The lattice fluid with the competing interactions on the square lattice

Ya. G. Groda[a], A. Ciach[b]

a) Belarusian State Technological University, Minsk, Belarus, **yar.groda@gmail.com**
b) Institute of Physical Chemistry PAS, Warsaw, Poland

Abstract.

The lattice system with competing interactions (attractive between nearest neighbors and repulsive between fourth order neighbors) on a square lattice is studied. It is shown that the competing interactions lead to the order-disorder phase transitions. The possibility of existence of two types of ordered phases in the system is established and investigated the conditions for the occurrence of each of these phases. The geometric order parameter for localizing the structural phase transition points is proposed. With its help, the critical value of the interaction parameter was established, and the dependence of the critical temperature of the model versus the ratio of intensities of competing interactions was studied. The Monte Carlo simulation data are compared with the results of the quasi-chemical approximation. It is shown that the quasi-chemical approximation allows one to determine the thermodynamic properties of the model with high accuracy.

1 The model and its order parameter

The model which is considered in this article is the lattice fluid consisting of n particles on the square lattice containing N lattice sites. Each of the lattice sites can be occupied by no more than one particle. Particles occupying the nearest lattice sites and sites that are fourth-order neighbors interact with each other. The energies of these interactions are equal to J_1 and J_4, respectively. The second, third, fifth and more distant neighbors are considered as non-interacting.

In the future, we will assume that $J_1<0$, and $J_4>0$

$$J_1 = -J, \quad J_4 = J^*J. \tag{1}$$

where $J>0$ is the energy parameter of the model and

$$J^* = \left|\frac{J_4}{J_1}\right|. \tag{2}$$

This choice of interaction energies corresponds to the attraction of the nearest neighbors and the repulsion of the fourth neighbors.

The simulation of the equilibrium characteristics of the system under consideration in the grand canonical ensemble using the Monte Carlo method is performed within the framework of the Metropolis algorithm [1]. For simulation, we used a lattice containing 2^{12} lattice sites with periodic boundary conditions. The total

length of the simulation procedure consisted of 70 000 steps of the Monte Carlo algorithm (MCS). The first 20 000 MCSs were used to equilibrate the system and not taken into account at subsequent averaging.

A MC simulation has shown that two different types of ordered phases are formed in the system at low temperatures (below the critical temperature T_c). The both types of ordered phases are shown in Figure 1.

In contrast, the similar system considered earlier with the interaction of the nearest and third neighbors [2], the type of arising ordered phase depends on the ratio of the intensities of the interparticle interactions, i.e. from the parameter J^*.

Since the total internal energy of the ordered phase which is presented on the right panel of the Fig. 1 is zero, the threshold value of the parameter J^* can be determined from the following relation

$$3J_1 + 2J_2 = -3J + 2J^*J = 0, \tag{3}$$

and equal $J^*=1.5$.

At $J^*<1.5$, the ordered phase is an alternation of double empty and double filled vertical or horizontal stripes. At the same time, for $J^*>1.5$ the system has the so-called "chess" order. Thus, for the system under consideration, there is no degeneracy of the basic energy state observed earlier [2].

The MC simulation showed that the change of the type of ordered phase does not occur abruptly. At $J^*\approx1.5$ the system breaks up on domains with different types of the ordered structures (see Fig. 2). This behavior of the system can be explained by the influence of entropy effects on the form of its ordered phase.

For describing the both types of ordered phases, the initial square lattice was divided into a system of 16 identical sublattices with the spacing $4a$, where a is the lattice spacing of the initial lattice. In the case of complete ordering of the system at the lattice concentration $c = 0.5$ and low temperatures, eight sublattices are completely filled (p-sublattice) and eight sublattices are completely vacant (v-sublattice). After determining the average particle concentration on each of the introduced sublattices, the order parameter of the system δc can be determined in accordance with the relation

$$\delta c = \frac{c_{\max} - c_{\min}}{2}, \tag{4}$$

where $c_{\max}$ and $c_{\min}$ are the particles concentrations on the most and least filled sublattices, respectively.

At the same time, it should be noted that to describe the "chess" order, a more simple approach can be proposed. In this case the initial lattice is divided into only two sublattices with the spacing $a\sqrt{2}$. These sublattices can be named as even and odd lattices, respectively. Such terminology is because the sum of the coordinates of the lattice site on the initial lattice is an even number in one case and an odd number in the other. After then, the corresponding sublattice concentrations c_{2k} and c_{2k+1} can be determined, and on their basis the order parameter δc can be calculated as

$$\delta c = \frac{|c_{2k} - c_{2k+1}|}{2}. \tag{5}$$

2
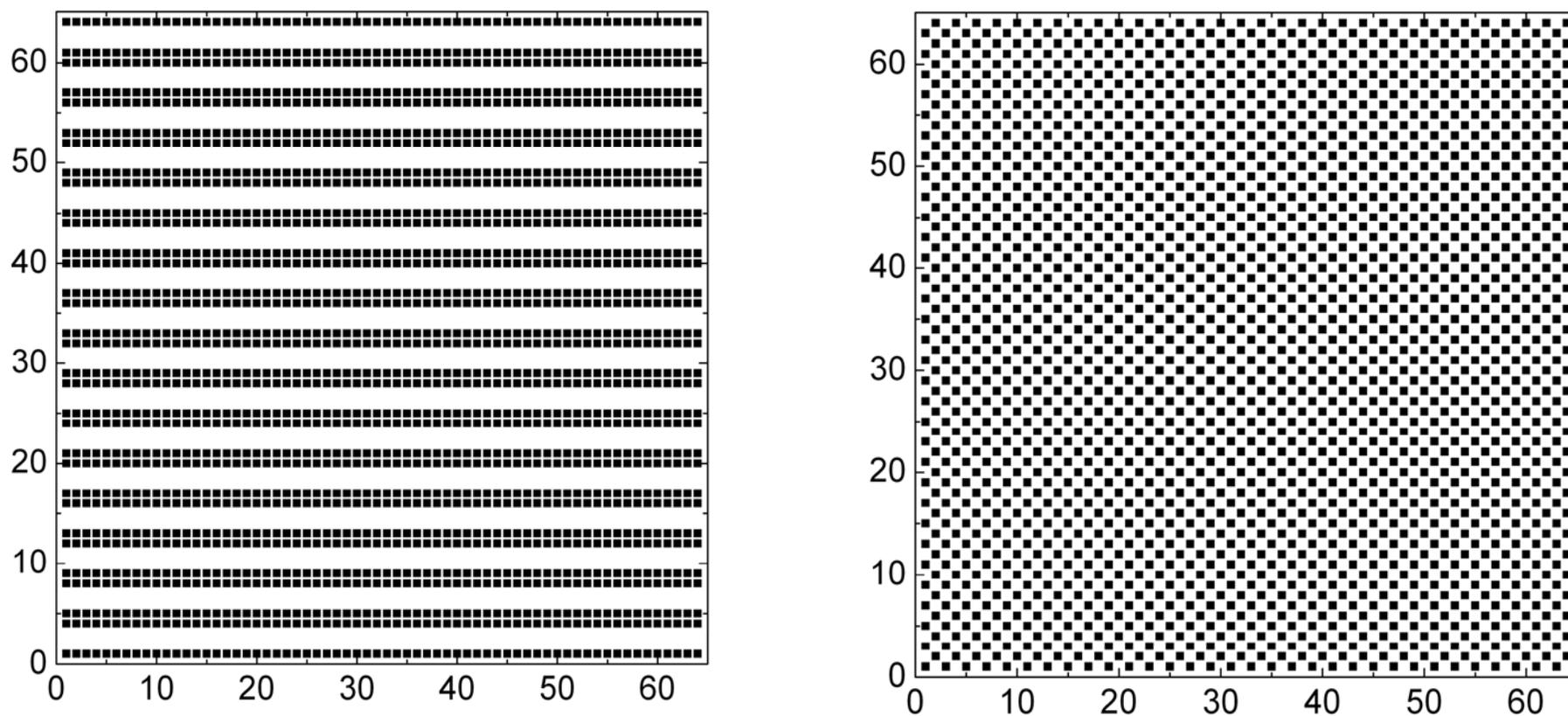
Figure 1. The final screenshot of the system at chemical potential $\mu = 10J$ (concentration $c = 0.5$), $J / k_B T_c = 2.0$. The left and right panels of the figure correspond to the $J^* = 1.2$ and 2.5, respectively
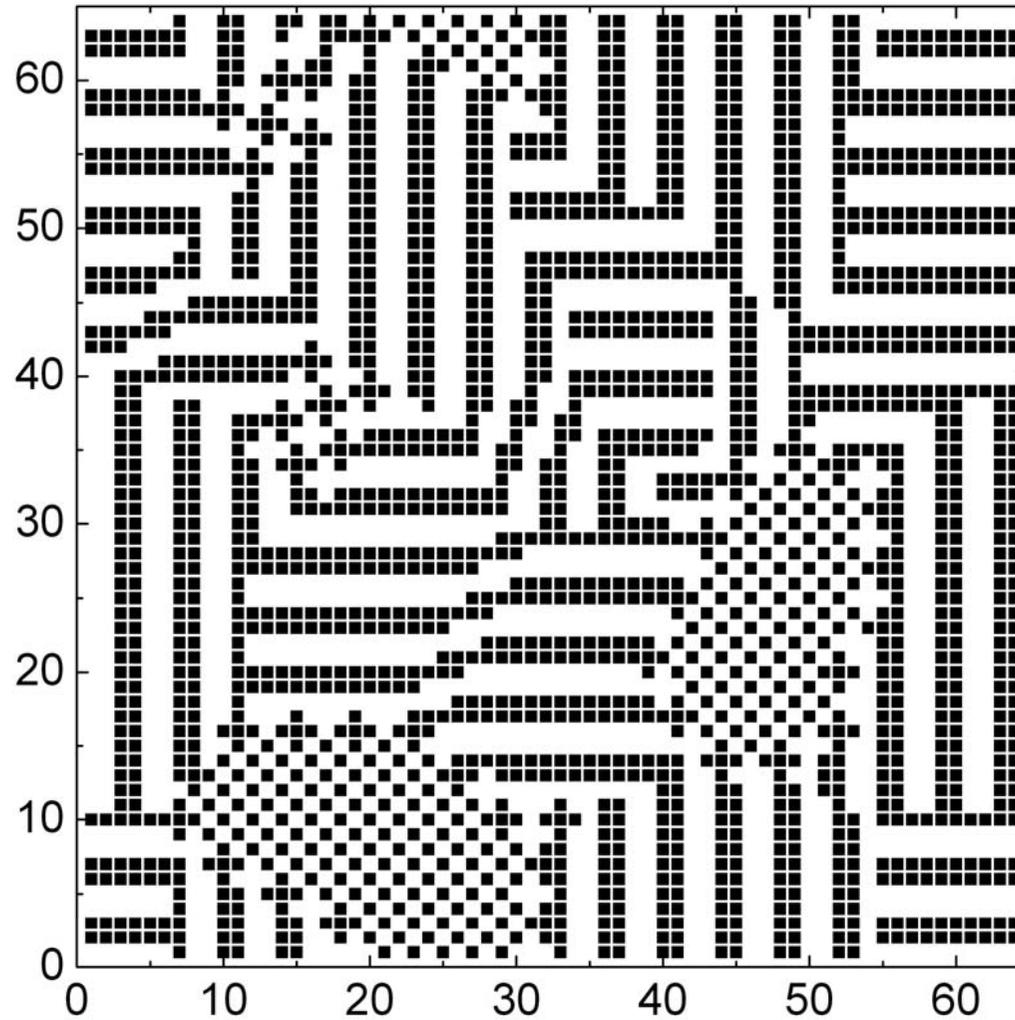
Figure 2. The final screenshot of the system at $\mu = 10J$ $(c = 0.5)$, $J / k_B T_c = 10.0$ and $J^* = 1.52$

It follows from the analysis of the left panel of the Fig. 1 that the second way to determining the order parameter is not universal. The order parameter according to the relation (5) is equal to 0 even in the case of complete ordered state, if this state corresponds to the alternation of double empty and double filled stripes.

Nevertheless, the presence of two different approaches to the description of the ordered states allows not only comparing their results, but also makes it possible to control the change of the type of the ordered phase in the system.

Another way to control of the type of the ordered phase is using the matrix of order parameters [2]

$$\delta c_{ij} = \frac{\left| c_i - c_j \right|}{2}.$$
(6)

where $c_{i(j)}$ is the concentration of particles on the sublattice $i(j)$.

This is a symmetric matrix (16×16) with the diagonal elements equal to zero and 120 independent nondiagonal elements equal to one or zero for the ordered structures. In this case, it is possible to distinguish the ordered phases by the structure of this matrix. However, this approach is rather cumbersome because of the size of the matrix of order parameters.

The order parameter characterizes the strength of the ordering of the ordered state and is equal to zero in a disordered state. The total lattice concentration c and the sublattice concentrations c_p and c_v satisfy the expressions (the subscripts 1 and 0 are related to particles and vacancies, correspondently)

$$c_p = c_1^p = c + \delta c, \quad c_0^p = 1 - c_1^p = 1 - c - \delta c,$$
(7)

$$c_v = c_1^v = c - \delta c, \quad c_0^v = 1 - c_1^v = 1 - c + \delta c,$$
(8)

$$c = c_1 = \frac{n}{N} = \frac{c_1^p + c_1^v}{2}, \quad c_0 = 1 - c_1.$$
(9)

2 The critical parameter of the system

The MC simulation shows (see Fig. 3) that in the case of the system with $J^* = 3.0$, the order parameter increases sharply at $J / k_B T_c = 0.266$ for the chemical potential $\mu = 10J$ that corresponds to the system with the average concentration $c = 0.5$.

Such an increase of the order parameter corresponds to the order-disorder phase transition. The value 0.266 can be interpreted as a critical parameter of the model, by analogy with the SALR system with the interaction of the first and third neighbors [2, 3] and the systems with repulsion interaction between the nearest neighbors [4, 5].

In a similar way, critical temperature of the system can also be determined for other values of the parameter J^*, which corresponds to various types of the ordering. Fig. 4 represents the dependence of the dimensionless critical temperature of the model on the parameter J^*. This dependence is approximately linear for a fixed type of ordering of the system and has a pronounced kink at $J^* \approx 1.5$. This point, as noted above, corresponds to the change in the type of the ordered state of the system.
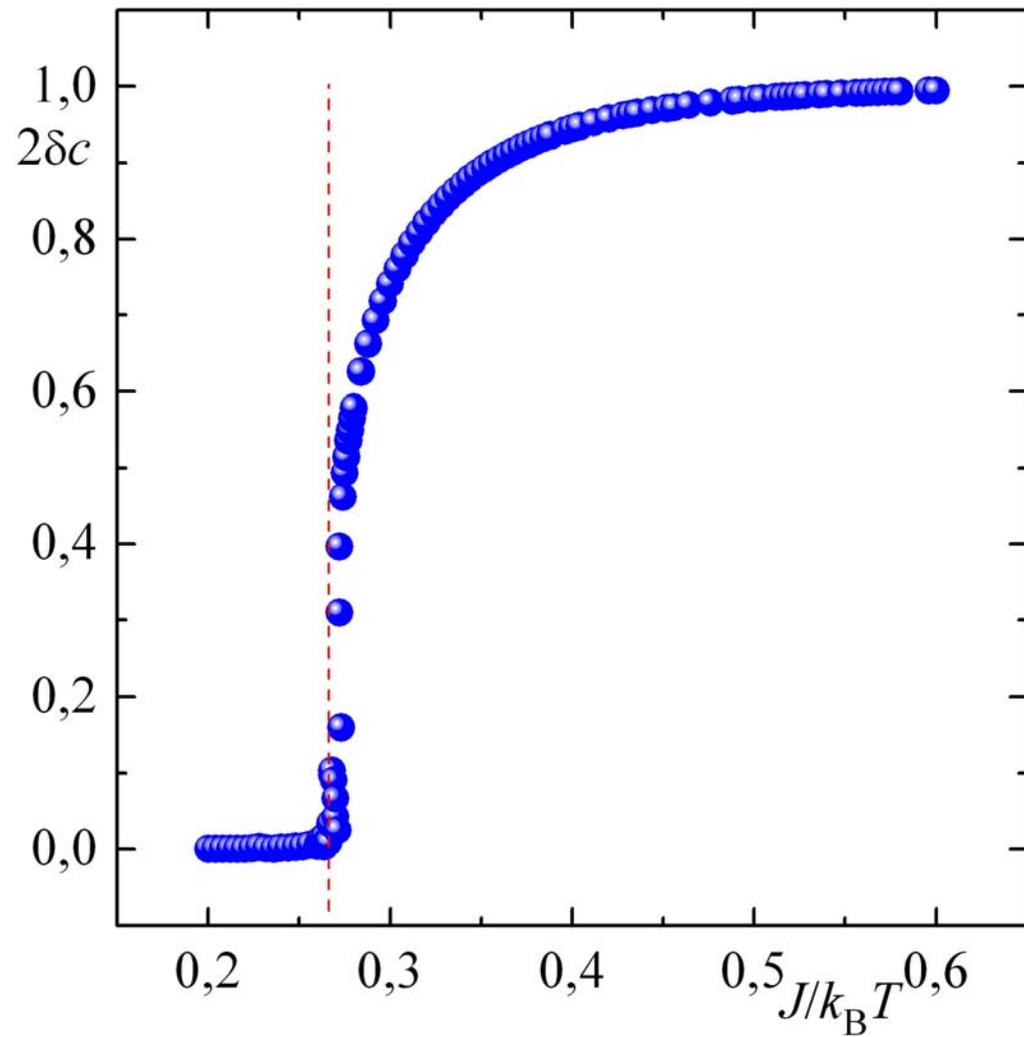
Figure 3. The order parameter versus the inverse temperature at $\mu = 10J$ ($c = 0,5$) and $J^* = 3$
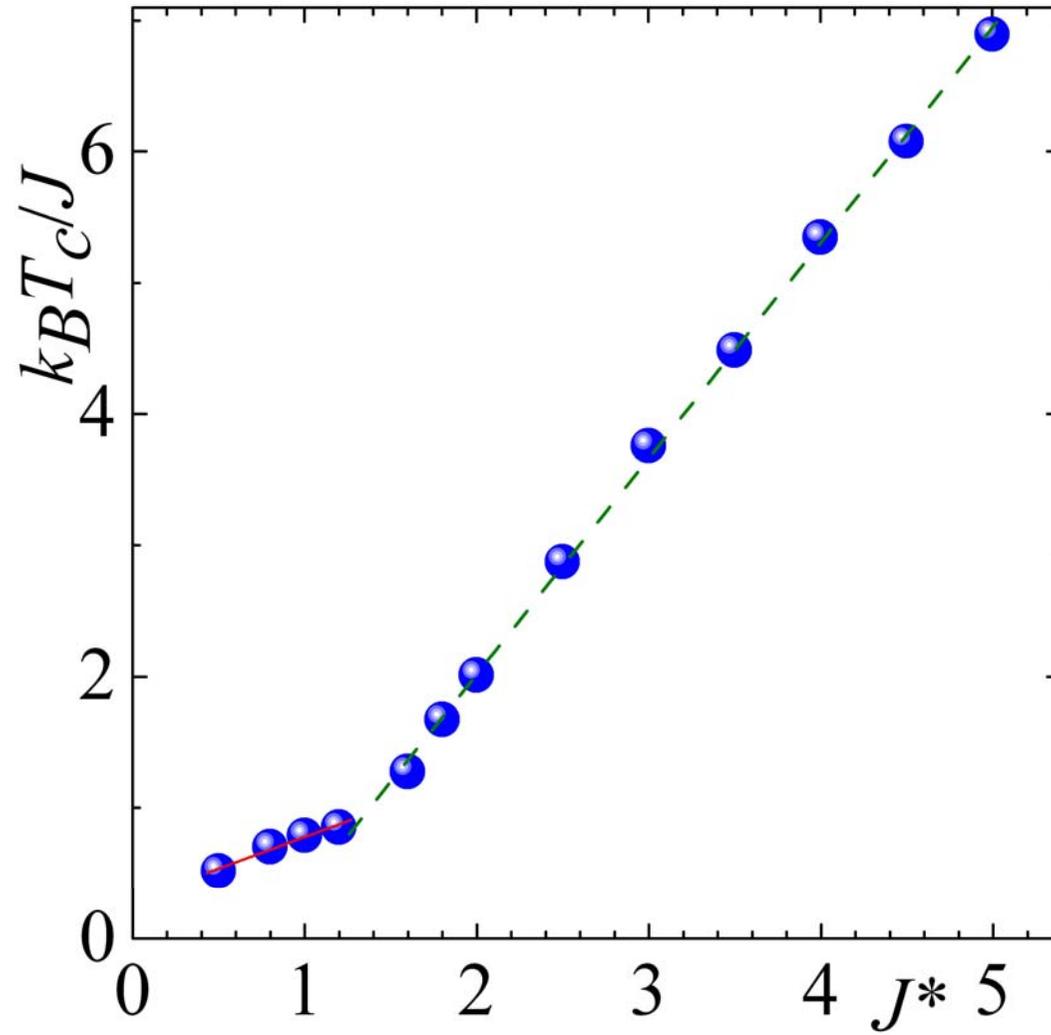
Figure 4. The dimensionless critical temperature of the model $k_B T_c / J$ versus the parameter J^*

3 The quasi-chemical approximation

The relatively simple quasi-chemical approximation (QChA) to estimate the equilibrium parameters of lattice systems with SALR interparticle interactions was proposed in [2].

The main idea of this approach is to present the free energy of initial system F as the sum of the free energy $F^{(r)}$ of the reference system (which is similar to the initial one) and the diagrammatic part $F^{(d)}$ of the free energy [5, 6]:

$$F = F^{(r)} + F^{(d)}. \tag{10}$$

The reference system is characterized by the mean potentials $\varphi_j^{\beta}(n_i^{\alpha})$ describing the interaction of a particle ($n_i^{\alpha} = 1$) or vacancy ($n_i^{\alpha} = 0$) on site i of the α-sublattice with the site j of the β-sublattice. The free energy of the system have not to depend on the choice of the mean potentials since equation (10) is an identity. This makes it possible to determine the mean potential from the minimal susceptibility principle [7]

$$\frac{\partial F}{\partial \varphi_i^{\alpha}} = 0. \tag{11}$$

Obviously, the free energy is the function of the concentration of particles on the sublattices $c_{p(v)}$ or the function of the average concentration of particles on the lattice c and the order parameter δc. The latter can be determined from the extremity condition

$$\frac{\partial F}{\partial \delta c} = 0, \tag{12}$$

which is equivalent to the requirement that the chemical potentials on all the sublattices are equal.

The quasi-chemical approximation corresponds to taking into account in the diagram part of the free energy the contributions only of the two-vertex graphs. In this case [2], the free energy of the system can be represented in the following form

$$F^{QChA}(c, \delta c) = \frac{k_B T}{2} \sum_i c_i \left(\ln\left(c_i^2 - \delta c^2 \right) - 2z_1 \ln X_i \right) -$$

$$- \frac{k_B T}{2} z_4 \left(\ln Z_0^p Z_0^v + c \ln \xi_v \xi_p \right) + \frac{k_B T}{2} \delta c \left(\sum_i \ln \frac{c_i + \delta c}{c_i - \delta c} - z_4 \ln \frac{\xi_p}{\xi_v} \right), \tag{13}$$

Where the coordination numbers $z_1 = 4$ and $z_4 = 8$ in the case of square lattice

$$W = \exp\left(-\frac{J_1}{k_B T} \right); \qquad \Omega = \exp\left(-\frac{J_3}{k_B T} \right); \tag{14}$$

$$\eta = -\frac{c_1 - c_0}{2c_0} + \sqrt{\left(\frac{c_1 - c_0}{2c_0} \right)^2 + \frac{c_1}{c_0} W}; \quad X_0 = \sqrt{c_0 + \frac{c_1}{\eta}}; \quad X_1 = \eta X_0; \tag{15}$$

$$\xi_{p(v)} = -\frac{c_1 - c_0 \pm 2\Omega\delta c}{2(c_0 \mp \delta c)} + \sqrt{\left(\frac{c_1 - c_0 \pm 2\Omega\delta c}{2(c_0 \mp \delta c)}\right)^2 + \frac{c_1 \pm \delta c}{c_0 \mp \delta c}\Omega} \; ; \tag{16}$$

$$Z_0^v Z_0^p = c_0^v + \frac{c_1^v}{\xi_v} = c_0^p + \frac{c_1^p}{\xi_p} . \tag{17}$$

All the thermodynamic characteristics can be investigated on the basis of equation (13) for the free energy. For example, the chemical potential μ, the thermodynamic factor χ_T and the correlation function $g_k(1;1)$ for two nearest neighbors ($k = 1$) and neighbors of kth order can be determine as [7]

$$\beta\mu = \left(\frac{\partial(\beta F)}{\partial c}\right)_T , \tag{18}$$

$$\chi_T = \frac{\partial(\beta\mu)}{\partial \ln c} , \tag{19}$$

$$g_k(1;1) = \frac{2}{z_k c^2}\left(\frac{\partial F}{\partial J_k}\right)_T . \tag{20}$$

4 The order parameter and phase diagram of the model

The most important structural feature, which describes the ordered state of the model is the order parameter. The comparisons of the calculation and simulation results for the order parameter are shown in Fig. 5 for the case $J^* = 3$.

As follows from Figure 5, the QChA reproduces the MC simulation results only qualitatively. Nevertheless, the introduced order parameter can be used to construct the phase diagram of the model, which is represented in Fig. 6.

In general, it can be noted that the constructed diagram is similar to the diagram for the lattice fluid with the attraction between the nearest neighbors and repulsion between the next-next-nearest neighbors [2]. Based on Figure 5, we should expect that the true phase diagram would be somewhat narrower than the results of the QChA.

It can also be noted that the critical temperature of the model in the framework of the QChA is overestimated by approximately 38% as compared to the MCS data $((J\beta_c)^{QchA} = 0.192)$.
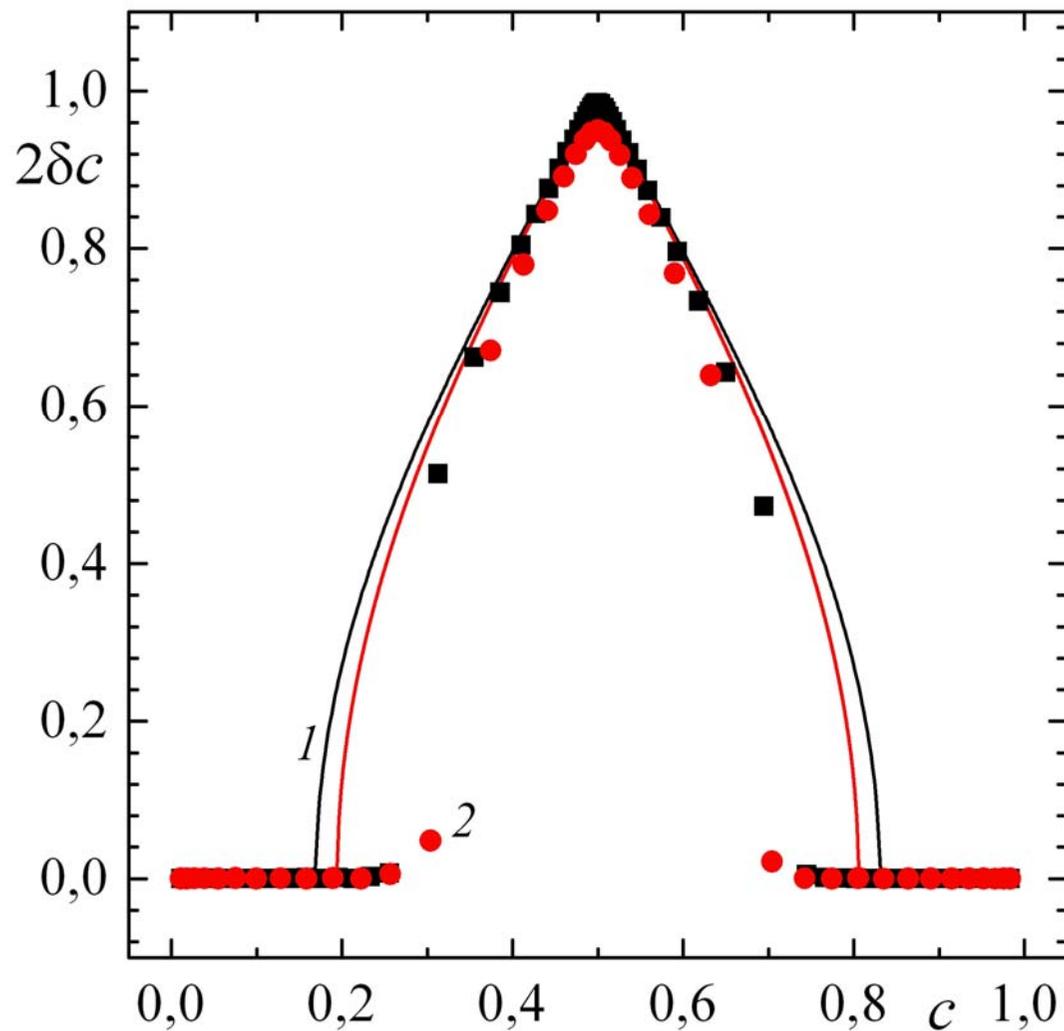
Figure 5. The order parameter versus concentration at $J^* = 3.0$, $\beta J = 0.5$ (*1*) and 0.4 (*2*). The solid lines represent the QChA results, the circles and squares are the MC simulation data
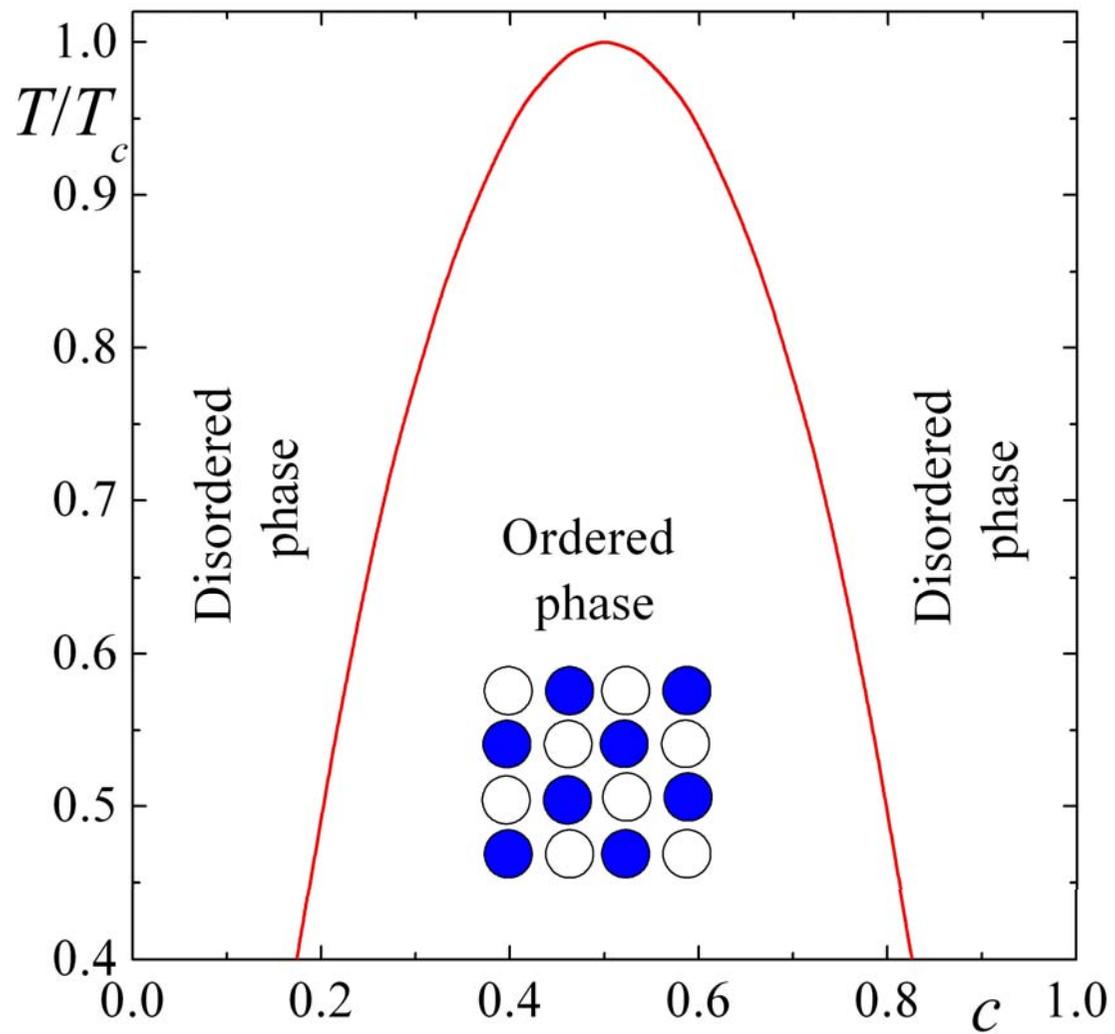
Figure 6. The order-disorder phase transition curve in the QChA at $J^* = 3$

5 The thermodynamic and structural features of the model

The chemical potential isotherms are shown in Fig. 7. The ordered phase exists at temperatures below critical ($\beta J = 0.50$; 0.40 and 0.30) where a steep increase of the chemical potential is observed.

The comparison of the QChA and MCS data is also shown in Fig. 7. From this comparison, it follows that the results of both methods are in a good quantitative agreement. In fact, differences in the chemical potential occur only in the region of the ordered phase in the system.

In accordance with expression (18), the increase of the chemical potential, which was noted above, leads to the sharp increase of the thermodynamic factor or, correspondingly, to the number of particles fluctuation decrease

$$\frac{\left\langle \left(n - \langle n \rangle \right)^2 \right\rangle}{\langle n \rangle} = \left(\chi_T \right)^{-1}.$$ (21)

This means that in the ordered state, the fluctuations are suppressed and the system becomes more rigid. Obviously, the minimum of fluctuations is achieved in the fully ordered state corresponding to the concentration of 0.5 on the square lattice. In turn, the thermodynamic factor in this conditions will be maximal.

In QChA, the chemical potential and the thermodynamic factor were calculated by numerical differentiating of the free energy expression (13). However, such a differentiation of the chemical potential extracted from MC simulations suffers from low precession. In this case, the thermodynamic factor can be calculated as the value inversely proportional to the mean square concentration fluctuations in accordance with Eq. (21).

It can also be noted that the parameter χ_T plays an important role in the description of diffusion processes in lattice fluids [8]. In particular, it establishes the relationship between the chemical (D_{ch}) and kinetic (D_J) diffusion coefficients

$$D_{\text{ch}} = \chi_T D_{\text{J}},$$ (22)

$$D_{\text{ch}} \nabla c = D_{\text{J}} c \nabla \beta \mu.$$ (23)
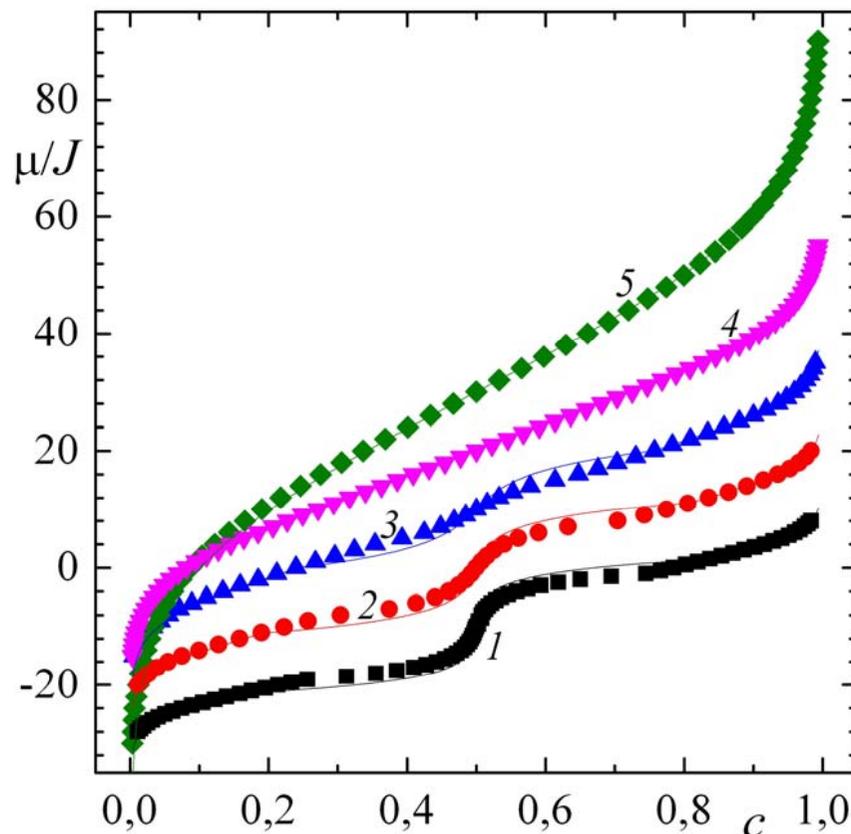
Figure 7. The chemical potential (in units of the nearest neighbor interaction energy J) versus concentration at $\beta J = 0.50$ (*1*); 0.40 (*2*); 0.30 (*3*); 0.20 (*4*) и 0.10 (*5*). The solid lines represent the QChA results, the symbols are the MC simulation data. Each group of curves is shifted down by 10 units along the μ axis with respect to the previous one for better visibility. The upshifted curve (*3*) is characterized by $\mu/J = 10$ at $c = 0.5$, and this point is the same for all the temperatures. Thus, the curves (1) and (2) are shifted down from their true position, while (4) and (5) are shifted up.
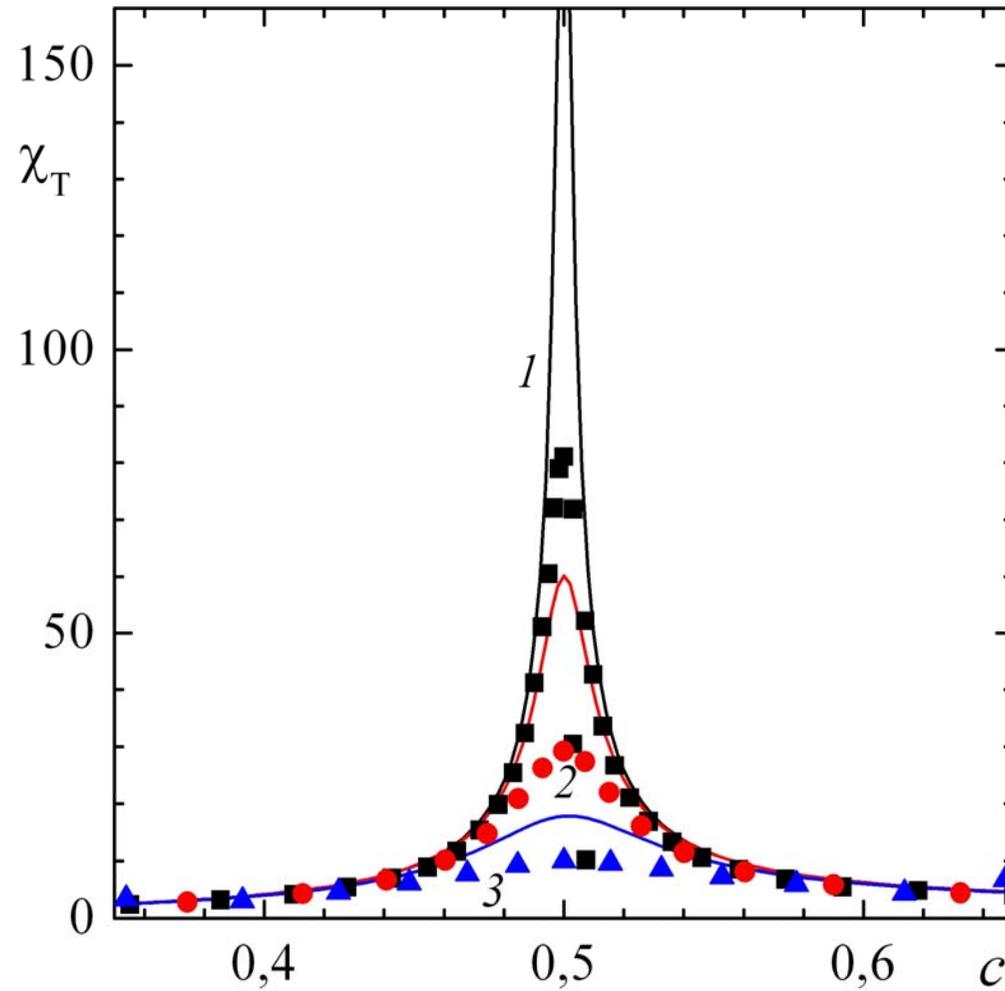
Figure 8. The thermodynamic factor versus concentration at $\beta J = 0.50$ (*1*, squares), 0.40 (*2*, circles) and 0.30 (*5*, triangles). The solid lines represent the QChA results, the symbols are the MC simulation data. The designation of the curves is the same as in Fig. 7.

The order parameter and the thermodynamic factor describe the global ordering of the system. In turn, the short range ordering can be described by the correlation function (20). Physically, the correlation function is the ratio of the probability of two nearest (or kth order) neighbor lattice sites to be occupied by particles to the same probability for the case of the Langmuir (non-interacting) lattice gases c^2.

The correlation functions for the nearest and fourth order neighbors are shown in Figs. 9 and 10, respectively.

The global ordering of the system also manifests itself at the local level, as for the lattice fluid with the interaction of the nearest and next-next-nearest neighbors. At temperatures below critical, the probability to find the two nearest neighbor sites and the two fourth order neighbor sites occupied by particles becomes very low. If the system is completely ordered, any lattice site occupied by a particle has neither the nearest nor the fourth-order neighbor as it is evident from the right panel of Fig. 1. Obviously, with the temperature increase, the distinction from the Langmuir lattice gas decreases.

In general, the results of QChA and MC simulation data satisfactorily correspond to each other in the disordered phase. At the same time, they differ significantly in the region of ordered phases due to problems associated with determining the order parameter and the critical temperature in the quasi-chemical approximation.

The most significant differences arise when considering correlations in the filling of the nearest lattice sites when noticeable qualitative differences between the results of the analytical approximation and the MC simulation data exist. The simulation results indicate the nonmonotonic dependence of the correlation functions on the concentration and the presence of the minimum of this function around the concentration 0.5. These features are not observed in the quasi-chemical approximation.
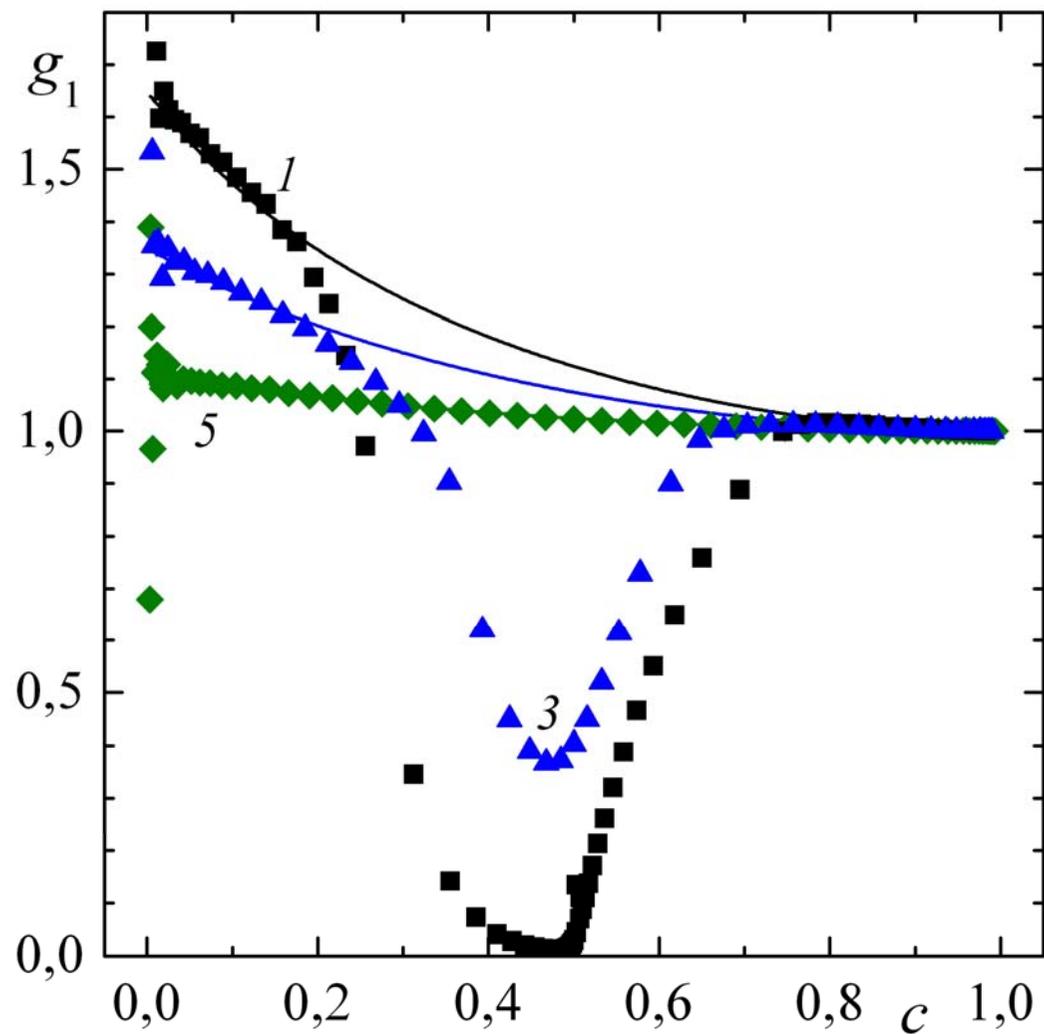
Figure 9. The correlation functions of the nearest neighbors versus concentration at $\beta J = 0.50$ (*1*, squares), 0.30 (*3*, triangulars) and 0.10 (*5*, diamonds). The solid lines represent the QChA results, the symbols are the MC simulation data.
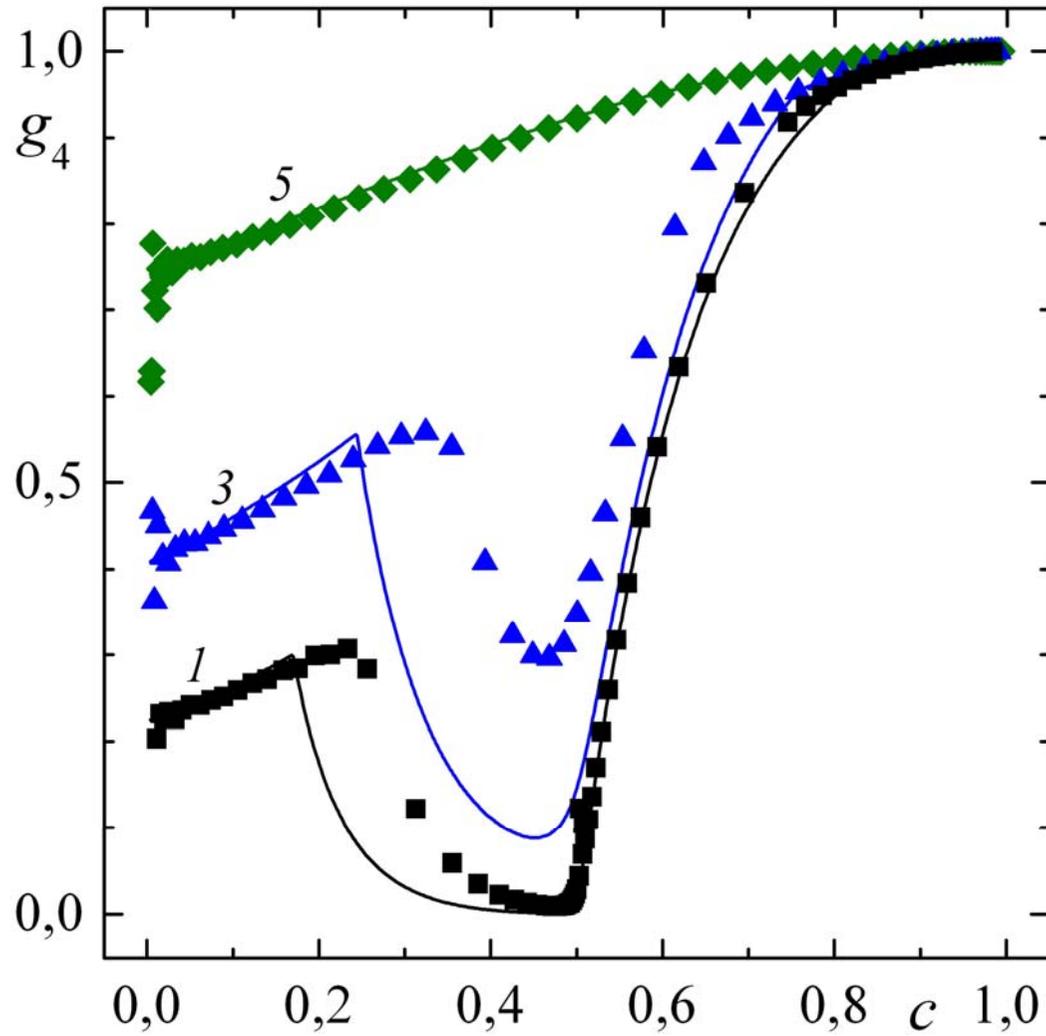
Figure 10. The correlation functions of the fourth order neighbors versus concentration at $\beta J = 0.50$ (*1*, square), 0.30 (*3*, triangular) and 0.10 (*5*, diamond). The solid lines represent the QChA results, the symbols are the MC simulation data.

Conclusion

The lattice system with attractive interaction between the nearest neighbors and repulsive interaction between the fourth order neighbors has been studied.

It is shown that the competing interactions lead to the order-disorder phase transitions. The structure of the ordered phase depends on the value of the parameter J^*, which is determined as the ratio of the intensities of repulsion and attraction interactions between particles. At $J^* < 1.5$, the ordered phase is the set of alternating double empty and double filled stripes. These stripes can be arranged vertically or horizontally. At $J^* > 1.5$, the vacant and filled lattice sites are staggered.

The separation of the initial lattice into a system of 16 sublattices was proposed to describe both types of the ordered phases. In the ordered phase, a half of these sublattices are predominantly vacant and the other half are predominantly filled. This gives the possibility to determine the order parameter of the model δc as the difference between the particle concentrations on the sublattices.

Subsequently, the order parameter is used as the indicator of the structural phase transitions. It was found that the dependence of the critical temperature $k_B T_c / J$ on the parameter J^* is linear both for $J^* < 1.5$ and for $J^* > 1.5$, but has a kink at $J^* \approx 1.5$.

The order parameter, chemical potential, thermodynamic factor and correlation functions are determined both in the QChA and in the Monte Carlo simulation. As before [2, 3] the order parameter of the system δc is determined in the QChA with significant errors. This leads to errors in determining the critical temperature of the system and to difficulties in studying the structural properties of the model in the framework of the QChA at low temperatures. At the same time, the thermodynamic properties of the system such as, for example, the chemical potential isotherms, are determined in this approximation with high accuracy.

Acknowledgments

References

1. Uebing C., Gomer R. A. Monte Carlo study of surface diffusion coefficients in the presence of adsorbate-adsorbate interactions // J. Chem. Phys. – 1991. – Vol. 95. – P. 7626–7652. https://doi.org/10.1063/1.461817.

2. Groda Ya. G., Vikhrenko V. S., di Caprio D. Equilibrium properties of the lattice system with SALR interaction potential on a square lattice: quasi-chemical approximation versus Monte Carlo simulation // Cond. Matt. Phys. – 2018. – Vol. 21, no. 4. – art. no. 43002 (10 p.). https://doi.org/10.5488/CMP.21.43002.

3. Groda Ya. G., Vikhrenko V. S., di Caprio D. Lattice fluid with attractive interaction between nearest neighbors and repulsive interaction between next-next-nearest neighbors on simple cubic lattice // Journal of the Belarusian State University. Physics. – 2019. – no. 2. – P. 84–95. https://doi.org/10.33581/2520-2243-2019-2-84-95 (in Russ.).

4. Binder K., Landau D. P. Phase diagrams and critical behavior in Ising square lattices with nearest- and next-nearest-neighbor interactions // Phys. Rev. B. – 1980. – Vol. 21. – P. 1941–1963. https://doi.org/10.1103/PhysRevB.21.1941.

5. Groda Ya. G., Argyrakis P., Bokun G. S., Vikhrenko V. S. SCDA for 3D lattice gases with repulsive interaction // Euro. Phys. Journ. B. – 2003. – Vol. 32. – P. 527–535. https://doi.org/10.1140/epjb/e2003-00118-3.

6. Groda Ya. G., Lasovsky R. N., Vikhrenko V. S. Equilibrium and diffusional properties of two-level lattice systems: quasichemical and diagram approximation versus Monte Carlo simula-tion results // Solid State Ionics. – 2005. – Vol. 176. – P. 1675–1680. https://doi.org/10.1016/j.ssi.2005.04.016.

7. Bokun G. S., Groda Ya. G., Belov V. V., Uebing C., Vikhrenko V. S. The self-consistent diagram approximation for lattice systems // Euro. Phys. Journ. B. – 2000. – Vol. 15. – P. 297–304. https://doi.org/10.1007/s100510051128.

8. Bokun G. S., Groda Ya. G., Uebing C., Vikhrenko V. S. Statistical-mechanical description of diffusion in interacting lattice gases // Physica A. – 2001. – Vol. 296. – P. 83–105. https://doi.org/10.1016/S0378-4371(01)00163-7.

9. Groda Ya. G., Grishina V. S., Ciach A., Vikhrenko V. S. Phase diagram of the lattice fluid with SRLA-potential on the plane triangular lattice // Journal of the Belarusian State University. Physics. – 2019. – no. 3. – P. 81–91. https://doi.org/10.33581/2520-2243-2019-3-81-91 (in Russ.).