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SCDA for 3D lattice gases with repulsive interaction

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Abstract. The selfconsistent diagram approximation (SCDA) is generalized for three-dimensional lattice gases with nearest neighbor repulsive interactions. The free energy is represented in a closed form through elementary functions. Thermodynamical (phase diagrams, chemical potential and mean square fluctuations), structural (order parameter, distribution functions) as well as diffusional characteristics are investigated. The calculation results are compared with the Monte Carlo simulation data to demonstrate high precision of the SCDA in reproducing the equilibrium lattice gas characteristics. It is shown that similarly to two-dimensional systems the specific statistical memory effects strongly influence the lattice gas diffusion in the ordered states.

PACS. 05.50.+q Lattice theory and statistics (Ising, Potts, etc.) – 05.60.-k Transport processes – 05.70.Ce Thermodynamic functions and equations of state

1 Introduction

Extensive applications of lattice models [1–7] for the description of a variety of physical systems and processes make it topical to improve statistical-mechanical methods of their investigation. The approaches developed earlier are characterized either insufficient precision (different mean field approximations [8,9]) or require tedious calculations (series expansions [4,10]) and cannot be used for most practical calculations. Although lattice models are described by a discrete vector of states and the Markovian master equation the strong interparticle interactions being accounted of lead to their complex properties and give rise to considerable difficulties well known in many body theories.

Properties of lattice systems crucially depend on the type of interparticle interactions. For example, attractive interactions lead to first order phase transitions while order – disorder phase transitions are ordinary observed for repulsive interactions. Therefore, many approaches appropriate for the former cannot be used for the later or at least must be considerably modified because the ordering in a lattice system lowers its symmetry and requires to divide the lattice into sublattices.

Recently [11] the selfconsistent diagram approximation (SCDA) was suggested and applied to lattice gases with attractive nearest neighbor interactions [11,12]. It was shown that SCDA well reproduces the thermodynamic (chemical potential *versus* concentration, its concentration derivative, phase transition curves) and structural (probabilities for a pair of lattice sites to be occupied by particles or vacancies) properties for two- (2D) as well as three-dimensional (3D) systems. Moreover, it was successfully used for describing the diffusional properties of lattice gases [12,13]. Here we generalize SCDA for nearest neighbor repulsive interactions on 3D low packed (simple cubic (SC) and body centered cubic (BCC)) lattices.

The paper is organized as follows. In the next section the necessary definitions are introduced and the free energy is represented as a diagram expansion in renormalized Mayer functions. Section 3 is devoted to evaluation of the mean potentials that renormalize the Mayer functions on the basis of the concept of minimal susceptibility. In Section 4 statistical mechanical calculations are compared with Monte Carlo simulation results. The last section concludes.

2 The free energy and the order parameter

For lattice gases with repulsive interparticle interactions at sufficiently low temperatures different ordered states can exist. The sublattice decomposition of the lattice is used for the analysis whether the system is in an ordered or disordered state [14]. We consider the simplest case when the lattice is represented by two sublattices (A and B). Lattice gases with repulsive nearest neighbor (NN) interactions on honeycomb, square, simple cubic and body centered cubic lattices are examples of such systems. The potential energy of the system of n particles on N lattice

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sites can be written as

$$U = \frac{J}{2} \sum_{i=1}^{N} \sum_{j=1}^{z} n_i^\alpha n_j^\beta, \tag{1}$$

where z is the coordination number of the lattice, $J > 0$ is the interaction energy of particles occupying NN sites. More distant interactions are not taken into account. $n_i^\alpha = 0$ or 1 is the occupation number of lattice site i, which belongs to sublattice $\alpha = A$ or B. In the canonical ensemble the occupation numbers obey the normalization conditions

$$n_A = \sum_{i=1}^{N/2} n_i^A, \qquad n_B = \sum_{j=1}^{N/2} n_j^B, \qquad n_A + n_B = n. \tag{2}$$

Concentrations of particles $c_\alpha = c_1^\alpha = 2n_\alpha/N$ and vacancies $c_0^\alpha = 1 - c_1^\alpha$ on the sublattices as well as the mean concentrations $c = c_1 = n/N$ and $c_0 = 1 - c$ over the lattice can be introduced. The order parameter

$$\zeta = (c_A - c_B)/2 \tag{3}$$

is equal to zero in a disordered state and characterizes the strength of the ordering of the ordered state.

The SCDA employs the reference system that in the case under consideration is characterized by mean potentials $\phi_j^\beta(n_i^\alpha)$ describing the interaction of a particle ($n_i^\alpha = 1$) or vacancy ($n_i^\alpha = 0$) on site i of α-sublattice with site j of β-sublattice. Its energy

$$U_{\mathrm{r}} = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{n_i^\alpha=0}^{1} \varphi_j^\beta(n_i^\alpha). \tag{4}$$

The interaction of a site with itself is equal to zero ($\varphi_j^\beta(n_j^\beta) = 0$). It is worth to note that although the nearest neighbor interactions are only taken into account the mean potentials can include more distant interactions. In fact, they reflect correlations between different sites of the system.

Equilibrium properties can be deduced from the partition function

$$Q = \mathrm{Sp}_{\{n_1, n_2, \ldots, n_N\}}[\exp(-\beta U)], \tag{5}$$

where $\mathrm{Sp}_{\{n_1, n_2, \ldots, n_N\}}$ designates summation over all possible combinations of the occupation numbers satisfying the normalization condition equation (2), $\beta = (k_{\mathrm{B}}T)^{-1}$ is inverse temperature, k_{B} the Boltzmann constant. The partition function can be rewritten [11] as

$$Q = Q_{\mathrm{r}} \left\langle \prod_{i=1}^{N} \prod_{j=i+1}^{N} (1 + f_{ij}^{\alpha\beta}) \right\rangle_{\mathrm{r}}, \tag{6}$$

where $\langle \ldots \rangle_{\mathrm{r}}$ means equilibrium averaging over states of the reference system, Q_{r} is the partition function of the latter and renormalized Mayer functions

$$\begin{aligned} f_{ij}^{\alpha\beta} &= f(n_i^\alpha, n_j^\beta) \\ &= \exp\left\{ -\beta \left[\Phi_{ij} n_i^\alpha n_j^\beta - \varphi_j^\beta(n_i^\alpha) - \varphi_i^\alpha(n_j^\beta) \right] \right\} - 1 \end{aligned} \tag{7}$$

are introduced. For nearest neighbor sites i and j the interaction potential $\Phi_{ij} = J$. For more distant neighbors $\Phi_{ij} = 0$.

Due to one-particle character of the reference system energy [Eq. (4)] its partition function is factored as follows

$$\begin{aligned} Q_{\mathrm{r}} = &\left[\prod_{l=0}^{1} \left(Q_l^A / (c_l - (-1)^l \zeta) \right)^{c_l - (-1)^l \zeta} \right]^{N/2} \\ &\times \left[\prod_{l=0}^{1} \left(Q_l^B / (c_l + (-1)^l \zeta) \right)^{c_l + (-1)^l \zeta} \right]^{N/2}, \end{aligned} \tag{8}$$

where

$$Q_{n_i^\alpha} = \prod_{j=1}^{N} X_j^\beta(n_i^\alpha), \qquad X_j^\beta(n_i^\alpha) = \exp\left[-\beta \varphi_j^\beta(n_i^\alpha) \right]. \tag{9}$$

According to equation (6) the free energy per lattice site is represented by two terms

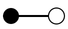
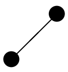
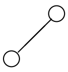
$$F = -(k_{\mathrm{B}}T/N) \ln Q = F_{\mathrm{r}} + F_{\mathrm{d}}, \tag{10}$$

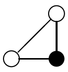
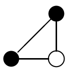
where F_{r} and F_{d} are the free energy of the reference system and the diagram part of the free energy, respectively

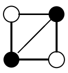
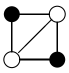
$$F_{\mathrm{r}} = -(k_{\mathrm{B}}T/N) \ln Q_{\mathrm{r}}, \tag{11}$$

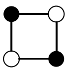
$$F_{\mathrm{d}} = -(k_{\mathrm{B}}T/N) \ln \left\langle \prod_{i=1}^{N} \prod_{j=i+1}^{N} \left(1 + f_{ij}^{\alpha\beta} \right) \right\rangle_{\mathrm{r}}. \tag{12}$$

The latter can be written as a diagram expansion [11] in the renormalized Mayer functions

$-\beta N F_{\mathrm{d}} = \frac{z_1}{2}$  $+ \frac{z_2}{4}$  $+ \frac{z_2}{4}$ 

$+ \frac{z_1}{4}(z_1 - 2)$  $+ \frac{z_1}{4}(z_1 - 2)$ 

$+ \frac{z_1(z_1 - 2)}{8}$  $+ \frac{z_1(z_1 - 2)}{8}$ 

$+ \frac{z_1(z_1 - 2)}{8}$  $+ \ldots,$ (13)

where the edges correspond to the renormalized Mayer functions, open and filled circles designate sites of sublattices A and B, respectively. The diagonal edges connect next nearest neighbor (NNN) sites.

The free energy can be considered as a function of the sublattice concentrations. However, it is advisable to consider it as a function of the lattice concentration c and the order parameter ζ. The latter can be determined from the extremity condition

$$\frac{\partial F}{\partial \zeta} = 0, \tag{14}$$

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

$$\mu_A = \frac{\partial F}{\partial c_1^A}, \qquad \mu_B = \frac{\partial F}{\partial c_1^B}, \qquad \mu_A = \mu_B = \mu = \frac{\partial F}{\partial c}\cdot \tag{15}$$

If the assumption of structural similarity of the original and reference systems (*i.e.*, their order parameters are equal) is accepted the extremity condition leads to the equation for the order parameter

$$\zeta^2 - \frac{\pi_A + \pi_B}{\pi_A - \pi_B}\zeta + c(1-c) = 0, \tag{16}$$

where

$$\pi_\alpha = \prod_{k=1}^{\infty} \left(\eta_k^\alpha\right)^{z_k}, \qquad \eta_k^\alpha = X_k^\alpha(1)/X_k^\alpha(0),$$
$$X_k^\alpha(m) = X_k(n_i^\alpha = m) \tag{17}$$

and it is taken into account that the mean potentials are identical for all the pairs of lattice sites that are neighbors of the same order k, z_k is the coordination number of kth coordination sphere. Thus, to calculate the free energy and the order parameter we need to calculate the mean potentials.

3 The mean potentials evaluation

Equation (6) is an identity and the partition function does not depend on the mean potentials. However, the mean potentials renormalize interparticle interactions and if properly found reduce values of the renormalized Mayer functions leading to better convergence of the free energy expansion (*i.e.* its diagram contribution) in these functions. To this end the self-consistency condition [11] can be formulated on the basis of the minimal susceptibility principle. One can consider a few first terms in the expansion equation (12) and find mean potentials requiring the independence of the truncated free energy expression on the mean potentials. It means that the partial derivatives of the free energy over the mean potentials are equal to zero. This approximation is justified in Section 4 by comparing the calculation and Monte-Carlo simulation results for different thermodynamical and structural characteristics.

For the NN mean potentials ($k = 1$) the lowest first order terms in the renormalized Mayer functions (that correspond to the first line in Eq. (13)) are kept in equation (12). It leads to the expressions

$$X_1^\alpha(n_i^\alpha) = \sum_{n_j^\beta=0}^{1} \frac{\exp\left(-\beta J n_i^\alpha n_j^\beta\right) c_j^\beta}{X_1^\beta(n_j^\beta)}, \tag{18}$$

where α and β belong to different sublattices. The solution of equation (18) can be written in a closed form

$$X_1^\alpha(n_i^\alpha) X_1^\beta(n_j^\beta) = (\eta_1^\alpha)^{n_i^\alpha} (\eta_1^\beta)^{n_j^\beta} (c_0^\alpha + c_1^\alpha/\eta_1^\alpha), \tag{19}$$

$$\eta_1^\alpha = -\frac{c_1^\beta - c_0^\alpha - W(c_0^\alpha - c_0^\beta)}{2c_0^\alpha} + \sqrt{\left(\frac{c_1^\beta - c_0^\alpha - W(c_0^\alpha - c_0^\beta)}{2c_0^\alpha}\right)^2 + \frac{c_1^\alpha}{c_0^\alpha}W}, \tag{20}$$

$$W = \exp(-\beta J). \tag{21}$$

For NN sites the products $X_1^\alpha(m)X_1^\beta(l)$ are only necessary to calculate the free energy. All these products can be calculated making use of equations (19, 20).

Equations (18–21) are equivalent to the quasichemical approximation. If more distant interactions are taken into account the mean potentials for arbitrary neighbors can be calculated by the same equations where subscripts 1 at X and η are replaced by the coordination sphere number k and the corresponding interaction constants are used. It leads to the generalized quasichemical approximation. When concentrations on both sublattices are equal these equations reduce to the form considered earlier [11,12] for attractive interactions where no ordered states exist.

The irreducible diagrams linear in the NNN renormalized Mayer functions and containing up to four vertices (the second, third and forth lines in Eq. (13)) are considered to calculate the mean potentials of the second neighbors ($k = 2$). In this case both lattice sites belong to the same sublattice (A or B). The calculations are rather tedious although straightforward, and they lead to the following equations for the mean potentials

$$X_2^\alpha(m) = (\eta_2^\alpha)^m \sqrt{c_0^\alpha W_{00}^{\alpha\alpha} + c_1^\alpha W_{01}^{\alpha\alpha}/\eta_2^\alpha}, \tag{22}$$

$$\eta_2^\alpha = -\frac{c_1^\alpha - c_0^\alpha}{2c_0^\alpha}\frac{W_{01}^{\alpha\alpha}}{W_{00}^{\alpha\alpha}} + \sqrt{\left(\frac{c_1^\alpha - c_0^\alpha}{2c_0^\alpha}\frac{W_{01}^{\alpha\alpha}}{W_{00}^{\alpha\alpha}}\right)^2 + \frac{c_1^\alpha}{c_0^\alpha}\frac{W_{11}^{\alpha\alpha}}{W_{00}^{\alpha\alpha}}}, \tag{23}$$

$$W_{lm}^{\alpha\alpha} = \left(\lambda B_{lm}^{\alpha\alpha} + 1\right)^2, \tag{24}$$

$$B_{lm}^{\alpha\alpha} = \sum_{k=0}^{1} \frac{W_{lk} W_{km} c_k^\beta}{X_1^\alpha(l) X_1^\alpha(m) \left(X_1^\beta(k)\right)^2} - 1, \tag{25}$$

$$W_{km} = 1 + (W-1)\delta_{1k}\delta_{1m}. \tag{26}$$

δ_{km} is the Kronecker's δ-symbol. In equation (24) λ is a parameter that indirectly takes into account contributions of more complex diagrams. This is the consequence of the assumption that the square diagram reasonably represents statistical correlations in the system under consideration because $(B_{lm}^{\alpha\alpha})^2$ corresponds to the square diagram. In contrast to the system with attractive interactions [11,12] the rescaling of the square diagram contribution should account of the presence of long range order and is carried out on the level of the reference system. In view of equation (22) it leads to an additional contribution to the NN mean potential $\Delta\varphi = -4k_\mathrm{B}T\ln\lambda$ when the NNN mean potentials are calculated.

It is worth to note that W in equation (21) is determined by direct interaction between NNs while $W_{lm}^{\alpha\alpha}$ in equation (24) is defined by quantities $B_{lm}^{\alpha\alpha}$ (Eq. (25)) that reflect indirect correlations between states of NNN sites through common nearest neighbors. Thus, the NNN mean potentials are not equal to zero although the direct interaction between NNNs is absent.

The NNN mean potentials defined by equations (22–26) allow one to sum the diagrams shown in equation (13) and to represent the free energy as

$$\frac{F}{k_\mathrm{B}T} = \frac{1}{2}\left(\sum_{\alpha=A}^{B}\sum_{m=0}^{1} c_m^\alpha \ln c_m^\alpha - \sum_{k=1}^{2} z_k \ln[X_k^\alpha(0)X_k^\beta(0)]\right) - \sum_{\alpha=A}^{B} c_1^\alpha \ln\pi_\alpha + \Lambda\lambda^2 \sum_{l,m=0}^{1}\sum_{\alpha=A}^{B}(B_{lm}^{\alpha\alpha})^2. \quad (27)$$

The last term here is the square diagram contribution in agreement with the case of attractive interactions [11,12]. The coefficient $\Lambda = 3$ or 6 for simple or body-centered cubic lattices, respectively. Accordingly, the coefficient $\lambda = 1.24$ or 1.47 is evaluated from the requirement that the critical temperature is equal to its best estimate.

4 Calculation and simulation results and discussion

4.1 Equilibrium properties

Equilibrium Monte Carlo (MC) simulations were carried out in the grand canonical ensemble on simple and body centered cubic lattices. A lattice site i is chosen at random. The number z_i of particles on the NN sites of site i, the energy difference $\Delta U = (-1)^{n_i}(Jz_i - \mu)$ and the probability $P = \exp(-\beta\Delta U)$ are calculated. If site i is field ($n_i = 1$) or vacant ($n_i = 0$) a trail is made to remove or insert the particle. The trail is accepted when $\Delta U < 0$. Otherwise a random number $0 \leq P_\mathrm{r} \leq 1$ is generated and the trail is accepted if $P \geq P_\mathrm{r}$. One Monte Carlo step (MCS) consists of n trails.

At a given values of adimensional temperature $k_\mathrm{B}T/J$ and the chemical potential μ/J first 10^4 MCSs are used to equilibrate the system. Then the number, square number of particles and number of NN pairs of particles and vacancies after each MCS are recorded and averaged over 10^5 MCSs to provide with mean concentration, mean square fluctuations, and the distribution functions of particles and vacancies. In ordered states fluctuations are very week and to preserve precision of simulations the square deviation of number of particles from an integer number that is close to the mean number of particles is used. The former is calculated during 2×10^4 MCSs just after the equilibration period while the latter is determined by averaging over full run. This square deviation is an integer and does not suffer from the loss of precision when the difference of close values is taken. In this way isotherms of different characteristics are produced.

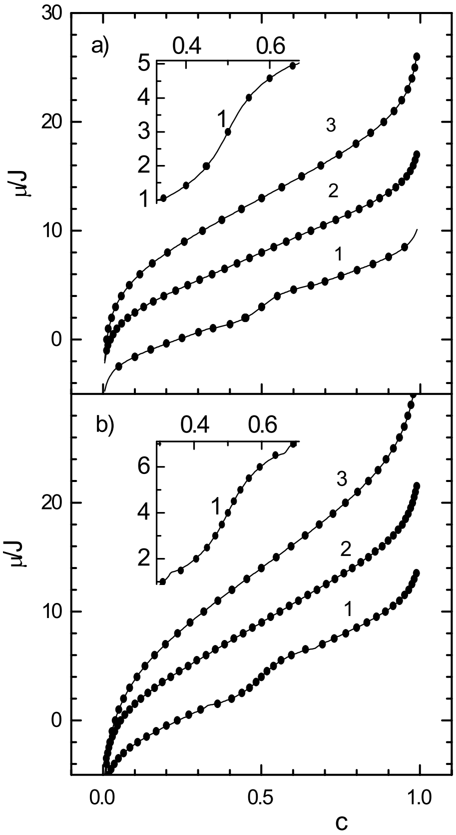


Fig. 1. Chemical potential *versus* concentration at several reduced temperatures for a lattice gas on SC (a) and BCC (b) lattices. MC simulation (full circles) and SCDA (solid lines) results are shown for T/T_c=0.8 (curves 1), 1.2 (2) and 2.0 (3). The curves are shifted by 5 from each other in vertical direction. The unshifted curves are characterized by $\mu/J = 3$ (SC lattice) or 4 (BCC lattice) at $c = 0.5$ for all temperatures. The inserts demonstrate the chemical potential behavior in the region of the ordered states in a bigger scale.

The chemical potential isotherms are shown in Figure 1. It is convenient to represent temperature $t = T/T_\mathrm{c}$ in units of the critical temperature T_c, which is equal to $1.128J/k_\mathrm{B}$ and $1.588J/k_\mathrm{B}$ for simple and body centered cubic lattices, respectively. At temperature below critical ($t = 0.8$) in the region of the ordered phase a steep increase of the chemical potential with concentration is observed. It manifests that the concentration fluctuations are week in this region

$$\left\langle (n-\bar{n})^2\right\rangle/\bar{n} = (\chi_T)^{-1}, \qquad \chi_T = c\partial(\beta\mu)/\partial c. \quad (28)$$

χ_T is a thermodynamic factor, which plays an important role in description of diffusion processes.

There are no visible peculiarities in the behavior of the chemical potential in the vicinity of the order-disorder phase transition. However, the concentration derivative of the chemical potential (Fig. 2) has a brake indicating the phase transition. Concentration fluctuations grow immediately just after the transition from the disordered to

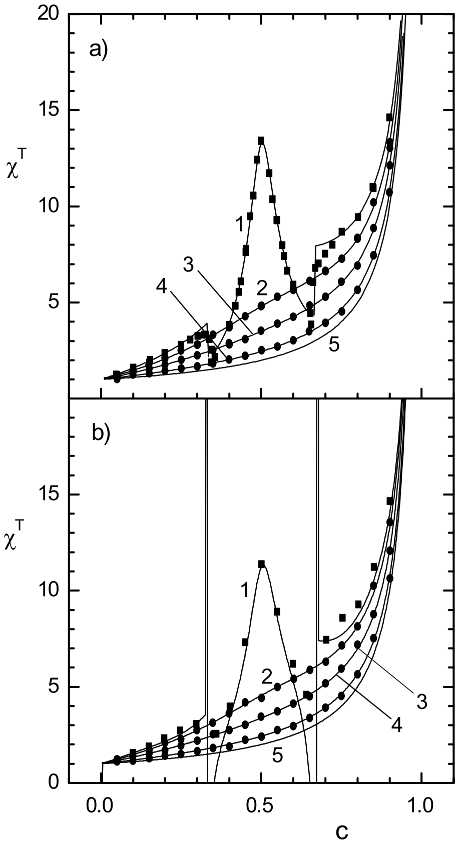


Fig. 2. Thermodynamic factor *versus* concentration at T/T_c=0.8 (curves 1), 1.2 (2), 2.0 (3), 6.0 (4) and for a non-interacting (5) lattice gas on SC (a) and BCC (b) lattices. MC simulation and SCDA results are shown by full circles (full squares at $T/T_c = 0.8$) and solid lines, respectively.

ordered state and then decrease systematically until concentration 0.5 is reached when ideal ordering is possible.

The chemical potential and the thermodynamic factor were calculated by differentiating the free energy equation (27). However, such a differentiation of the chemical potential extracted from MC simulations may not be used because of computer time and precision limitations. Thus, concentration mean square deviations were directly obtained from MC simulations and then the thermodynamic factor was calculated according to equation (28). The calculation and simulation results are in a good agreement except for the close vicinity of the second order phase transition curve. MC simulations were performed for the simulation box of 32^3 and 16^3 lattice sites. The results were almost indistinguishable from each other indicating that there are no size effects beginning from the box of 16^3 lattice sites. However, the results become different in the vicinity of the second order phase transitions. Again, the thermodynamic factor calculated as the concentration derivative of the chemical potential, on one hand, and as the inverse value of concentration fluctuations, on the other hand, coincide with each other for most states but the nearest vicinity of the second order phase transition curve where better statistics as well as bigger simulation boxes are required to get higher accuracy of the simulation results.

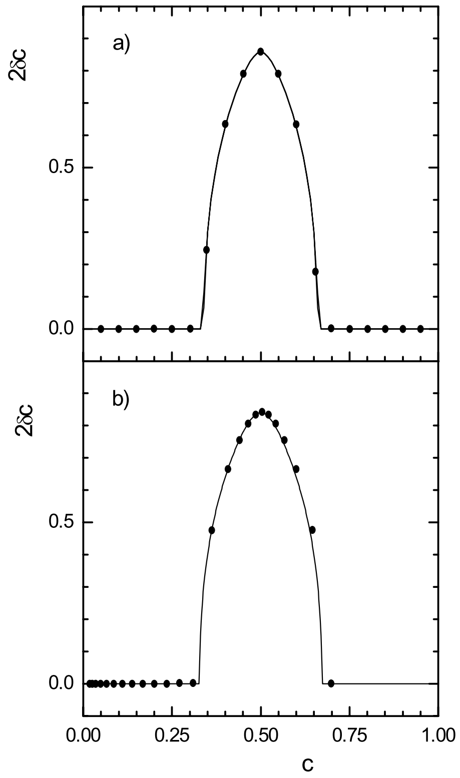


Fig. 3. Order parameter *versus* concentration at T/T_c=0.8 for SC (a) and BCC (b) lattices. MC simulation and SCDA results are shown by full circles and solid lines, respectively.

In the systems under consideration $\chi_T > 1$ that differs from systems with attractive interactions [11,12] where at low and intermediate concentrations the thermodynamic factor is less than one up to twice critical temperature. It means that the concentration fluctuations in systems with attractive interactions are much stronger than for repulsive interactions. However, in the phase transition range the density fluctuations can be quite strong. Bigger MC simulation boxes are required for their investigation (see, *e.g.* Ref. [15]).

The most important structural characteristics of an ordered state is the order parameter. The comparison of calculated (Eq. (16)) and simulated results are shown in Figure 3. The order parameter alongside with the concentration fluctuations are used for detecting the phase transition curve by Monte Carlo simulation. Both methods lead to identical results that are shown in Figure 4.

The short range ordering is characterized by distribution functions or probabilities $F(l,m)$ for NN lattice sites to be occupied by particles ($l,m = 1$) or vacancies ($l,m = 0$). They are calculated by differentiating the free energy over the interaction parameter

$$F(1,1) = \frac{2}{z_1}\left(\frac{\partial F}{\partial J}\right)_{c,T}, \qquad (29)$$

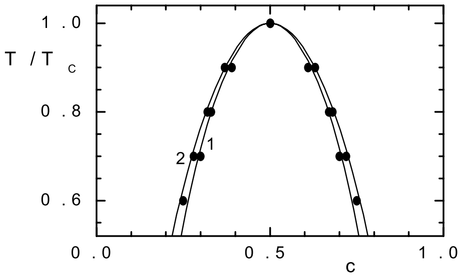


Fig. 4. The order-disorder phase transition curves for SC (curve 1) and BCC (2) lattices.

$$F(0,1) = c - F(1,1), \qquad F(0,0) = 1 - 2c + F(1,1). \tag{30}$$

However, the correlation functions

$$g(m,l) = F(m,l)/c_m c_l, \tag{31}$$

are more informative objects because they manifest the deviation of the short range correlations in interacting systems from the case of noninteracting (Langmuir) lattice gases. For the latter $g(m,l) = 1$ for all possible values of $m, l = 0$ or 1. The symmetry conditions are that $g(0,0)$ at concentration c is equal to $g(1,1)$ at concentration $1 - c$ and $g(1,0)$ has the same values at c and $1 - c$.

The correlation functions are shown in Figure 5. The long range ordering reflects itself in a short range structure as well. At temperatures below critical (see curves 1 and 2 for $T/T_\mathrm{c} = 0.8$) the probability to find two NN sites occupied by particles becomes very low while for a particle and a vacancy it is high in ordered states due to difference in the mean particle concentrations on the sublattices. Of course, the higher the temperature the less pronounced difference from the Langmuir gas behavior is observed.

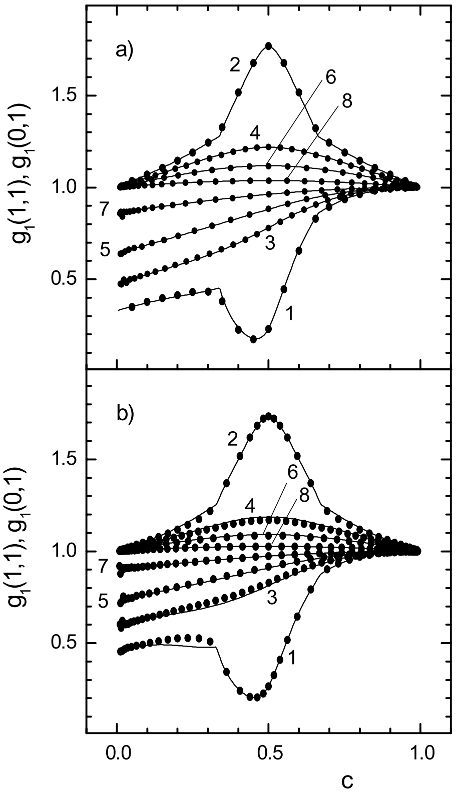


Fig. 5. Correlation functions *versus* concentration for SC (a) and BCC (b) lattices. The particle-particle $g(1,1) > 1$ and vacancy-particle $g(0,1) < 1$ correlation functions are shown for T/T_c=0.8 (curves 1 and 2), 1.2 (3 and 4), 2.0 (5 and 6), and 6.0 (7 and 8).

For simple and quite accurate calculations of the equilibrium characteristics the diagram approximation [16] can be used. It represents the chemical potential in an analytical form with the accuracy that is only slightly less precise as compared to SCDA.

4.2 Diffusion characteristics

The lattice gas diffusion has been the subject of considerable attention during last decades. Although extensive Monte-Carlo simulations were performed [14,17,18] the deep understanding of the phenomenon can only be attained on the basis of statistical mechanics. Intuitively, the quasiequilibrium distribution function in presence of the concentration gradient should give a ground basis for evaluating the diffusion coefficients. This approach was used in references [19–21] and the diffusion coefficient was represented in terms of the average hopping rate of a particle [20,21]. In this line simple expressions for the lattice gas diffusion coefficients were derived [22].

However, more careful statistical-mechanical considerations based on the Markovian theory of the lattice gas dynamics [23] and Zwanzig-Mori projection operator techniques applied to the dynamical structure factor [24,25] or concentration fluctuations [13,26] have shown that the diffusion coefficient expression contains the instantaneous contribution of the average hopping rate as well as the term that represents specific statistical memory effects. The latter are frequently associated with the correlation between successive jumps of particles that strongly influence the tracer diffusion coefficient even in the case of noninteracting lattice gases [27,28]. The contribution of the correlation between jumps to the chemical (or collective) diffusion coefficient was already anticipated by Reed and Ehrlich [20]. The direct Monte-Carlo simulations for a model of oxygen adsorption layer on a wolfram surface [29] and for an interacting lattice gas on a square lattice [13,26] have demonstrated that the memory effects are important in the ordered states, which appear as a result of the second order phase transition at repulsive interparticle interactions. These memory effects were included [30] by considering the dynamics of defects of the ordered states [14] (vacancies in the filled sublattice or particles in the empty one) that allow one to take into account correlations between the particles jumps. Below we analyze the situation for 3D lattices.

Diffusion coefficients are simulated for the model of traps [31] on a SC lattice according to the method described in references [17,18]. $n = cN$ particles are distributed over N lattice sites at random. Then, a site i is randomly selected. If filled, a NN destination site j is chosen at random and, if j is vacant, a jump may occur with probability

$$P_{\text{jump}} = \exp[\beta(\varepsilon_i - 5J)], \qquad \varepsilon_i = J s_i, \tag{32}$$

otherwise no jump occurs. Here ε_i is the interaction energy of a particle on site i with its s_i nearest neighbors. The multiplier $\exp(-5\beta J)$ ensures the probability P_{jump} to be less than one. This rescales the time intervals that is taken back into account when the diffusion coefficients are evaluated by equation (33). One MCS represents the consideration of n filled lattice sites. Before starting the diffusion runs the equilibration of the system is performed for 2000 MCS. The diffusion runs typically go up to 10^5 MCS. The lattice size was M=30. Simulations for smaller ($M = 10, 20$) and larger lattices (up to $M = 50$) were used exemplarily and it was shown that size effects are negligible for $M = 30$ and larger, except, perhaps in the vicinity of second order phase transitions.

The jump diffusion coefficient is calculated by the Green-Kubo expression [1,3]

$$D_{\text{JGK}} = D_0 \lim_{\tau\to\infty} \frac{\exp(5\beta J)}{2\tau n d} \left\langle \left(\sum_{i=1}^{n} \Delta\mathbf{r}_i \right)^2 \right\rangle,$$
$$D_0 = (z_1/2d) w_0 a^2, \tag{33}$$

where $\Delta\mathbf{r}_i$ stands for the displacement of the ith particle from its initial (at $\tau = 0$) position and τ is the number of MCSs. D_0 is the diffusion coefficient at zero concentration, w_0 is the frequency of particle jumps in the low concentration limit, a is the nearest neighbor distance, $d = 3$ the space dimensionality.

Unlike Hamiltonian systems, where transport coefficients are represented by time correlation functions of the corresponding fluxes, lattice gas dynamics is described by irreversible master equation and static correlation functions contribute significantly to lattice gas diffusion coefficients [12,13,25].

When static correlations are only taken into account (through the quasiequilibrium distribution function) in the model of traps the chemical diffusion coefficient D_{ch} can be represented as [12,13,22]

$$D_{\text{ch}} = \chi_T D_{\text{J}}, \tag{34}$$

$$D_{\text{J}} = D_0 \exp(\beta\mu)(F(0,0)/c), \tag{35}$$

where D_{J} is the jump diffusion coefficient. The latter being multiplied by the chemical potential gradient is equal to the particle flux density. Of course, equation (34) is an exact representation for the chemical diffusion coefficient if D_{J} is considered as Onsager transport coefficient [32] that includes memory contribution.

Equation (35) is an average jump rate approximation that takes into account spatial correlations exactly. It can be given a form

$$D_{\text{J}} = (z_1/2d) a^2 w(c) F(1,0)/c, \tag{36}$$

$$w(c) = \exp(\beta\tilde{\mu}) g(0,0)/g(0,1), \tag{37}$$

where $\tilde{\mu}$ is the chemical potential excess of the noninteracting gas value, $w(c)$ is the concentration dependent average rate of hopping attempts and $F(1,0)/c$ is the availability factor, *i.e.* the probability for a particle to have an empty nearest neighbor destination site. In accordance with the last expression the chemical potential excess represents the density and temperature dependent contribution of interparticle interactions to the average activation energy of particle jumps. However, the additional contribution to $w(c)$ comes from the short range correlation functions that reflect peculiarities of a many-body interacting system. It is evident from Figure 5 that the latter contribution becomes very important in the ordered states where the correlation functions ratio entering equation (37) attains rather low values. For noninteracting lattice gas all the correlation functions are equal to one.

Equations (34) through (37) are derived within the linear response approximation and contain equilibrium characteristics (the chemical potential and distribution functions). They can be applied for describing the noneqilibrium diffusional processes at small gradients of the chemical potential or concentration. It is difficult to establish the limits of the applicability of these equations by analytical means and experimental or computer simulation results have to be invoked. At least, the first Fick's law must be valid with a reasonable accuracy. Otherwise, the chemical diffusion coefficient as a quantity that is independent on concentration gradient cannot be used for characterizing the process of particles migration. For describing strongly nonequilibrium states it is necessary to average over the corresponding nonequilibrium distribution and equations (35) can be used with nonequilibrium correlation functions and chemical potential as a first approximation.

There exists a variety of experimental methods for determining the diffusion coefficients in solid solutions, solid electrolytes and intercalation compounds [3,33–35]. Electrochemical methods [5,35,36] are especially powerful because they provide with information about equilibrium as well as nonequilibrium characteristics, *e.g.* jump and chemical diffusion coefficients can be separately measured. Lattice gas models are used for clarifying the transport mechanisms and evaluating the microscopic interaction parameters [5,36–39]. The mean field approximation for the chemical diffusion coefficient is frequently considered [35,36] when in equation (34) the jump diffusion coefficient is put equal to its noninteracting lattice gas value $D_0(1-c)$ and the thermodynamic factor takes into account interactions in the simplest form $\chi_T = 1 + qc(1-c)$, q being the interaction constant. Although this approximation provides with very simple expressions for the diffusion coefficients it can at most give a qualitative description of the phenomenon [39].

For lattice gases with attractive interparticle interactions the static contribution represents well the diffusion coefficients at arbitrary values of thermodynamical variables [12,13]. On the other hand, it is shown above that SCDA represents equilibrium lattice gas characteristics for repulsive interactions with a high precision. Thus, it is

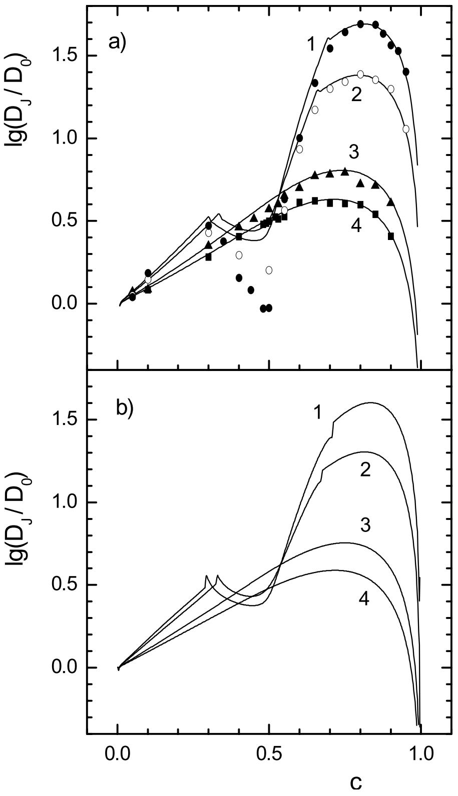


Fig. 6. Jump diffusion coefficient for SC (a) and BCC (b) lattices. Lines represent SCDA results at T/T_c=0.7 (curves 1), 0.8 (2), 1.11 (3), and 1.27 (4). NC simulation results are shown by full circles (T/T_c=0.7), open circles (0.8), triangles (1.11), and squares (1.27). No simulations were done for a BCC lattice.

possible to test whether in 3D lattice gases with repulsive interactions memory effects are important.

Figure 6a demonstrates that equation (35) represents well the jump diffusion coefficient for a SC lattice everywhere outside the region of the ordered states where memory effects are important. Identical concentration dependence of the diffusion coefficient for lattice gases on SC and BCC lattices is evident from comparison of Figures 6a and b. The diffusion coefficients isotherms for these two lattices differ insignificantly when they are calculated at the same reduced temperatures.

In the ordered states the decrease of the hopping rate due to spatial correlations is only a part of the jump diffusion coefficient decrease and not only the concentration dynamics but also the evolution of the order parameter has to be considered for proper evaluation of the diffusion coefficient. The corresponding calculations that involve dynamics of the defect structures mentioned above for a simple cubic lattice were performed in reference [40]. The calculation results describe well the decrease of the jump diffusion coefficient in the ordered phase as compared to its value calculated in the quasiequilibrium approximation.

The chemical diffusion coefficient is calculated as the product of the jump diffusion coefficient and the thermodynamic factor (see Eq. (34)).

5 Conclusion

The free energy diagram expansion in terms of the renormalized Mayer functions for a lattice gas with long range ordering is considered. The mean potentials renormalizing the interparticle interaction potentials are selfconsistently determined on the basis of the minimal susceptibility principle. In the lowest (generalized quasichemical) approximation they make the two-vertices diagrams as well as the diagrams that contain a vertex with the only outgoing edge equal to zero. Thus, the generalized quasichemical approximation is applicable for interparticle interactions of an arbitrary range.

In the SCDA the mean potentials allow one to sum the diagrams containing up to four vertices and represent them in terms of the lowest order irreducible square diagram. In the assumption that the latter reasonably represents correlation properties of the lattice gas the equilibrium characteristics (the free energy, the chemical potential, the distribution functions, the order parameter, the concentration mean square fluctuations, the phase transition curves) are expressed through a system of algebraic equations that can be easily solved on a personal computer. In contrast to the lattice gas with attractive NN interactions the corrections for the square diagram contribution have to be introduced on the level of the reference system, which is described by the mean potentials.

Monte Carlo simulations were performed to justify the assumptions used. It is shown that the equilibrium properties calculated on the basis of the SCDA coincide within a few per cent with the MC simulation results for all thermodynamic states but the nearest vicinity of the second order phase transition curves. All the quantities investigated behaves similarly for SC and BCC lattices when the reduced temperature scales are used.

The lattice gas diffusion coefficient is evaluated in the assumption that the specific statistical memory effects can be neglected while the spatial correlations are exactly accounted for. The expression for the jump diffusion coefficient is represented by equilibrium quantities (the chemical potential and the probability for two NN sites to be vacant) and the diffusion coefficient in the low density limit. By comparing with MC simulation results it is shown that similarly to 2D lattice gases the memory effects are important in the ordered states.

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