the system structure at high densities. In particular, when ρ approaches unity, the concentrations of differently bonded and unbonded particles ($c_b(i)$, $i = 0, 1,$

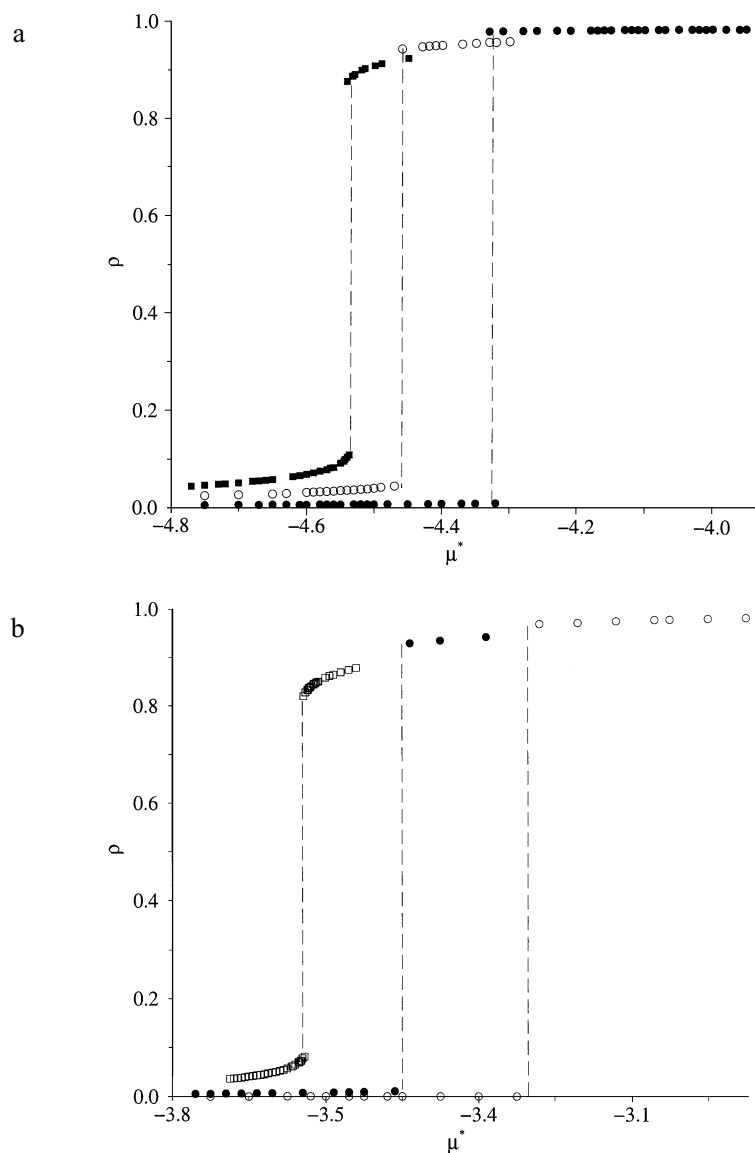


Figure 2. Adsorption isotherms at various temperatures. Part a shows results for $c = 0$ at $T^* = 0.6$ (filled squares); $T^* = 0.8$ (open circles) and at $T^* = 1$ (filled circles). Part b is for $c = 1$ and at $T^* = 0.4$ (open squares); $T^* = 0.8$ (filled circles) and at $T^* = 0.75$ (open circles).

2 and 3) are expected to reach the values $p_o(i)$, predicted by (5). The above prediction is quite well supported by the results shown in Figure 4, which presents the changes of $c_b(i)$ versus chemical potential at two different temperatures below the critical point for the system with $c = 1.0$. On the other hand, when the bond weakening parameter c is equal to zero, the condensed phase behaves differently, as it demonstrates Fig. 5. In particular, the number of bonded particles is considerably higher than in the previous

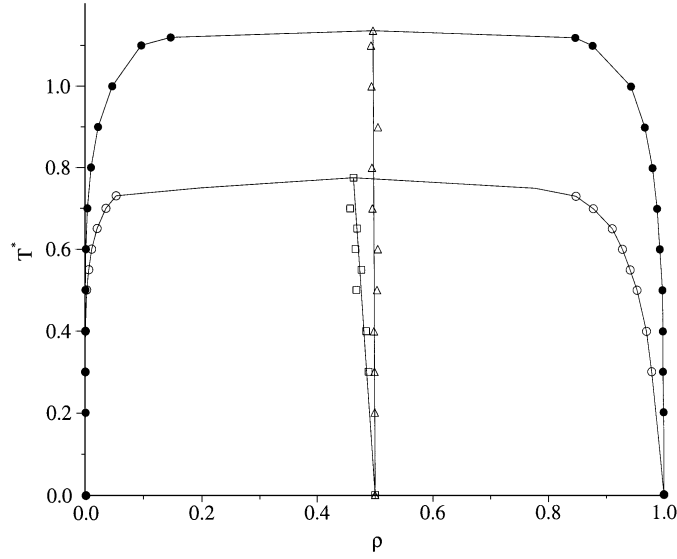


Figure 3. Phase diagram for $c = 1$ (open circles) and for $c = 0$ (filled circles). Triangles and squares denote the line $(\rho_l + \rho_g)/2$.

case. We also observe that the contribution of particles, which form three bonds, increases when the temperature becomes lower. From the above discussion it follows that the effect of cooperativity is rather quantitative only. In particular, we expect that the both systems studied here belong to the same universality class of 2D Ising model [29]. In order to verify this hypothesis, we have estimated the critical exponents ν and β , using the finite size scaling analysis. Figure 6 presents the density distribution functions $\hat{P}(\rho)$ along the coexistence curve, obtained at different temperatures (near T_c^*) for both systems. It is quite well seen that in the case of $c = 0$ the distribution $\hat{P}(\rho)$ is fully symmetric, while for $c = 1$ the distribution lacks a full symmetry. Thus, the peak at the gas phase side is sharper and higher than the peak at the liquid phase side. The critical temperatures have been estimated from the plots of U_L for different L versus temperature (see Fig. 7). In both cases ($c = 0$ and $c = 1$) the fixed point value U^* of the cumulants U_L has been found to be equal to 0.61. This is exactly the value of U^* for the two-dimensional Ising model [24]. The critical temperature for the system with $c = 0$ has been estimated as equal to 1.137 ± 0.001 , while in the case of $c = 1$ $T_c^* = 0.7755 \pm 0.0005$. One should remember that the above method is not biased by any assumptions concerning the universality class and the knowledge about of the critical exponents is not required. The critical exponent ν can be also evaluated from the behavior of cumulants for systems of different size. When the values of L are big enough and the corrections to scaling are negligible, the exponent ν can be found from

$$\nu^{-1} = [\ln(\delta U_{bL}/\delta U_L)/\ln(b)]_{U^*} \quad (9)$$

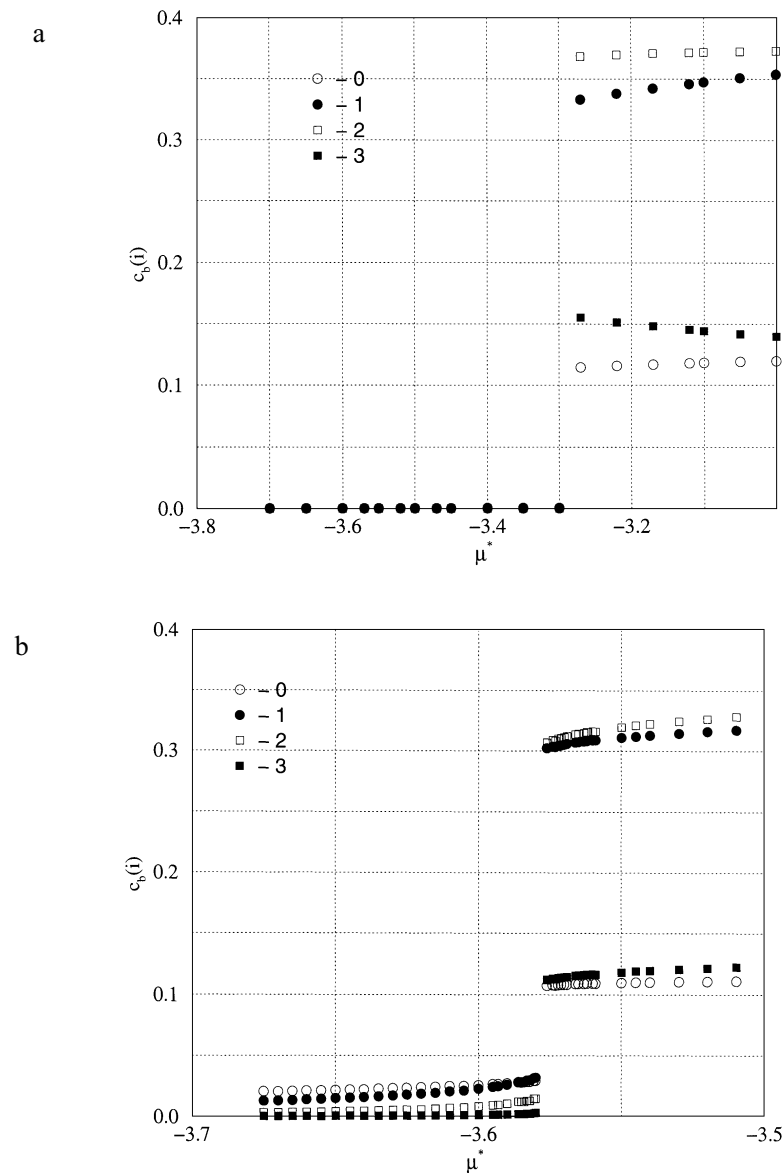


Figure 4. Concentrations of differently bonded and unbonded particles *versus* chemical potential for the system with $c = 1$ at two reduced temperatures: 0.4 (part a) and 0.75 (part b).

where $b = L'/L$. Figure 8 demonstrates that in both cases of $c = 0$ and 1 the exponent ν is very close to 1.0. Having the value of ν , we can also estimate the critical exponent β , which describes the behavior of the order parameter (m) near the critical point. Namely, the finite size scaling of the second moment of the order parameter leads to the equation [24]

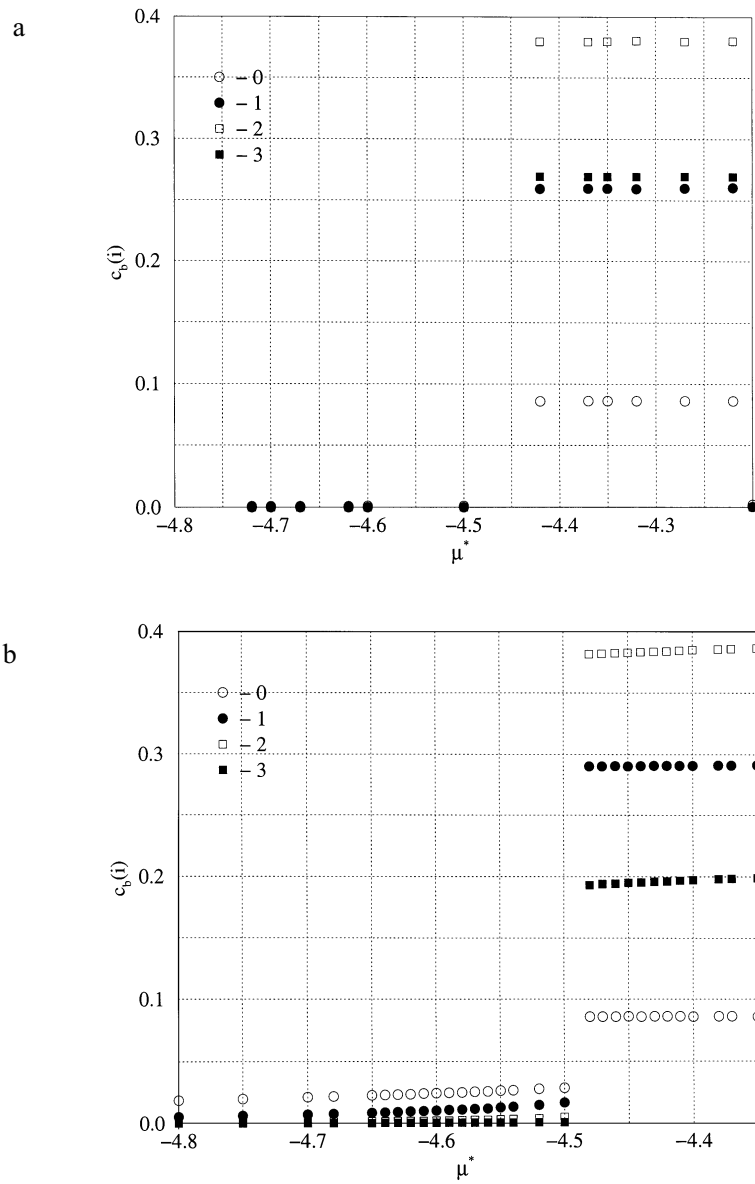


Figure 5. The same as in Fig. 4, but for the system with $c = 0$ at the reduced temperature 0.6 (part a) and 1.0 (part b).

$$2\beta/\nu = -\ln[\langle m^2 \rangle_{bL,T_c} / \langle m^2 \rangle_{L,T_c}] / \ln(b) \quad (10)$$

The results of our calculations are presented in Figure 9 and show that in both systems we have $2\beta/\nu \approx 0.25$ and hence $\beta \approx 0.125$. The estimated exponents ν and β confirm that our systems belong to the universality class of the two-dimensional Ising model

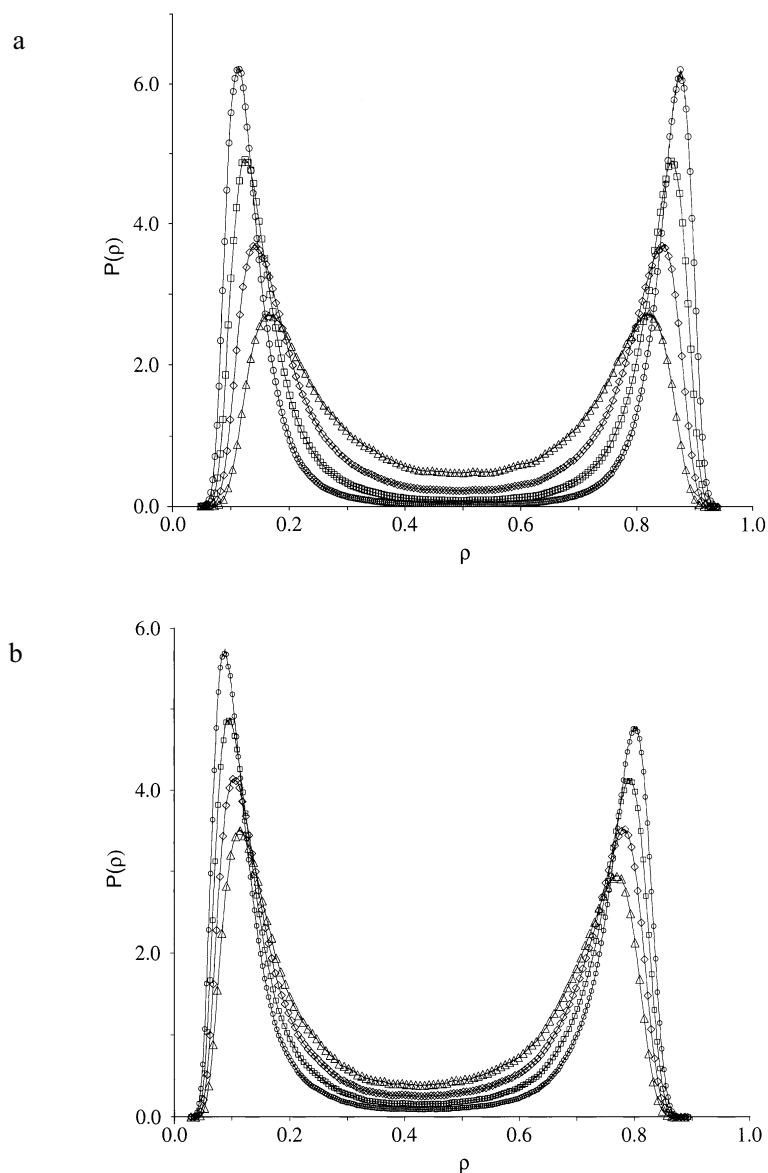


Figure 6. The distributions $P(\rho)$ at different temperatures close to the critical temperature. Parts a and b are for the systems with $c = 0$ and $c = 1$, respectively.

[29]. The results shown in Figs. 7–9 demonstrate also, that the critical temperature and exponents can be evaluated with a very high precision. In this paper we present the results of extensive Monte Carlo simulation of two-dimensional lattice model of associating fluid. Our primary aim was to check, how the histogram reweighting technique, together with the finite size scaling analysis, works in the case of such complex systems. It should be emphasized that the histogram reweighting method has not been

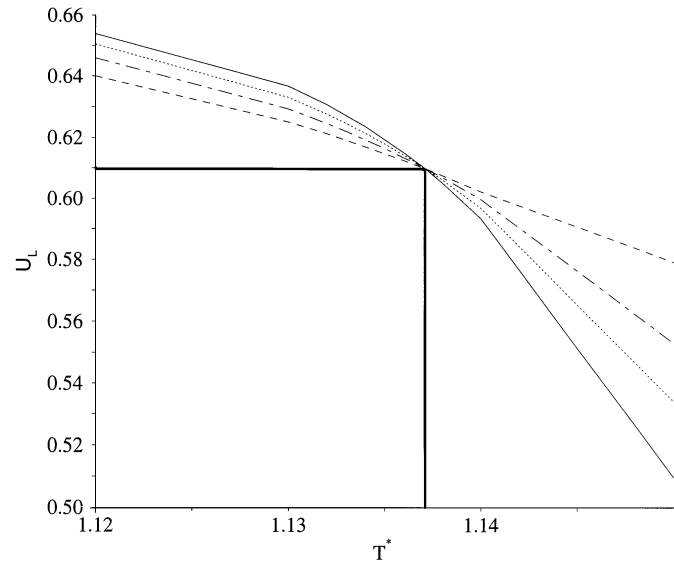


Figure 7. Cumulant intersection plot for the systems of different size: $L = 72$ (solid line), $L = 60$ (dotted line); $L = 48$ (long-dashed line) and $L = 36$ (dashed line).

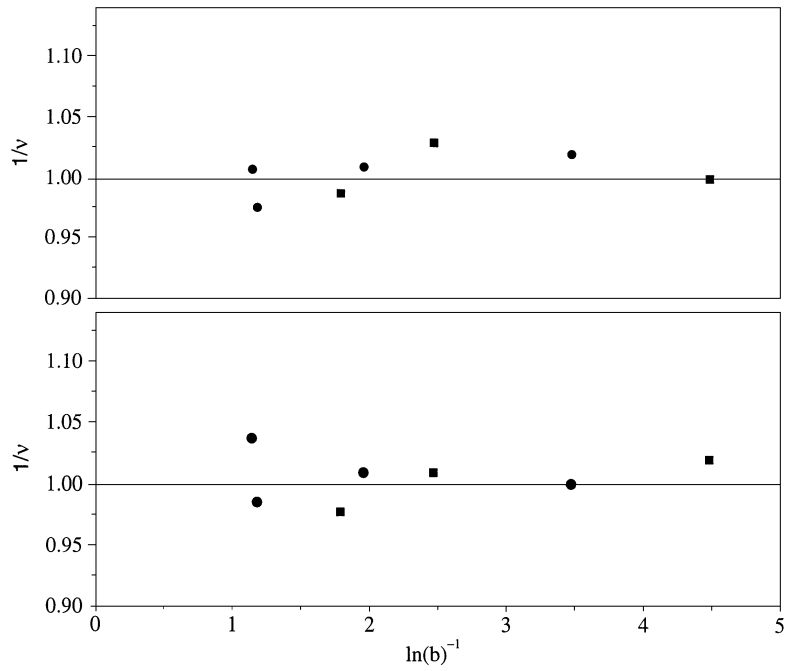


Figure 8. Evaluation of the critical exponent $1/\nu$. Lower panel is for the system with $c = 0$, whereas upper panel – for the system with $c = 1$.

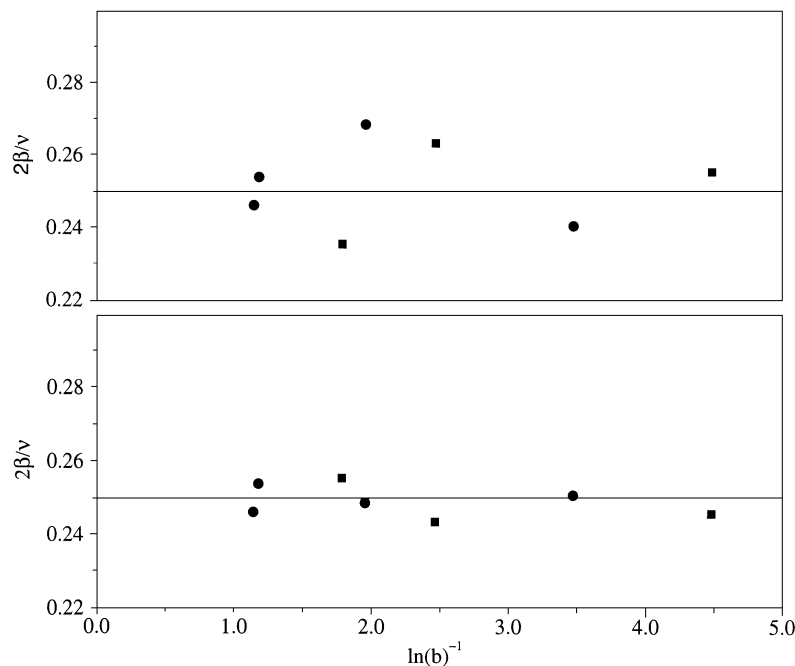


Figure 9. Evaluation of the critical exponent $2\beta/\nu$. Lower panel is for the system with $c = 0$, whereas upper panel – for the system with $c = 1$.

previously used to study models, which take into account association between the particles [30–32].

We estimate the critical temperatures and critical exponents for two different systems and find that both belong to the universality class of the two-dimensional Ising model. Of course, the results presented here correspond to a rather simple situation. In particular, the model predicts that for higher energy of association [7] the topology of the phase diagram changes and that there is more than one condensed phase. Already the ground state analysis suggests that in such cases the model belongs to different universality class. We plan to apply similar techniques to investigate strongly associating systems and the results of our study will be presented in the next paper.

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