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The self-consistent diagram approximation for lattice systems

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Abstract. We apply the self-consistent diagram approximation to calculate equilibrium properties of lattice systems. The free energy of the system is represented by a diagram expansion in Mayer-like functions with averaging over states of a reference system. The latter is defined by one-particle mean potentials, which are calculated using the variational condition formulated. As an example, numerical computations for a two-dimensional lattice gas on a square lattice with attractive interaction between nearest neighbours were carried out. The critical temperature, the phase coexistence curve, the chemical potential and particle and vacancy distribution functions coincide within a few per cent with exact or with Monte Carlo data.

PACS. 05.50.+q Lattice theory and statistics (Ising, Potts, etc.) – 05.70.Ce Thermodynamic functions and equations of state – 64.60.-i General studies of phase transitions

1 Introduction

Two- and three-dimensional lattice models are frequently used for the description of equilibrium and kinetic properties of solid state ionics, solid electrolytes, solid solutions, magnetic materials and surface phenomena [1–9], just to name a few. These relatively simple models of many-body systems are widely used for clarifying different aspects of critical phenomena [10] and thus different approaches for their investigation are developed. Nevertheless, for most lattice models general analytical solutions are not known.

Series expansions which in principle may yield exact equilibrium characteristics frequently suffer from very slow convergence requiring tedious calculations [11] and are not suitable for numerical problems. In recent years, interest has grown in the lattice gas modeling of non-equilibrium phenomena such as surface diffusion [12–14], intercalation [15], crystal growth and surface roughening [16], phase transitions under non-equilibrium conditions [17], etc. and there is, therefore, a need to develop simplified approximate methods for their sufficiently accurate description. In contrast with the conventional point of view, which mainly addresses lattice systems to investigating critical phenomena, this modeling requires the knowledge of equilibrium lattice gas characteristics at different thermodynamic conditions.

One of the best known approaches for equilibrium phenomena is the mean field approximation. It can be used in the most simple Bragg-Williams form or in the form of the Bethe-Peierls (or quasi-chemical) approximation [18]. However, the critical temperature for the two-dimensional square lattice gas with nearest neighbour interaction (in units of the interaction parameter) in Bragg-Williams (1.0) and quasi-chemical (0.721) approximations sufficiently deviate from the exact value (0.567). In addition, the coexisting curve in the phase diagram, the chemical potential and other equilibrium properties of such systems are badly represented by these approximations, both at attractive and repulsive interactions. Different discretized versions of integral equations successfully used in the theory of liquids [19] have shown restricted applicability to specific values of lattice concentration and temperature [20]. The Kikuchi's cluster variation method [21–23], although very powerful in principle, cannot be applied in some cases [24] since cumbersome calculations are required. Hence, the development of other approximate schemes is highly desirable.

In this paper we propose a new approximate method for equilibrium characteristics based on the diagram expansion of the lattice gas free energy in terms of Mayer-like functions and the variational condition for the self-consistent calculation of mean potentials. We apply this self-consistent diagram approximation (SCDA) for the calculation of thermodynamic quantities (*i.e.* chemical potential, heat capacity and phase transition curve for two-dimensional lattice gases with nearest neighbour interactions) and distribution functions as well. These quantities were also calculated by means of Monte Carlo (MC) simulations. The comparison between SCDA and MC data demonstrates the high accuracy of our approach.

The reasons for this consideration are that (a) two-dimensional lattice gases are widely used for modeling surface phenomena (see Refs. [5,6,12–14,16,17]) and (b) the main characteristics of an interacting lattice gas on a

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square lattice are very badly reproduced by different approximate approaches. For example, critical temperatures for Bragg-Williams, quasi-chemical approximations and the best estimations on the basis of the high temperature series expansions (see [25]) are consecutively, as follows, for simple (1.0; 0.822; 0.752) and face centered (1.0; 0.914; 0.816) cubic lattices, *i.e.* the discrepancies are much lower than for the two-dimensional case. The SCDA describes quite satisfactorily two- as well as three-dimensional lattices.

The organization of the paper is as follows. In Section 2 we describe the concept of mean potentials and formulate the variational conditions. The quasi-chemical approximation (QChA) in terms of our approach is considered in Section 3. First order corrections to the QChA (*i.e.* the SCDA) are discussed in Section 4. In Section 5 we present and compare calculated and MC results. Conclusions are given in the final section.

2 The concept of mean potentials and the variational conditions

The potential energy of a lattice gas system of n particles on a regular lattice of N sites is given by

$$U_N = \sum_{i=1}^{N}\sum_{j>i}^{N} \Phi_{ij} n_i n_j, \tag{1}$$

where Φ_{ij} is the interaction energy of particles on lattice sites i and j. The number of independent interaction constants can be substantially reduced taking into account the symmetry of a particular lattice. Thus for the interaction energies the notation $J_k = \Phi_{ij}$ is used frequently for sites i and j, which are neighbours of kth order ($k = 1, 2, \ldots$ for nearest, next nearest and more distant neighbours, respectively). The occupation of a lattice site by more than one particle is prohibited, *i.e.* the occupation numbers $n_i = 0, 1$ obey the normalisation condition

$$\sum_{i=1}^{N} n_i = n. \tag{2}$$

We also consider a reference system, which is defined by one-particle mean potentials $\varphi_j(n_i)$ describing the interaction of a particle ($n_i = 1$) or a vacancy ($n_i = 0$) at site i with site j, so that its potential energy can be written as

$$U_N^0 = \sum_{i=1}^{N}\sum_{j=1,}^{N} \varphi_j(n_i). \tag{3}$$

We assume $\varphi_j(n_j) = 0$, *i.e.* there are no interactions of a particle or a vacancy with itself.

The equilibrium properties of the lattice gas system can be extracted from the partition function

$$Q_N = \mathrm{Sp}_{\{n_1,\ldots,n_N\}}\{\exp(-\beta U_N)\}, \tag{4}$$

where $\mathrm{Sp}_{\{n_1,\ldots,n_N\}}$ designates the summation over all possible distributions of particles or over all allowed permutations of occupation numbers satisfying equation (2). $\beta = (k_\mathrm{B}T)^{-1}$ is inverse temperature and k_B the Boltzmann constant.

The free energy F of the system per lattice site is defined as

$$F = -(k_\mathrm{B}T/N)\ln Q_N. \tag{5}$$

The partition function of the reference system can easily be factorised due to the one-particle character of its potential energy

$$\begin{aligned} Q_N^{(0)} &= \mathrm{Sp}_{\{n_1,\ldots,n_N\}}\left\{\exp\left(-\beta U_N^0\right)\right\} \\ &= \mathrm{Sp}_{\{n_1,\ldots,n_N\}}\left\{\prod_{i=1}^{N}\exp\left[-\beta\sum_{j=1,j\neq i}^{N}\varphi_j(n_i)\right]\right\} \\ &= \left[\prod_{l=0}^{1}\left(Q_l/\theta_l\right)^{\theta_l}\right]^N \end{aligned} \tag{6}$$

with

$$Q_{n_i} = \exp\left[-\beta\left(\sum_{j=1,j\neq i}^{N}\varphi_j(n_i)\right)\right] \tag{7}$$

and

$$\theta_0 = (N-n)/N, \quad \theta_1 = n/N, \quad \text{and} \quad \theta_0 + \theta_1 = 1, \tag{8}$$

where θ_0 and θ_1 represent lattice concentrations of vacant and occupied sites (vacancies and particles), respectively. The Stirling formula was used to calculate the number of equivalent terms in equation (6):

$$\frac{N!}{n!(N-n)!} \cong \frac{1}{\theta_1^n\theta_0^{N-n}}\,. \tag{9}$$

In turn, the partition function of the initial system can be identically expressed as

$$\begin{aligned} Q_N &= Q_N^{(0)}\mathrm{Sp}_{\{n_1,\ldots,n_N\}}\left\{\exp\left[-\beta\left(U_N - U_N^{(0)}\right)\right]\right. \\ &\quad \left.\times\exp\left(-\beta U_N^{(0)}\right)/Q_N^{(0)}\right\} \\ &= Q_N^{(0)}\left\langle\exp\left[-\beta\left(U_N - U_N^{(0)}\right)\right]\right\rangle_0, \end{aligned} \tag{10}$$

where the angular brackets with subscript 0 represent mean values over states of the reference system

$$\langle A_{mkl\ldots}\rangle_0 = \sum_{m,k,l,\ldots}^{N} A_{mkl\ldots}\theta_m\theta_k\theta_l\ldots. \tag{11}$$

Here shortcut notations are used so that subscripts m, k, l, ... designate lattice sites and occupation numbers as well, *i.e.* the sum in equation (11) represents the summation over all lattice sites and over all occupation numbers satisfying equation (2). Due to the simple structure of the potential energy of the reference system (Eq. (3)) its distribution functions can be written as products of mean concentrations of vacancies and particles.

Equation (10) allows us to introduce Mayer-like functions

$$f_{ij}(n_i, n_j) = \exp\left\{-\beta\left[\Phi_{ij} n_i n_j - \varphi_j(n_i) - \varphi_i(n_j)\right]\right\} - 1, \tag{12}$$

and to rewrite the partition function in the form

$$Q_N = Q_N^{(0)} \left\langle \prod_{i=1}^{N} \prod_{j=i+1}^{N} (1 + f_{ij}) \right\rangle_0 . \tag{13}$$

The introduction of Mayer-like functions is advantageous as compared to standard ones [18,19]. The mean potentials if properly found reduce values of the Mayer-like functions leading to better convergence of the free energy expansion in these functions. Equations (6) and (10–12) reformulate the initially one-component lattice gas problem in terms of a two-component system. Mayer functions defined by equation (12) at $\varphi = 0$ are equal to 0 if at least one of the sites i or j is vacant. In general, mean potentials for a vacant site $\varphi_j(0)$ are not equal zero. Then equation (13) comprises three Mayer-like functions for each pair of lattice site occupation numbers, as is the case for the Mayer functions of a two-component system.

It is well-known that for fluids the diagram expansion of the free energy in terms of Mayer functions can be represented by irreducible diagrams [19]. Particular calculations of these irreducible diagrams, for the case of lattice gases where multiparticle site occupations are forbidden, result in appearing reducible diagrams due to excluded volume restrictions [11]. Fortunately, our self-consistency conditions (see below) lead to zero values of these reducible diagrams so that we can use only irreducible ones calculating weight coefficients by means of simple combinatorial arguments.

On the basis of equation (13) the free energy of the system can be calculated and its expansion in the Mayer-like functions truncated at some level can be used to develop a self-consistent scheme for proper determination of the mean potentials. Transformation (10) is an identity and the partition function as well as the free energy of the system does not depend on the mean potentials. As an approximation, ultimately justified by its success (see Sects. 5 and 6), the same requirement can be applied to the truncated part of the expansion. It means that its variations (or partial derivatives) with respect to the mean potentials have to be equal to zero. In the next two sections this technique is demonstrated deriving QChA and its first order corrections.

3 The quasi-chemical approximation

An explicit expression for the free energy follows from equations (5, 10)

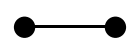
$$\begin{aligned} F &= -\frac{k_\mathrm{B}T}{N}\ln Q_N \\ &= -k_\mathrm{B}T\left(\theta_0 \ln\frac{Q_0}{\theta_0} + \theta_1 \ln\frac{Q_1}{\theta_1} + \sum_{i=2}^{N} b_i\right), \end{aligned} \tag{14}$$

where b_i stands for the contribution of graphs (diagrams) defined on i vertices (lattice sites). Graph edges correspond to the Mayer-like functions, whereas filled vertices mean multiplication by concentration and averaging over the site states (occupied and vacant).

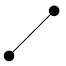
As a first step in the free energy expansion we consider the free energy of the reference system and the two-vertex graph contributions (b_2) only,

$$F = -k_\mathrm{B}T\left(\theta_0 \ln\frac{Q_0}{\theta_0} + \theta_1 \ln\frac{Q_1}{\theta_1}\right)$$

$$- 2k_\mathrm{B}T \Bigg($$



$$+$$



$$+ \ldots \Bigg) . \tag{15}$$

Here values Q_0 and Q_1 are defined by equation (7). The explicit form of equation (15) in view of definitions similar to equation (11) for the mean values of the Mayer-like functions

$$\begin{aligned} F &= k_\mathrm{B}T\left(\theta_0 \ln\theta_0 + \theta_1 \ln\theta_1\right) \\ &+ \sum_{k=1}^{k_\mathrm{max}} (\theta_0 \varphi_0^{(k)} + \theta_1 \varphi_1^{(k)}) z_k - \frac{k_\mathrm{B}T}{2} \sum_{k=1}^{k_\mathrm{max}} \sum_{i,j=0}^{1} f_{ij}^{(k)} \theta_i \theta_j z_k \end{aligned} \tag{16}$$

contains mean potentials $\varphi_0^{(k)}$ and $\varphi_1^{(k)}$ of interaction of a vacancy or a particle, respectively, with kth order neighbour site. z_k denotes the number of such sites. We use notations

$$f_{ij}^{(k)} = \frac{W_{ij}^{(k)}}{X_i^{(k)} X_j^{(k)}} - 1, \tag{17}$$

$$\exp(-\beta\Phi_{ij}^{(k)}) = W_{ij}^{(k)}, \tag{18}$$

$$\exp(-\beta\varphi^{(k)}(i)) = X_i^{(k)}, \tag{19}$$

to simplify equation (16) as much as possible. Due to translational and point group symmetries of the lattice it is possible to replace the summation over mutual positions of two particles belonging to the same coordination sphere by the multiplication with the co-ordination number z_k of this sphere. The subscripts i, j indicate site states (vacant or occupied), whereas the superscript k designates the neighbour order of interacting objects. Hence $f_{ij}^{(k)}$ defines three types (in accordance with the set (0,0), (0,1) and (1,1) of values of subscripts i and j) of the Mayer-like functions for neighbours of different order $k = 1, 2, ...$ The interaction potential $\Phi_{ij} = 0$ and $W_{ij} = 1$, if at least one of their subscripts is zero. However, due to the mean potentials the Mayer-like functions are not equal to 0 in these cases.

In accordance with the variational condition formulated in the previous section the variation of equation (16) with respect to the mean potentials results in a system of equations

$$X_i^{(k)} = \sum_{j=0}^{1} \frac{W_{ij}^{(k)}\theta_j}{X_j^{(k)}}, \quad i = 0, 1; \quad k = 1, 2, ... \tag{20}$$

These equations show that the mean potentials for different neighbours are independent of each other and the interaction range of the mean potentials is the same as for the interaction potential Φ. The solution of equation (20) can be written in a closed form

$$X_0^{(k)} = \sqrt{\theta_0 + \theta_1/\eta_k}, \quad X_1^{(k)} = X_0^{(k)}\eta_k, \tag{21}$$

where

$$\eta_k = -\frac{\theta_1 - \theta_0}{2\theta_0} + \sqrt{\left(\frac{\theta_1 - \theta_0}{2\theta_0}\right)^2 + \frac{\theta_1}{\theta_0}W_k} \tag{22}$$

is the positive root of a quadratic equation

$$\eta_k^2 + \frac{\theta_1 - \theta_0}{2\theta_0}\eta_k - W_k\frac{\theta_1}{\theta_0} = 0, \tag{23}$$

$$W_k = W_{11}^{(k)} = \exp(-\beta J_k), \quad J_k = \Phi_{11}^{(k)}. \tag{24}$$

J_k is an interaction parameter between neighbours of kth order. For a system with nearest neighbour interactions only, equations (21–24) at $k = 1$ represent ordinary QChA. For the case of more distant interactions, $J_k \neq 0$ at $k \geq 2$, these equations can be considered as a generalization of QChA.

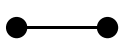
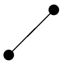
Due to the normalization condition for lattice concentrations, equation (20) can be rewritten in terms of the Mayer-like functions

$$\sum_{j=0}^{1}\left(\frac{W_{ij}^{(k)}}{X_j^{(k)}X_i^{(k)}} - 1\right)\theta_j = \sum_{j=0}^{1} f_{ij}^{(k)}\theta_j = 0, \tag{25}$$

which shows that a two-vertex graph is equal to zero if the Mayer-like function is averaged over states of one of its vertices, *i.e.* the two-vertex graphs with one free vertex are zero graphs. Hence in QChA all graphs which contain a vertex linked to others by only one edge do not contribute to the free energy. This circumstance tremendously reduces the number of graphs which have to be considered in the free energy expansion in the Mayer-like functions. QChA accounts for contributions of such graphs *via* mean potentials.

As a consequence of equation (25) the two-vertex graphs are given zero values by the mean potentials of the quasi-chemical approximation

$$\sum_{i=0}^{1}\sum_{j=0}^{1}\left(\frac{W_{ij}^{(k)}}{X_j^{(k)}X_i^{(k)}} - 1\right)\theta_j\theta_i = \sum_{i=0}^{1}\sum_{j=0}^{1} f_{ij}^{(k)}\theta_j\theta_i = 0,$$

$\Rightarrow$  $= 0,$  $= 0, ...$ (26)

Hence the graph contribution to equation (16) is equal to zero and the free energy in QChA is entirely defined by the reference system contribution

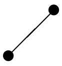
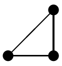
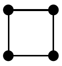
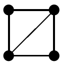
$$F \cong F_0 = k_{\rm B}T(\theta_0 \ln\theta_0 + \theta_1 \ln\theta_1) + \sum_{k=1}^{k_{\max}}(\theta_0\varphi_0^{(k)} + \theta_1\varphi_1^{(k)})z_k. \tag{27}$$

Nevertheless, through the mean potentials this expression indirectly accounts for contributions of a large number of zero graphs. This may explain why QChA already yields semi-quantitative results for the free energy or the chemical potential of lattice systems (see Sect. 5). However, this approximation fails in the description of phase transitions which are very sensitive to small variations of these thermodynamic quantities.

4 Beyond QChA - the SCDA

Although more distant neighbours can be handled in a straightforward way, we consider here a system of particles with nearest neighbour attractive interactions on a square lattice since up to now there is no method giving a simple and at the same time accurate description of this system.

As it was discussed in the previous section the mean potentials of QChA have the same range as the interaction potential. Hence only nearest neighbour mean potentials have non-zero values and it is convenient to use their quasi-chemical values defined by equations (21–24) in the approximation under consideration too. Second neighbour mean potentials may be treated as corrections and thus in the free energy diagram expansion we retain only terms linear in $f^{(2)}$. Bearing in mind that all graphs containing first neighbour edges with a free vertex give zero contributions, we can write an approximate equation that contains only irreducible two-, three- and four-vertex graphs

$\frac{F}{k_{\rm B}T} = \frac{F_0}{k_{\rm B}T} - 2$  $- 4$  $-$  $- 2$  $- ...$ (28)

In the Appendix the diagrams entering equation (28) are represented *via* the mean potentials. It allows the summation of them, and to write for the free energy

$$\begin{aligned}\frac{F}{k_\mathrm{B}T} &= \sum_{i=0}^{1}\theta_i\ln\theta_i + \sum_{i=0}^{1}\theta_i\sum_{k=1}^{2}\frac{z_k\varphi_i^{(k)}}{k_\mathrm{B}T}\\ &\quad - 2\sum_{i=0}^{1}\sum_{j=0}^{1}\left(\frac{W_{ij}^{(2)}}{X_j^{(2)}X_j^{(2)}}-1\right)\left(B_{ij}+1\right)^2\theta_i\theta_j\\ &\quad - \sum_{i=0}^{1}\sum_{j=0}^{1}B_{ij}^2\theta_i\theta_j \end{aligned}\tag{29}$$

where

$$B_{ij} = \sum_{k=0}^{1}\frac{\theta_k W_{ik}^{(1)}W_{jk}^{(1)}}{X_i^{(1)}X_j^{(1)}\left(X_k^{(1)}\right)^2} - 1. \tag{30}$$

The first derivative of equation (29) with respect to the next nearest neighbour mean potentials

$$\frac{\partial F}{\partial\varphi_i^{(2)}} = z_2\theta_i\left[1-\frac{1}{X_i^{(2)}}\sum_{j=0}^{1}\left(\frac{W_{ij}^{(2)}}{X_j^{(2)}}-1\right)\left(B_{ij}+1\right)^2\theta_j\right] \tag{31}$$

with the variational condition to be taken into account results in the equation

$$X_i^{(2)} = \sum_{j=0}^{1}\frac{W_{ij}^{(2)}}{X_j^{(2)}}\left(B_{ij}+1\right)^2\theta_j, \tag{32}$$

which defines the second neighbour mean potentials. With this equation rewritten in the form

$$\sum_{i=0}^{1}\sum_{j=0}^{1}\frac{W_{ij}^{(2)}}{X_j^{(2)}X_j^{(2)}}\left(B_{ij}+1\right)^2\theta_i\theta_j = 1 \tag{33}$$

and equation (30) rewritten as

$$\sum_{j=0}^{1}B_{ij}\theta_j = 0 \tag{34}$$

the third term in equation (29) gives the doubled value of the square graph, and the free energy takes a simple form

$$\begin{aligned}\frac{F}{k_\mathrm{B}T} &= \sum_{i=0}^{1}\theta_i\ln\theta_i + \sum_{i=0}^{1}\theta_i\sum_{k=1}^{2}\frac{z_k\varphi_i^{(k)}}{k_\mathrm{B}T}\\ &\quad + \sum_{i=0}^{1}\sum_{j=0}^{1}B_{ij}^2\theta_i\theta_j + \ldots\\ &= \frac{F_0}{k_\mathrm{B}T} + \square - \ldots \end{aligned}\tag{35}$$

Equation (32) has the same structure as equation (20) with $W_{ij}^{(2)}(B_{ij}+1)^2$ instead of $W_{ij}^{(1)}$. Thus the solution of equation (32) can be obtained in a closed form

$$X_1^{(2)} = X_0^{(2)}\eta_2, \tag{36}$$

$$X_0^{(2)} = \sqrt{V_{00}\theta_0 + (V_{01}\theta_1/\eta_2)}, \tag{37}$$

where

$$\eta_2 = \frac{-V_{01}(\theta_1-\theta_0)+\sqrt{V_{01}^2(\theta_1-\theta_0)^2+4V_{00}V_{11}\theta_0\theta_1}}{2V_{00}\theta_0}, \tag{38}$$

$$V_{ij} = W_{ij}^{(2)}(B_{ij}+1)^2. \tag{39}$$

In the case of nearest neighbour interactions, $W_{ij}^{(2)} = 1$ for all combinations of subscripts. However, the quantities B_{ij} are different from zero, and the second neighbour mean potentials acquire non-zero values due to statistical effects.

On the basis of the mean potentials additional diagrams entering the free energy expansion equation (14) can be taken into account. The main contribution occurs from the 6-vertex graph containing first neighbour links only. A detailed analysis has shown that its values amount to about 70% of the square graph entering equation (35), in a wide range of temperatures and concentrations between 0.2 and 0.8 where mean potentials are important. Hence, having in mind contributions from other graphs the expression

$$\begin{aligned}\frac{F}{k_\mathrm{B}T} &= \frac{F_0}{k_\mathrm{B}T} + b\,\square = \sum_{i=0}^{1}\theta_i\ln\theta_i\\ &\quad + \sum_{i=0}^{1}\theta_i\sum_{k=1}^{2}\frac{z_k\varphi_i^{(k)}}{k_\mathrm{B}T} + b\sum_{i=0}^{1}\sum_{j=0}^{1}B_{ij}^2\theta_i\theta_j \end{aligned}\tag{40}$$

for the free energy can be used with $b \cong 0.25$.

Equation (40) with equations (21–24) for $k = 1$ and equations (36–39) for $k = 2$ with definitions (18, 19, 30) represent a simple approximate description – the SCDA – of the lattice system with attractive nearest neighbour interactions. These expressions are valid for repulsive interactions outside the ordered region of the phase diagram too. The transcription from the lattice gas to magnetic systems or binary alloys can be easily done with the help of respective analogies [1,18]. The SCDA despite its simplicity yields a surprisingly accurate description (see the next section) of the lattice gas except in the nearest vicinity of critical points.

5 Results and discussion

All thermodynamic characteristics of the system can be investigated using equation (40) for the free energy. For example, the chemical potential μ is defined by the derivative

$$\mu = \left(\frac{\partial F}{\partial\theta_1}\right)_T. \tag{41}$$

This derivative is calculated analytically. However, the resulting complicated expression can hardly be analyzed without numerical computations. In Figure 1 calculated chemical potential isotherms are compared with corresponding MC simulation results [26]. SCDA and MC data

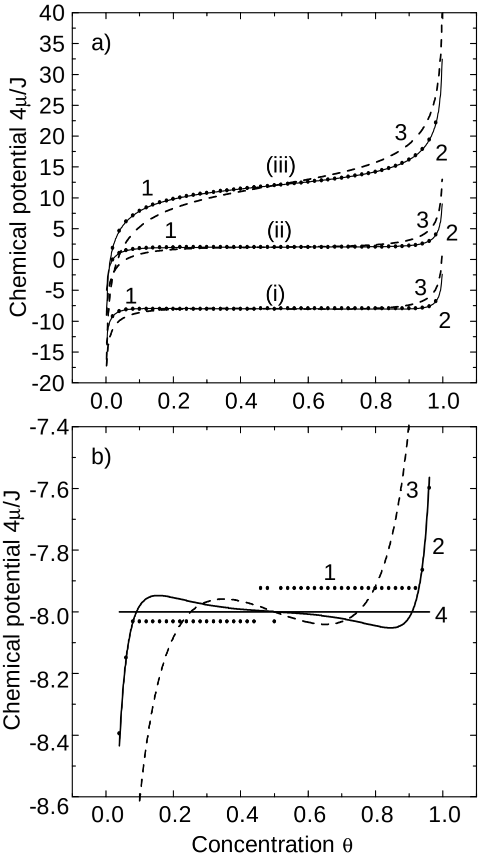


Fig. 1. Chemical potential (in units of the twice nearest neighbour interaction energy) *versus* concentration. (a) $T/T_c = 0.95$ (i), 1.05 (ii), 2.00 (iii). (1) Monte Carlo (MC) simulation (solid circles), (2) self-consistent diagram approximation (SCDA, solid line), (3) quasi-chemical approximation (QChA, dashed line) results. Each group of curves is shifted up by 5 units along the μ axis with respect to the previous one. (b) $T/T_c = 0.95$. (1) MC, (2) SCDA, (3) QChA, (4) $\mu = 2J$. The intersections of line (4) with the left and right branches of the chemical potential curves define the phase transition points in QChA and SCDA.

agree in the limits of accuracy of the latter for all values of the thermodynamical parameters. At slightly supercritical temperatures the SCDA and MC isotherms display a very wide plateau in contrast to the quasi-chemical approximation.

Even in the two-phase region (curves (*i*) in Figs. 1a and 1b) the difference between MC and SCDA results is very small. MC simulations show an almost constant value of the chemical potential, whereas theoretical results obtained from equation (41) demonstrate the well-known Van der Waals kink. It should be noted that this kink is weakly manifested. The theoretical curve deviates only slightly from a horizontal straight line and the positions of its points satisfying the Maxwell construction are very sensitive to the accuracy of approximations. This is the reason why the phase transition curve is reproduced with difficulty by many approximate approaches.

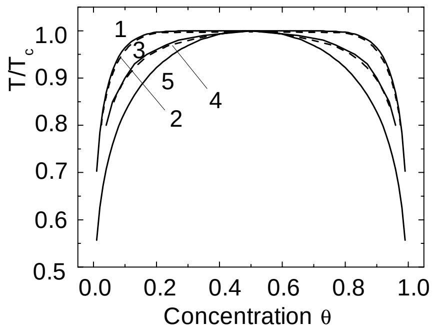


Fig. 2. The phase diagram of the lattice gas with an attractive nearest neighbour interaction. (1) Yang expression [18,27], (2) SCDA, (3) Kikuchi approximation, (4) consolidation site 4×4 approximation [28] and (5) QChA.

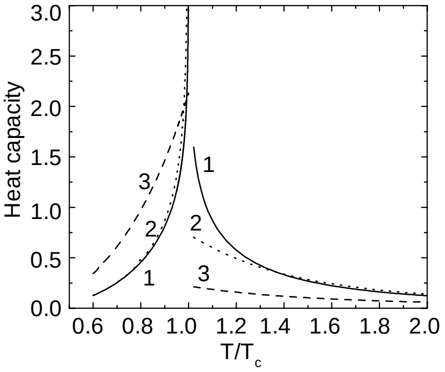


Fig. 3. Heat capacity *versus* temperature at $\theta = 0.5$. (1) Onsager solution, (2) SCDA and (3) QChA.

The lattice gas – Ising magnet analogy [18]

$$m = 1 - 2\theta \tag{42}$$

allows comparison of the SCDA phase transition curve with corresponding values for the magnetization m in zero magnetic field given by Yang [18,27] on the basis of the exact Onsager solution. In Figure 2 the lattice gas phase diagrams in quasi-chemical, Kikuchi, consolidation site [28], and self-consistent diagram approximations are compared with the data obtained from Yang's exact expression. Again, a high accuracy of the SCDA is noticeable. Moreover, the critical temperature $k_B T_c/J = 0.565$ of SCDA coincides within several tenths of a per cent with the exact (0.567) value, and can be compared with the corresponding values of QChA (0.721) and Kikuchi approximations (0.606).

The heat capacity below (along the coexistence curve) and above (at constant concentration $\theta = 0.5$) the critical temperature is shown in Figure 3. The sharp increase of the SCDA heat capacity values in the vicinity of the critical point, especially below the critical temperatures, indicates that the higher order SCDA may be used for an adequate description of critical phenomena.

It is worthwhile to note that Figures 1–3 are given in reduced temperature units T/T_c with absolute values of T_c specified for each approach. All critical temperatures in reduced units are equal to 1. However,

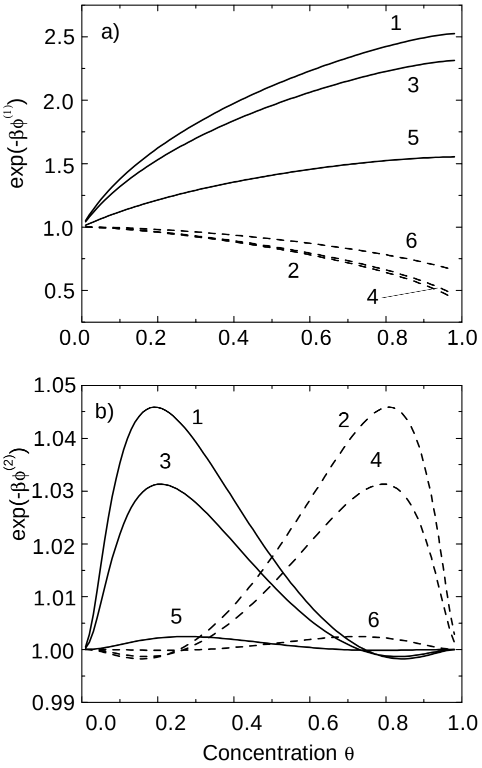


Fig. 4. Mean potential exponents $\exp(-\beta\varphi^{(k)})$ *versus* concentration. (a) For the interaction of a particle (solid lines, odd indices) or a vacancy (dashed lines, even indices) with a nearest neighbour site; $T/T_c = 0.95$ (1, 2), $T/T_c = 1.20$ (3, 4), $T/T_c = 2.00$ (5, 6). (b) The same as (a) for the interaction of a particle or a vacancy with a next nearest neighbour site.

the absolute critical temperature of QChA, for example, is $0.721/0.567 = 1.27$ times higher than the exact value. Thus in the temperature region $T \cong T_c$ different approximations represent the coexistence curves, chemical potentials and other thermodynamic and structural quantities much better in reduced units than in the absolute temperature ones. At the same time, many approximations (*e.g.*, QChA, Kikuchi, SCDA) in the high temperature or low concentration limit become exact, requiring the usage of the absolute temperature units at these conditions. Therefore it is very important for any approximation to get as best an estimation of the critical temperature as possible, to satisfactorily represent equilibrium characteristics at different thermodynamic conditions. SCDA values of lattice gas critical temperatures for the two-dimensional system considered, as well as for all cubic three-dimensional lattices (simple, body and face centered), [29] coincide with their best estimations within a per cent ensuring practical needs for most applications.

Figure 4 proves that the next nearest neighbour mean potentials can be considered as small corrections to the nearest neighbour ones. Nevertheless, their contributions to the free energy are very important and considerably improve the concentration and temperature dependences of the free energy and the chemical potential.

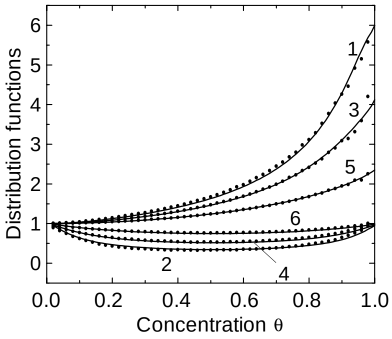


Fig. 5. MC and SCDA results for the concentration dependence of the distribution functions for two nearest neighbour vacancies ($F(0,0)/(1-\theta)^2$, odd indices) or for a particle and a vacancy ($F(0,1)/\theta(1-\theta)$, even indices) at $T/T_c = 0.95$ (1, 2), $T/T_c = 1.20$ (3, 4) and $T/T_c = 2.00$ (5, 6). These quantities define the ratios of the probabilities for interacting and noninteracting lattice gases. The solid curves represent SCDA results. MC results are shown by solid circles.

It follows from the definitions of the interaction energy (Eq. (1)), the partition function (Eq. (4)), and the free energy (Eq. (5)) that the probability $F_k(1,1)$ for two lattice sites to be occupied is defined by the derivative

$$F_k(1,1) = \frac{2}{z_k}\left(\frac{\partial F}{\partial J_k}\right)_{\theta,T}. \qquad (43)$$

Here the subscripts $k = 1, 2, \ldots$ are used to indicate nearest, next nearest and more distant neighbours. The other two-site distribution functions can be calculated from the normalization conditions

$$F_k(0,1) = \theta - F_k(1,1), \qquad (44)$$

$$F_k(0,0) = 1 - \theta - F_k(0,1). \qquad (45)$$

The probabilities for two nearest sites to be vacant $F_1(0,0)$ or for a vacancy and a particle to be nearest neighbours $F_1(0,1)$ divided by their values for a non-interacting (Langmuir) gas are represented in Figure 5. These values show the deviation of the system from the ideal Langmuir gas behavior. At all values of thermodynamic parameters the SCDA values coincide with the MC results within the precession of the latter. Strong deviations of these functions from their Langmuir values are observed at middle and high concentrations and at low temperature. Although at $T = 0.95T_c$ the SCDA data mostly correspond to thermodynamically unstable states their coincidence with MC results is as good as in stable states. It can be explained by very small deviations of the chemical potential from its actual constant value $\mu = 2J$ in the two-phase region at this temperature.

6 Conclusions

The SCDA of the first order represented by equation (40), with equations (21–24) at $k = 1$ and equations (30, 36–39) at $k = 2$, provides a simple and accurate description of the lattice gas system with nearest neighbour attractive interactions in most areas of the thermodynamical parameters. It takes several tenths of a second to calculate on a personal computer thermodynamic characteristics of the system in a hundred points along an isotherm.

The quasi-chemical approximation can be considered as a zero order SCDA. The nearest neighbour mean potentials are found in such a way that the two-vertex graph with the Mayer-like functions becomes zero valued after averaging over states of only one of its vertices. It means that all graphs, which contain a nearest neighbour edge with a free vertex at its end, do not directly contribute to the free energy expansion. Their contributions are taken into account through the mean potentials.

It is convenient to keep the quasi-chemical definition of the nearest neighbour mean potentials for the first order SCDA. The considerable improvement of the results for the thermodynamic characteristics is attained by introducing the next nearest neighbour mean potentials. The SCDA can easily be generalized for more distant interactions introducing more distant mean potentials and calculating additional diagrams.

The advantage of the SCDA is connected with the renormalization of the interaction potential by the mean potentials, which substantially reduces values of the Mayer-like functions as compared to the Mayer functions. Thus the convergence of expansions in the Mayer-like functions seems to be sufficiently rapid in a wide area of thermodynamic variables. Also, it promises progress in the investigation of critical phenomena on the basis of higher order SCDA.

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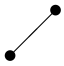
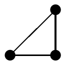
Appendix: Summation of particular diagrams

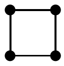
In accordance with the definitions of the Mayer-like functions (Eqs. (12, 17)), the diagrams in equation (28) can be represented in terms of the mean potentials



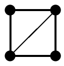
$$= \sum_{i=0}^{1}\sum_{j=0}^{1} f_{ij}^{(2)}\theta_i\theta_j, \qquad \text{(A.1)}$$



$$= \sum_{i=0}^{1}\sum_{j=0}^{1} f_{ij}^{(2)}B_{ij}\theta_i\theta_j, \qquad \text{(A.2)}$$



$$= \sum_{i=0}^{1}\sum_{j=0}^{1} B_{ij}^{2}\theta_i\theta_j, \qquad \text{(A.3)}$$



$$= \sum_{i=0}^{1}\sum_{j=0}^{1} f_{ij}^{(2)}B_{ij}^{2}\theta_i\theta_j, \qquad \text{(A.4)}$$

where

$$B_{ij} = \sum_{k=0}^{1}\theta_k f_{ik}^{(1)} f_{jk}^{(1)}. \qquad \text{(A.5)}$$

To explain the derivation of these expressions it is sufficient to note that equation (A.5) defines the average value of the product of Mayer-like functions given for two pairs of nearest neighbours (ki) and (kj) over the states of site k. Then, in order to derive, for example, equation (A.2), it is necessary to multiply equation (A.5) by the Mayer-like function for a pair of second neighbour sites (ij) and average this product over the states of sites i and j. Equation (30) follows after using the definition (17), equation (25) and the normalization condition equation (6) in equation (A.5). The sum of diagrams (A.1, A.4) with doubled diagram (A.2) yields the third term in equation (29).

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