PHYSICAL REVIEW E, VOLUME 64, 066108

Thermodynamics and diffusion of a lattice gas on a simple cubic lattice

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(Received 24 October 2000; revised manuscript received 29 March 2001; published 14 November 2001)

A lattice gas model with nearest neighbor attractive interactions on a simple cubic lattice is considered. The method of nonequilibrium statistical ensembles due to Zubarev is used to derive expressions for jump and chemical diffusion coefficients. For thermally activated hopping dynamics in the hydrodynamical (low frequency, long wavelength) limit, and neglecting specific memory effects, these expressions are represented in a simple form in terms of the zero concentration limit of the chemical diffusion coefficient and equilibrium characteristics, i.e., the chemical potential, and the probability for two nearest neighbor sites to be vacant. These equilibrium characteristics are calculated by means of the self-consistent diagram approximation. The equilibrium characteristics and diffusion coefficients are in a good agreement with extensive Monte Carlo simulation results.

DOI: 10.1103/PhysRevE.64.066108 PACS number(s): 05.50.+q, 05.10.Ln, 66.30.Dn

I. INTRODUCTION

Many important properties, equilibrium as well as nonequilibrium, of interacting many-body systems can be understood considering relatively simple lattice systems [1–6]. However, even for these simplified systems exact solutions of numerous important problems do not exist except for several well known cases such as, for example, Onsager's result for the free energy of the Ising two-dimensional model [7]. Thus, there has been a considerable effort to develop approximate approaches, mainly for calculating equilibrium properties.

The best known approaches for investigating equilibrium characteristics are based on the mean field approximation. The latter can be used in the most simple Bragg-Williams form or in the form of the Bethe-Peierls-Weiss (or quasichemical) approximation (see [7]). However, these approximations, as well as a newly suggested one [8] can give only semiquantitative results. The Kikuchi cluster variation method [9,10] in its simplest form also cannot be used for quantitative investigations, or it requires cumbersome calculations. Moreover, the methods based on different series expansions [11] that can in principle yield as exact results as necessary suffer from a weak series convergence and cannot be used for applications if results at different thermodynamic conditions are required.

Diffusion coefficients represent the most important nonequilibrium characteristics of lattice gas systems. These coefficients were considered for spin dynamics by Kawasaki [12] and by Kadanoff and Swift [13] in the framework of Kubo's linear response theory. For systems where dynamics may be described on the basis of simple model Hamiltonians the quantum mechanical formalism was widely exploited [14–18]. Similar techniques were used for lattice models with transition rates defined by kinematic conditions or in the simplest mean field approximations [19–22]. However, the transition rates of lattice gas models have more complicated structures and do not allow us to use this formalism in a straightforward manner. Several different approaches are used that employ thermally activated particle hopping, which is the basic characteristic of a lattice gas. For the two-dimensional case important results were obtained considering the quasiequilibrium distribution [23] and by a semiphenomenological approach [24]. Monte Carlo (MC) simulations of two-and three-dimensional interacting lattice gases have also appeared [25–27]. With the progress of computational techniques extensive and more sophisticated two-dimensional simulations were performed [28,29].

In spite of the above progress, much less attention has been given to the statistical mechanical description of nonequilibrium processes in lattice gases. Kutner *et al.* [26] developed a mean field treatment with emphasis on the critical behavior of the chemical (collective) diffusion coefficient in three-dimensional lattice gases obeying Kawasaki dynamics. For two-dimensional lattice gases, a simple and rather general derivation of the microscopic expression for the chemical diffusion coefficient was given by Zhdanov [30]. The quasiequilibrium distribution of mobile particles similar to Refs. [23], [24] was used in this derivation. The dynamical structure factor was used to represent the chemical diffusion coefficient [31] in terms of the Mori's continuous fractions [32] and for the two-dimensional lattice gas the calculations were performed on the basis of Kikuchi's approximation [9]. Some general results concerning diffusion in lattice gases were obtained [33,34] on the basis of the theory of Markov processes.

Recently [35,36], general expressions for the jump [3,4] and chemical diffusion coefficients were derived in the frame of the nonequilibrium statistical ensemble method (NESEM) due to Zubarev [37,38]. This method is in line with modern nonequilibrium statistical mechanical theories developed by Kubo [39], Mori [32], Zwanzig [40], McLennan [41], and many others, and may be considered as the most suitable technique for applications. For thermally activated hopping dynamics when specific memory effects are neglected the diffusion coefficients are represented in terms of the transi-

1063-651X/2001/64(6)/066108(11)/$20.00

tion rate at zero concentration and thermodynamical characteristics (the chemical potential and the vacancy distribution function) only. Here these expressions are used to investigate lattice gas diffusion of interacting particles in an attractive field on a three-dimensional simple cubic (SC) lattice. The equilibrium characteristics are calculated within the self-consistent diagram approximation (SCDA) [42] that was shown to be quite accurate for a two-dimensional square lattice. This approximation is extended now to the three-dimensional case.

The paper is organized as follows: The derivation of the chemical diffusion coefficient is outlined in the next section. The SCDA expressions for calculating the chemical potential and distribution functions are derived in Sec. III. MC simulation techniques for equilibrium characteristics and diffusion coefficients are described in Sec. IV. Also the results for attractive interactions from the calculations and the comparison between the statistical mechanical and MC simulation data are discussed in this section. Section V presents the conclusions. The derivation of the expression for the mean transition rate and the expressions defining the SCDA mean potentials are given in Appendixes A and B, respectively, for attractive interactions.

II. GENERAL EXPRESSIONS FOR THE DIFFUSION COEFFICIENTS

A. Description of the model

We consider a lattice gas system of n particles on a SC lattice with nearest neighbor (NN) interactions described by a potential energy

$$U=J\sum_{i=1}^{N}\sum_{j=1}^{z}\hat{n}_j\hat{n}_i+u\sum_{i=1}^{N}\hat{n}_i, \tag{1}$$

where N is the number of lattice sites. The interaction constant J is positive for repulsive and negative for attractive interactions. The external site potential u is usually negative to capture a particle at a lattice site. The occupation numbers $\hat{n}_i$ are considered as dynamical variables whose distribution over the lattice sites defines a microscopic state of the system. The summation on j runs over the z nearest neighbor sites of site i. For a SC lattice $z=6$. Double occupancy of a site is forbidden, i.e.,

$$\hat{n}_i=\begin{cases}1 & \text{if the lattice site } i \text{ is occupied}\\ 0 & \text{otherwise,}\end{cases} \tag{2}$$

$$n=\sum_{i=1}^{N}\hat{n}_i=\text{const.} \tag{3}$$

A nonequilibrium state of the lattice gas is determined by a probability distribution vector

$$\mathbf{P}(t)=\sum_{\{\underset{\sim}{\alpha}\}}P_\alpha(t)\underset{\sim}{\alpha}, \tag{4}$$

where $\{\underset{\sim}{\alpha}\}$ is an orthonormalized set of vectors $\underset{\sim}{\alpha}$ representing all the particular states of the system. P_α is the probability to find the lattice gas system in the state α.

We assume that the evolution of the lattice gas is governed by the master equation (see [5,12,22])

$$\frac{d\mathbf{P}(t)}{dt}=\mathbf{WP}(t), \tag{5}$$

where the matrix elements

$$W(\alpha,\alpha')=w(\alpha,\alpha')-\delta_{\alpha,\alpha'}\sum_{\alpha''}w(\alpha'',\alpha') \tag{6}$$

represent the transition matrix $\mathbf{W}$ and $w(\alpha,\alpha')$ is the transition rate from state α' to state $\alpha(\alpha'\neq\alpha)$. The transition matrix $\mathbf{W}$ satisfies the detailed balance condition

$$\mathbf{WP}_{\text{eq}}=\mathbf{0}, \tag{7}$$

where $\mathbf{P}_{\text{eq}}$ represents the equilibrium probability distribution.

The lattice gas dynamics is specified by the model of traps [2] at constant (zero) level of barriers (which need to be overcome by diffusing particles) when the transition (hopping) rate from site i to a NN site j is given by

$$w_{ji}=\nu\exp[\beta(\varepsilon_i+u)]=w_0\exp(\beta\varepsilon_i), \tag{8}$$

where $\beta=(k_{\text{B}}T)^{-1}$ is an inverse temperature, k_{B} the Boltzmann constant,

$$w_0=\nu\exp(\beta u) \tag{9}$$

is the transition rate of a single particle on the lattice, and ν is a frequency determining the time scale of the diffusion process. The potential well depth in Eq. (8) is created by the external field potential u and the interactions of a particle on site i with the neighboring particles

$$\varepsilon_i=J\sum_{k=1}^{z}\hat{n}_k. \tag{10}$$

Longer range than NN transitions are forbidden. The hopping dynamics is widely used in considerations of lattice gas diffusion processes by different methods [2–5,23,25,27–29,31]. We note that according to Eqs. (6) and (8)–(10) the transition matrix is a strongly nonlinear operator.

B. The evolution equation for concentration fluctuations

The chemical potential μ_i is considered to be the thermodynamic conjugate quantity to $\hat{n}_i$. In general, μ_i depends on the site position and is a function of time. The deviations (fluctuations) of the chemical potential and mean occupation numbers (concentration) from their equilibrium values

$$\delta\mu_i=\mu_i-\mu,$$

$$\delta\hat{n}_j=\hat{n}_j-c,\quad c=\langle\hat{n}_j\rangle \tag{11}$$

are interconnected by the thermodynamic relations [37,38]

$$\delta(\beta\mu_i)=\frac{1}{c}\sum_j \chi_{ij}\delta n_j ,$$

$$\delta n_j=\langle \delta\hat{n}_j\rangle_r=\langle \hat{n}_j\rangle_r-c, \tag{12}$$

where $\langle\,\rangle$ and $\langle\,\rangle_r$ denote averaging over the equilibrium and the relevant (or quasiequilibrium) probability distributions [37,38], respectively. μ and c are equilibrium values of the chemical potential and the lattice concentration. χ_{ij} is a $N\times N$ matrix. Its inverse value is related to the static correlation function of concentration (density) fluctuations

$$\chi_{ij}^{-1}=c^{-1}\langle \delta\hat{n}_i\delta\hat{n}_j\rangle. \tag{13}$$

According to the NESEM [37,38] the evolution of the mean value deviation of the occupation numbers from their equilibrium values (in the thermodynamic limit $N\to\infty,n\to\infty$ at $n/N=c=\text{const}$) obeys the Mori type [32] integro-differential equation

$$\frac{d\,\delta n_i(t)}{dt}-\beta c\sum_{j=1}^{N} \Omega_{ij}\delta\mu_j+\beta c\sum_{j=1}^{N}\int_0^\infty \Theta_{ij}(\tau)\,\delta\mu_j(t-\tau)d\tau =0, \tag{14}$$

where Ω_{ij} and Θ_{ij} are a static correlation matrix and a memory matrix, respectively. The former can be written as

$$\Omega_{ij}=c^{-1}\langle \delta\dot{\hat{n}}_i\delta\hat{n}_j\rangle, \tag{15}$$

where the microscopic particle flux is defined according to the master equation (5) and the occupation number restriction Eq. (2)

$$\dot{\hat{n}}_i=\sum_{j=1}^{z} [w_{ij}\hat{n}_j(1-\hat{n}_i)-w_{ji}\hat{n}_i(1-\hat{n}_j)]. \tag{16}$$

The mean particle flux at equilibrium is equal to zero, which has a consequence that the total and the fluctuation fluxes are equal: $\delta\dot{\hat{n}}_i=\dot{\hat{n}}_i$. For lattices with equivalent directions *ij* and *ji* the matrix Ω_{ij} is a symmetric matrix.

Since the master equation (5) is irreversible the equilibrium mean value of a product of quantities of different time symmetry is not equal to zero. Hence, in contrast to systems with reversible dynamics the matrix Ω_{ij} in Eq. (14) plays an important role in the irreversible evolution of lattice systems. This peculiarity and the possibility to calculate kinetic coefficients of lattice systems using the relevant (or quasiequilibrium) distribution was already considered by Kawasaki [12]. The formal solution of the master equation has the form being characteristic for a linear differential equation,

$$\mathbf{P}(t)=\exp(\mathbf{W}t)\mathbf{P}(0) \tag{17}$$

that enables us to represent the memory matrix

$$\begin{aligned}\Theta_{ij}(\tau)&=c^{-1}\langle Q\,\delta\dot{\hat{n}}_i\exp(\tau Q\mathbf{W}Q)\,Q\,\delta\dot{\hat{n}}_j\rangle\\ &=c^{-1}\langle Q\,\delta\dot{\hat{n}}_i(0)\,Q\,\delta\dot{\hat{n}}_j(\tau)\rangle\end{aligned} \tag{18}$$

through the bare evolution operator $\mathbf{W}$ and the operator

$$Q=1-P, \tag{19}$$

where the Mori projection operator P acts [32,38,43] on a function $\hat{b}_i$ of the dynamical variables as

$$P\hat{b}_i=\langle\hat{b}_i\rangle+\frac{1}{c}\sum_{i,k} \chi_{ij}\langle\hat{b}_j\delta\hat{n}_k\rangle\delta\hat{n}_k . \tag{20}$$

From Eq. (20) for $\hat{b}_i=\delta\dot{\hat{n}}_i=\dot{\hat{n}}_i$ it follows

$$P\,\delta\dot{\hat{n}}_i=\sum_{j,k} \chi_{ij}\Omega_{jk}\delta\hat{n}_k . \tag{21}$$

Thus, the memory matrix contains subtracted fluxes $J_i=(1-P)\dot{\hat{n}}_i$, the time evolution of which is described by the modified evolution operator $(1-P)\mathbf{W}(1-P)$. The latter circumstance substantially complicates the explicit evaluation of the memory matrix.

C. Jump and chemical diffusion coefficients

It has recently been shown [35,36] that for the two-dimensional lattice gas with attractive interactions in the hydrodynamic (long wave, low frequency) limit the memory matrix contribution to the diffusion coefficients is negligibly small. We neglect this contribution for a SC lattice as well. This approximation will be later verified by comparison with MC simulation results.

To calculate the static correlation matrix Ω_{ij} we substitute Eq. (16) into Eq. (15)

$$\Omega_{ij}=c^{-1}\left\langle \hat{n}_j\sum_{l=1}^{z} [w_{il}\hat{n}_l(1-\hat{n}_i)-w_{li}\hat{n}_i(1-\hat{n}_l)]\right\rangle. \tag{22}$$

For two conjugated system states that differ from each other by the states of the two sites *i* and *l* (from which only one is occupied by a particle) the detailed balance condition Eq. (7) can be written as

$$w_{il}P_{\alpha_{li}}=w_{li}P_{\alpha_{il}}. \tag{23}$$

Here α_{li} and α_{il} designate system states with the occupied site *l* or *i*, respectively, and equivalent states of the other lattice sites; $P_{\alpha_{li}}$ is an equilibrium probability of the state α_{li}. A particle move from site *l* to site *i* corresponds to a change of the system state from α_{li} to α_{il}, and vice versa. Equation (23) implies that at equilibrium the sum of direct and reverse particle fluxes between two lattice sites is equal to zero, and does not depend on the particular states of the other lattice sites.

Thus, if neither *i* nor *l* coincide with *j* the two terms in the right-hand side (rhs) of Eq. (22) cancel each other. For $l=j$ the identities $\hat{n}_j^2=\hat{n}_j$ and $\hat{n}_j(1-\hat{n}_j)=0$ lead to the disappearance of the second term in Eq. (22) but preserve the first one. Then, the nondiagonal matrix element Ω_{ij} can be written in the form

$$\Omega_{ij}=w_1, \tag{24}$$

where the mean transition rate between NN sites i and j

$$w_1=c^{-1}\langle w_{ji}\hat{n}_i(1-\hat{n}_j)\rangle \tag{25}$$

is introduced. Because of the symmetry of the lattice the mean transition rates between all NN sites are equal.

Due to the same identities for occupation numbers only the second term of Eq. (22) contributes to the diagonal matrix elements,

$$\Omega_{ii}=-zw_1. \tag{26}$$

The matrix Ω_{ij} obeys the sum rule

$$\sum_{j=1}^{N}\Omega_{ij}=0 \tag{27}$$

because of the mutual cancellation of the diagonal and nondiagonal matrix elements.

Although it is possible to investigate the wave vector dependence of the diffusion coefficients on the basis of Eq. (14) (see Refs. [35,36]) we restrict our considerations to the hydrodynamic limit. Due to the sum rule and Eqs. (24) and (26) the second term in Eq. (14) can be represented as a second finite difference of the chemical potential with respect to lattice site positions that corresponds to the Laplacian ($\triangle$) in continuous (hydrodynamics) representation. Taking into account that the number density $\rho=c/a^3$, where a is a lattice parameter, Eq. (14) can be rewritten as

$$\frac{\partial\rho}{\partial t}=w_1a^2\chi_T\Delta\rho, \tag{28}$$

where the thermodynamic factor (compressibility) is introduced as

$$\chi_T=\rho\frac{\partial(\beta\mu)}{\partial\rho}=c\frac{\partial(\beta\mu)}{\partial c}. \tag{29}$$

The derivative $\partial(\beta\mu)/\partial c$ is calculated at constant temperature.

Equation (28) represents Fick's second law, which gives the chemical diffusion coefficient

$$D_{\mathrm{ch}}=\chi_T D_{\mathrm{J}}, \tag{30}$$

where the jump [3] (or kinetic [4]) diffusion coefficient is given in terms of the mean transition rate

$$D_{\mathrm{J}}=w_1a^2. \tag{31}$$

In a more general case in the rhs of Eq. (31) the multiplier $z/2d$ appears, where d is a space dimensionality. For square and SC lattices this multiplier is equal to one.

The calculation of the mean transition rate according to Eq. (25) for interacting lattice gases requires averaging over a statistical ensemble. It is an important point that for thermally activated hopping dynamics described by Eq. (8) the mean transition rate as defined by Eq. (25) can be expressed in terms of its zero concentration limit w_0 and equilibrium characteristics only (see Appendix A)

$$w_1=w_0\exp(\beta\mu)F(0,0)/c, \tag{32}$$

where $F(0,0)$ is a probability for two NN sites (i and j) to be vacant. With this expression Eq. (31) transforms to the form

$$D_{\mathrm{J}}=D_0\exp(\beta\mu)F(0,0)/c,\quad D_0=w_0a^2. \tag{33}$$

Such an expression for a two-dimensional gas on a square lattice was derived by Zhdanov [30]. The quasiequilibrium distribution was used in his derivation. Our derivation shows that in the frame of hopping dynamics the only necessary approximation leading to Eq. (33) is the neglecting of specific memory effects described by the memory matrix Θ. No approximations like mean field ones are necessary. Due to the complicated character of the matrix Θ, which may not be handled by analytical means, the accuracy of Eq. (33) has to be tested by alternative methods, e.g., by MC simulations.

III. SCDA FOR SC LATTICE

Equilibrium properties of the lattice gas can be extracted from the free energy F of the system per lattice site

$$F=-(k_{\mathrm{B}}T/N)\ln Q_n. \tag{34}$$

We now introduce a reference system, which is defined by one-particle mean potentials $\varphi_j(\hat{n}_i)$ describing the interaction of a particle ($\hat{n}_i=1$) or a vacancy ($\hat{n}_i=0$) at site i with site j. Its potential energy can be written as

$$U^{(0)}=\sum_{i=1}^{N}\sum_{j=1}^{N}\varphi_j(\hat{n}_i). \tag{35}$$

We assume $\varphi_j(\hat{n}_j)=0$, i.e., there are no interactions of a particle or a vacancy with itself.

The partition function of the initial system can be identically expressed as [42]

$$Q_n=Q_n^{(0)}\left\langle\prod_{i=1}^{N}\prod_{j=i+1}^{N}(1+f_{ij})\right\rangle_0, \tag{36}$$

where the angular brackets with subscript 0 represent mean values over states of the reference system and the partition function of the latter

$$Q_n^{(0)}=\left\{\prod_{n_i=0}^{1}c_{n_i}^{-1}\exp\left[-\beta\sum_{j=1}^{N}\varphi_j(\hat{n}_i)\right]\right\}^N,\quad n_i=\hat{n}_i=0,1, \tag{37}$$

is written through concentrations of vacancies and particles

$$c_0=(N-n)/N,\quad c_1=c=n/N. \tag{38}$$

Mayer-like functions

$$f_{ij}(\hat{n}_i,\hat{n}_j)=\exp\{-\beta[\Phi_{ij}\hat{n}_i\hat{n}_j-\varphi_j(\hat{n}_i)-\varphi_i(\hat{n}_j)]\}-1 \tag{39}$$

are advantageous as compared to standard ones [7,44] because the mean potentials, if properly found, will reduce values of the Mayer-like functions leading to better convergence of the free energy expansion in these functions.

On the basis of Eqs. (34) and (36) the free energy of the system can be calculated. 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 [42]. In the case under consideration all irreducible graphs up to four vertices are taken into account. Transformation (36) is an identity and the partition function as well as the free energy of the system do not depend on the mean potentials. As an approximation, the same requirement can be applied to the truncated part of the expansion. This means that its variations (or partial derivatives) with respect to the mean potentials have to be equal to zero.

As a first step in the free energy expansion we consider the free energy of the reference system

$$F_0 = k_{\mathrm{B}}T\left[\sum_{i=0}^{1} c_i \ln c_i + \sum_{i=0}^{1} c_i \sum_{k=1}^{2} \frac{z_k \varphi_i^{(k)}}{k_{\mathrm{B}}T}\right] \tag{40}$$

and the two-vertex graph contributions only,

$$F = F_0 - 3k_B T\left(\{\bullet\!-\!\bullet\} + 2\{\diagup\} + \ldots\right), \tag{41}$$

The two graphs in Eq. (41) represent mean values of the Mayer-like functions for nearest and next nearest neighbor lattice sites, respectively. For example,

$$\{\bullet\!-\!\bullet\} = \sum_{i,j=0}^{1} f_{ij}^{(1)} c_i c_j, \tag{42}$$

where the superscript shows that the diagram is written for NN sites.

The variation condition formulated above and applied to Eq. (41) results in the NN mean potentials, which lead to zero value of the graph represented by Eq. (42) with one of its vertices opened, i.e., when the sum over one of the indices i or j is omitted. It means that all graphs for Mayer-like functions that include at least one vertex connected to the graph by one line are zero graphs and the quasichemical approximation takes implicitly into account contributions of all such graphs.

At the previous step the mean potentials between next NN sites were found to be equal to zero. In the next step we preserve the quasichemical expressions for the NN mean potentials (which are explicitly written in Appendix B) and take into account all two-, three-, and four- vertex irreducible graphs, which include one next NN Mayer-like function at most because the latter are considered as the first order corrections. Then the free energy is represented as

$$\frac{F}{k_{\mathrm{B}}T} = \frac{F_0}{k_{\mathrm{B}}T} - 6\{\diagup\} - 12\{\triangle\} - 3\{\square\} - 6\{\boxslash\} - \ldots. \tag{43}$$

The last expression differs from the free energy expansion for a square lattice by the graph coefficients only because a SC lattice consists of three plains with a square lattice in each of them and the structure of graphs with up to four vertices is the same for both lattices.

According to the variational condition the derivatives of Eq. (43) with respect to the mean potentials for next NN sites are equal to zero. This idea is used to derive the complete set of expressions for the mean potentials (see Appendix B). With these expressions, similarly to the two-dimensional case (see Appendix in Ref. [42]) the graphs entering Eq. (43) can be summed up. Then, the free energy of the system acquires the form

$$\frac{F}{k_{\mathrm{B}}T} = \frac{F_0}{k_{\mathrm{B}}T} + 3\{\square\}. \tag{44}$$

Again, the coefficient in front of the square graph is three times larger than for a square lattice. It is also possible to take into account graphs with more vertices, but it is difficult to calculate them explicitly. Thus, we suggest that these contributions are proportional to the square graph and adopt the coefficient of this graph in Eq. (44) in such a way that the critical temperature is close to its best estimation. The final expression for the free energy is as follows (quantities B_{ij} are given in Appendix B):

$$\frac{F}{k_{\mathrm{B}}T} = \frac{F_0}{k_{\mathrm{B}}T} - 0.42\sum_{i=0}^{1}\sum_{j=0}^{1} B_{ij}^2 c_i c_j. \tag{45}$$

The best estimation of the critical temperature (in units of the interaction parameter) is 1.128 and Eq. (45) yields the same result that can be compared with 1.19 for Eq. (44) and 1.23 for the quasichemical approximation.

The chemical potential μ and the probability $F(1,1)$ for two NN sites to be occupied by particles are defined by the derivatives

$$\mu = (\partial F/\partial c)_T, \tag{46}$$

$$F(1,1) = (\partial F/\partial J)_{T,c}. \tag{47}$$

The probability for two NN sites to be vacant can be calculated from the normalization condition

$$F(0,0) = 1 - 2c + F(1,1). \tag{48}$$

In spite of its simplicity, the SCDA yields a surprisingly accurate description (see the next section) of lattice gas equilibrium as well as diffusion characteristics.

IV. NUMERICAL RESULTS

A. Monte Carlo simulation techniques

In the two preceding sections quite simple statistical mechanical expressions for investigating equilibrium (chemical potential and distribution functions) as well as nonequilibrium (jump and chemical diffusion coefficients) lattice gas characteristics were derived on the basis of SCDA. The specific memory effects were neglected as well. However, it is not possible to test the validity of these approximations by strict analytical calculations, and thus we resort to MC simulations as the most appropriate means for testing these expressions.

The grand canonical ensemble is used for simulating the equilibrium characteristics. The lattice gas system under consideration is realized by a three-dimensional array of $M\times M\times M$ lattice sites with periodic boundary conditions. For given values of the chemical potential (which includes the external potential u) and temperature the grand canonical distribution function

$$P_N=\text{const}\cdot\,\exp\left[-\beta\left((J/2)\sum_{i=1}^{N}\sum_{j=1}^{z}\hat{n}_i\hat{n}_j-\mu\sum_{i=1}^{N}\hat{n}_i\right)\right] \tag{49}$$

is modeled by changing the number and positions of particles. A lattice site (say, site i) is chosen at random. An attempt is made in that the particle is placed (removed) on the site depending on whether it is vacant (occupied). The energy difference

$$\Delta U=J\sum_{j=1}^{z}\hat{n}_j-\mu \tag{50}$$

and the transition probability

$$P_{\text{tr}}=\exp(\mp\beta\Delta U) \tag{51}$$

are calculated. The sum on j runs over nearest neighbors of site i. Upper/lower sign in Eq. (51) is chosen if site i is vacant/occupied. If the exponent in the last equation is positive the change of the system state is accepted. In the opposite case a random number $0\leqslant P_{\text{ran}}\leqslant 1$ is generated and the change is accepted if $P_{\text{ran}}\leqslant P_{\text{tr}}$. Otherwise the trial is rejected. After this the procedure is repeated again. One Monte Carlo step (MCS) consists of n trials.

Thermodynamic equilibrium is established before the averaging procedure starts. The approach to equilibrium is monitored by following the total energy and number of particles, and it is assumed to occur when these quantities begin to fluctuate around their average values. In most cases it is found that at $M=50$ attaining equilibration requires no more than 2000 MCSs. After the equilibration process is finished the average concentration and probabilities for two particles or two vacancies or a particle and a vacancy to occupy NN sites are calculated over additional 10^4 MCSs. The same procedure was used to calculate the phase transition points. In the vicinity of the critical point $(0.99T_c<T<T_c)M=100$ and up to 10^5 realizations were used.

Nonequilibrium characteristics are simulated in the canonical ensemble. $n=cN$ 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

$$P_{\text{jump}}=\exp(\beta\varepsilon_i), \tag{52}$$

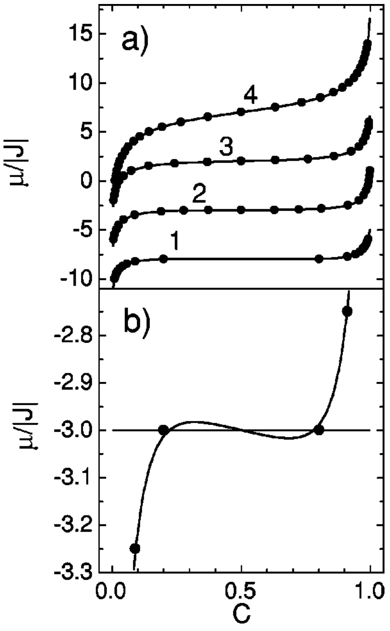

FIG. 1. Chemical potential versus concentration at $T/T_c=0.95$ (1); 1.05 (2); 1.2 (3); 2.0 (4). The solid lines represent the SCDA results, the full circles are the MC simulation data (at $M=50$). The data points in (a) are moved along the vertical axis by a factor of 5 from each other (the original position of each curve is determined by $\mu/|J|=-3$ at $c=0.5$). Curve 1 in (b) is shown in larger scale and its intersections with the line $\mu=3J$ define the phase transition points.

otherwise no jump occurs. One MCS represents the consideration of n lattice sites. Before starting the diffusion runs the equilibration of the system is performed for 2000 MCS. The diffusion calculations 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 [3,5]

$$D_{\text{JGK}}=\lim_{t\to\infty}\frac{1}{2tnd}\left\langle\left(\sum_{i=1}^{n}\Delta r_i\right)^2\right\rangle, \tag{53}$$

where $\Delta\mathbf{r}_i$ stands for the displacement of the ith particle from its initial (at $t=0$) position and t is the number of MCS.

B. Equilibrium properties

In Fig. 1 the chemical potential (absorption) isotherms are shown. The temperature is given in reduced units T/T_c, where the critical temperature for a SC lattice is taken equal to the best estimates from the high temperature free energy series expansion [45] $(T_c=1.128|J|/k_B)$, which is the result of the SCDA Eq. (45) as well. At all temperatures considered (from 0.95 till 6.0) the SCDA and MC simulation results are in a good agreement.

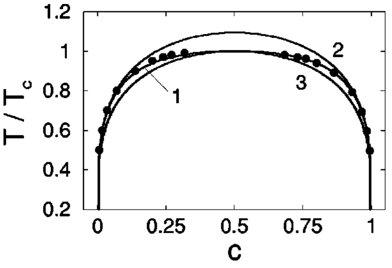

FIG. 2. Phase diagram for a system of particles with NN attractive interactions on a SC lattice. The full circles are the MC simulation data. The curves represent the SCDA (1) and quasichemical approximation [in units of the exact T_c (2) or specific for this approximation $T_{cq}=1.094T_c$ (3) critical temperatures] results.

Below T_c the SCDA chemical potential isotherms demonstrate the well known van der Waals kink. The Maxwell construction allows us to determine the phase transition points. Figure 1(b) demonstrates that the chemical potential isotherms have to be calculated with very high accuracy in order to construct reasonably the phase transition curve. At $T=0.95T_c$ the deviations of the value of μ/J from 3.0 are of the order of 0.01 when states between the phase transition points are considered (see the range $0.2<c<0.8$). At temperatures closer to T_c these deviations are even smaller. However, the range of the μ/J values is at least two orders of magnitude larger. This is the reason why many approximate approaches are unable to accurately describe phase transitions in lattice gas systems.

On the other hand, the small isothermal deviations of the chemical potential from its constant value in the two-phase region mean that the instability of the corresponding thermodynamical states is very weak [in Fig. 1(a) the corresponding part of the isotherm at $T=0.95T_c$ looks like a horizontal line]. The canonical ensemble simulations of the lattice gas on a square lattice have shown [46] that the system at thermodynamically unstable conditions even at temperatures as low as $T=0.6T_c$ creates structures from an initially homogeneous state rather slowly.

Due to the high accuracy of the SCDA we can use it for further analysis instead of the MC simulations. This is especially important for three-dimensional lattices for which even the equilibrium simulations are rather time consuming and many characteristics are defined in terms of free energy or chemical potential derivatives.

The phase diagram displaying the first order lattice gas–lattice liquid phase transition is shown in Fig. 2. The deviations of the SCDA phase transition temperatures from the MC simulation data are within a percent that can be compared to roughly a 10% difference for the quasichemical approximation in the absolute (see Fig. 2, curve 2) or in its own (curve 3) critical temperature units.

At near critical temperatures the phase diagram for a SC lattice is not as flat as for a two-dimensional square lattice. Thus, the chemical potential isotherms at temperatures slightly above critical ($T/T_c=1.05$ and 1.2) in their central parts show not as pronounced flat segments as for the two-dimensional case (see [42]). This feature is demonstrated in Fig. 3 by the comparison of the thermodynamic factor for the two systems. The inverse of the thermodynamic factor is a measure of concentration fluctuations. These fluctuations are much stronger in the two-dimensional system where low values of the thermodynamic factor in a wide concentration range are well pronounced, especially on the lowest temperature isotherm $T=1.05T_c$. Such a difference disappears almost completely at $T=2T_c$.

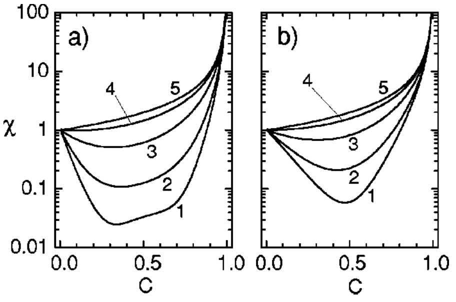

FIG. 3. The thermodynamic factor (SCDA results) versus concentration for square (a) and simple cubic (b) lattices at reduced temperatures $T/T_c=1.05$ (1), 1.2 (2), 2.0 (3), 6.0 (4), and for a noninteracting lattice gas (5).

The static correlations can be investigated by means of the distribution functions, i.e., the probabilities for particles and vacancies to occupy different lattice sites. The probabilities for two particles $F(1,1)$ or a particle and a vacancy $F(1,0)$ to occupy NN sites are plotted in Fig. 4. To demon-

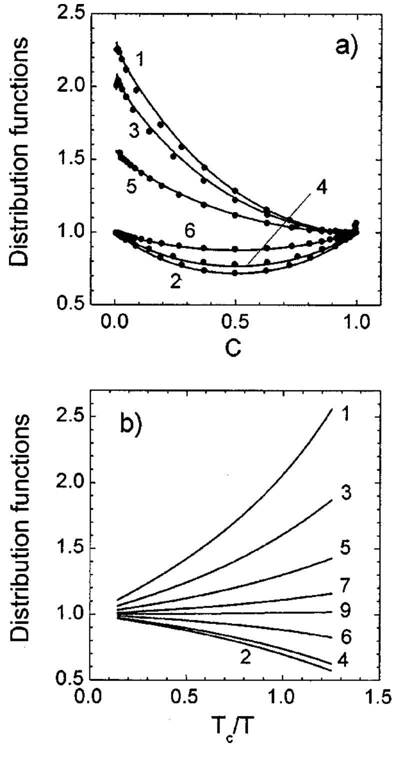

FIG. 4. Distribution functions versus concentration (a) and inverse temperature (b). Curves 1, 3, 5, 7, and 9 represent $F(1,1)/c^2$; curves 2, 4, and 6 represent $F(1,0)/c(1-c)$. (a) $T/T_c=1.05$ (curves 1,2); 1.2 (3,4); 2.0 (5,6). (b) $c=0.1$ (1,2); 0.3 (3,4); 0.5 (5,6); 0.7 (7,4); 0.9 (9,2). The solid lines represent the SCDA results; the filled circles are the MC simulation data.

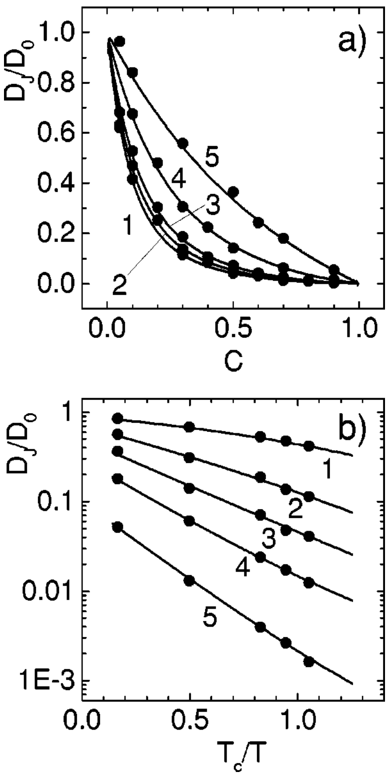

FIG. 5. The jump diffusion coefficient versus (a) concentration at $T/T_c=0.95$ (1); 1.05 (2); 1.2 (3); 2.0 (4); 6.0 (5) and (b) inverse temperature at $c=0.1$ (1); 0.3 (2); 0.5 (3); 0.7 (4); 0.9 (5). The lines are the calculation results according to Eq. (37); the full circles are the MC simulation data.

strate the influence of interactions and make the results more transparent at high concentrations, where their values are close to zero, these probabilities are divided by the Langmuir gas values c^2 and $c(1-c)$, respectively. It follows from the symmetry arguments that the probability $F(0,0)$ for two NN sites to be vacant at concentration c is equal to $F(1,1)$ at concentration $1-c$. Again, these probabilities agree with MC simulation results within a percent. We can see that the deviations from the Langmuir gas correlation functions are considerably reduced as compared to the square lattice at the same reduced temperatures (see Fig. 5 in Ref. [42]). The reason is that the critical temperature for the two-dimensional system $(0.567|J|/k_B)$ is considerably lower due to the difference in the number of nearest neighbors.

C. Diffusion coefficients and activation energies

Equation (33) relates the jump and chemical diffusion coefficients to equilibrium lattice gas characteristics except for a rather trivial factor representing the diffusion coefficient at zero concentration or the transition rate of a single particle on the lattice. As equilibrium characteristics are represented by SCDA quite accurately, the comparison of the jump diffusion coefficients calculated by Eq. (33) and simulated according to Eq. (53) allows one to test whether the contribution of the memory matrix Θ can be neglected as it was suggested in Sec. II. Figure 5 demonstrates that this is valid for the system under consideration. Although we have used lattices with size $30^3=27000$ lattice sites and runs as long as 10^5 MCS performing averaging over 500–2000 realizations the MC simulation data fluctuate around the curves corresponding to Eq. (33). Probably, at better MC simulation statistics the coincidence between the data could be even better.

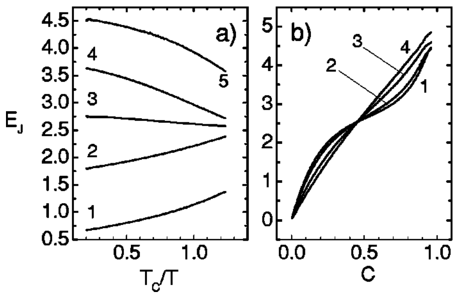

FIG. 6. The jump diffusion activation energies (SCDA results, in units of the interaction parameter $|J|$) versus (a) concentration at $T/T_c=0.95$ (1); 1.05 (2); 1.2 (3); 2.0 (4); 6.0 (5) and (b) inverse temperature at $c=0.1$ (1); 0.3 (2); 0.5 (3); 0.7 (4); 0.9 (5).

Statistical mechanics calculations were in part performed for temperatures and concentrations below the coexistence curve shown in Fig. 2 that correspond to thermodynamically metastable or unstable states. Up to temperatures as low as $0.8T_c$ the distribution functions and jump diffusion coefficient in Figs. 4(b) and 5(b) do not show any indication of the phase transition. In the past [46] MC simulations of an unstable two-dimensional system has shown that although mean square displacements of particles are not linear functions of time, the deviations from the linear behavior are not strongly pronounced at temperatures slightly below critical. In the present MC simulations at $T=0.95T_c$ [not shown in Fig. 5(a)] the jump diffusion coefficient agrees with the results of Eq. (33) with the same accuracy as at $T=1.05T_c$. Thus, the jump diffusion coefficient calculated, for example, by Green-Kubo Eq. (53) can be a measure of mobility of the system in strongly nonequilibrium conditions. The chemical diffusion coefficient does not exist at unstable conditions at all because the thermodynamic factor becomes negative.

Equation (33) allows us to investigate the concentration and temperature dependence of the diffusion coefficients in detail. Figure 5(b) shows that the jump diffusion coefficient obeys Arrhenius behavior almost perfectly at a half coverage while it deviates at other concentrations. The measure of such deviations may be understood by considering the temperature dependence of the diffusion activation energy.

The activation energy for diffusion can be defined as

$$U=-\partial(\ln D)/\partial\beta. \tag{54}$$

This quantity is widely used for the interpretation of experimental diffusion results and, therefore, we will discuss it in some detail.

For the kinetic diffusion coefficient Eq. (33) yields

$$U_J=-\partial(\ln D_J)/\partial\beta=-\mu-\beta(\partial\mu/\partial\beta)-\partial\ln F(0,0)/\partial\beta. \tag{55}$$

The dependence of the activation energy on the inverse temperature and concentration is presented in Figs. 6(a) and

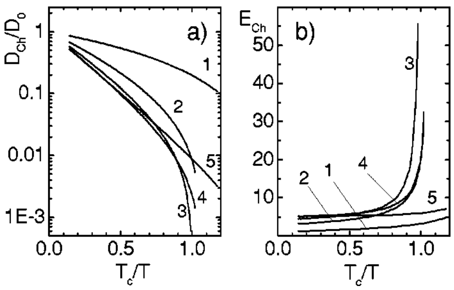

FIG. 7. SCDA results for the chemical diffusion coefficient (a) and its activation energy (b) versus inverse temperature. $c=0.1$ (1), 0.3 (2), 0.5 (3), 0.7 (4), 0.9 (5). From the low temperature side the curves are terminated at the phase transition line, see Fig. 2.

6(b), respectively. It is obvious that (i) the temperature dependence of the activation energy is largely pronounced at low ($c\approx 0.1-0.2$) and high ($c\approx 0.8-0.9$) lattice concentrations, and (ii) the activation energy at low temperatures changes more significantly at low and high concentrations and is nearly independent of coverage at middle concentrations. Due to the fact that only pairwise interactions are considered (maintaining the particle-hole symmetry of the corresponding lattice gas Hamiltonian) the chemical potential is symmetric around half coverage at any particular temperature. The corresponding part of the activation energy is represented by the symmetrically arranged curves. However, the contribution from the distribution function slightly violates the symmetry of the activation energy distribution.

At low concentrations the activation energy approaches zero while in the opposite limiting case of high concentrations the limiting value of $5J$ is reached. Five is the maximal number of nearest neighbors still permitting a particle jump in analogy with the two-dimensional case discussed in Refs. [28], [36] where this number is equal to 3. At high temperatures the concentration dependence of the activation energy is approximately linear, $U_J\cong 5|J|c$ [see Fig. 6(b) for $T=6T_c$]. Deviations from this linear dependence at lower temperatures are not as pronounced as for the lattice gas on a square lattice (see Ref. [36]).

According to Eqs. (32), (33) the total activation energy consists of the external site potential u, which enters the Langmuir gas diffusion coefficient D_0 [see Eq. (9)], and the contribution of the interparticle interactions that is discussed above. Evidently, D_0 obeys Arrhenius behavior. Thus, the deviations of the jump diffusion coefficient from Arrhenius behavior become significantly weaker if the site potential is considerably stronger than the interparticle interaction ($|u|\gg|J|$).

At the same time, the chemical diffusion coefficient deviates from the Arrhenius law much more strongly [Fig. 7(a)] than the jump diffusion coefficient due to the thermodynamic factor, which demonstrates strongly non-Arrhenius behavior. The activation energy for chemical diffusion depends on temperature much more than for jump diffusion [see Fig. 7(b)], especially at intermediate concentrations and not too high temperatures. Concentration fluctuations create extremely high barriers for collective diffusion but do not influence the jump diffusion coefficient. It is evident that the chemical diffusion activation energy as a function of concentration exhibits a bell-shaped structure with a maximum at a half coverage. The maximum strongly increases when temperature decreases. Such a bell-shaped structure was described by Uebing and Gomer [28] on the basis of the MC simulation results for the two-dimensional square lattice gas.

V. CONCLUSIONS

Thermodynamics and diffusion of the lattice gas with nearest neighbor attractive interactions on a simple cubic lattice are investigated by statistical mechanics and Monte Carlo simulation means. It is shown that the SCDA results coincide within 1% with the Monte Carlo simulation data for the lattice gas equilibrium characteristics (the chemical potential and probabilities for particles and vacancies to occupy nearest neighbor sites). The jump diffusion coefficient calculated by Eq. (33) accurately reproduces the MC simulation data, too. This implies that the contribution to the diffusion coefficients of the specific statistical memory effects represented by the time correlation matrix of the subtracted fluxes is negligibly small and can be disregarded. Thus, SCDA and Eq. (33) can be used to investigate the lattice gas equilibrium and diffusion characteristics with good accuracy.

The chemical potential along near critical isotherms does not contain as pronounced flat segments as for the two-dimensional square lattice gas and concentration derivatives of the chemical potential are not so small as well. Thus, for the lattice gas on a SC lattice the concentration fluctuations at near critical conditions are not as strong as in the case of the square lattice gas.

Although the jump diffusion activation energy is within the range (0 to $5J$) for the lattice gas on a SC lattice compared to the range (0 to $3J$) on a square lattice, deviations of the former from Arrhenius behavior are less pronounced and can be attributed to the considerably higher critical temperature in the three-dimensional case. The temperature dependence of the chemical diffusion coefficient is strongly non-Arrhenius except for the cases of low and high concentrations or high temperatures.

Finally, we note that the jump diffusion coefficient is a characteristic quantity for which it is not required to be calculated at equilibrium. In Eq. (53) the averaging over a nonequilibrium ensemble can be performed and the result may be considered to represent a mobility characteristic for a nonequilibrium system.

ACKNOWLEDGMENTS

This work was in part supported by INTAS Grant No. 96-0533 and by the Ministry of Education of Belarus. The visits of V.S.V. and Y.G.G. at the University of Thessaloniki were supported by the NATO Fellowship Program and an INTAS grant, Grant No. YSF 00-4154, respectively. Fruitful discussions with Dr. C. Uebing are gratefully acknowledged.

APPENDIX A

In the canonical ensemble the explicit expression for the mean value entering Eq. (25) is given by

$$\langle w_{ji}\hat{n}_i(1-\hat{n}_j)\rangle = Q_n^{-1}\sum_{\alpha} w_{ji}\hat{n}_i(1-\hat{n}_j)\exp(-\beta U_{n\alpha}), \tag{A1}$$

$$Q_n=\sum_{\alpha} \exp(-\beta U_{n\alpha}), \tag{A2}$$

where Q_n is the partition function, and $U_{n\alpha}$ the interaction energy of the system of n particles in a microscopic state α. The summation is carried out over all states of the system.

In fact, ε_i in Eqs. (8) and (10) represents the interaction energy of a particle on site i with the other $n-1$ particles of the system. Hence

$$\begin{aligned} w_{ji}\exp(-\beta U_{n\alpha}) &= w_0 \exp[-\beta(U_{n\alpha}-\varepsilon_i)] \\ &= w_0 \exp(-\beta U_{n-1,\alpha}), \end{aligned} \tag{A3}$$

i.e., the energy $U_{n-1,\alpha}$ of $n-1$ particles appears here. In the last expression α designates the distribution of $n-1$ particles over $N-1$ lattice sites (site i cannot be occupied by these particles). It is possible to sum over the values of $\hat{n}_i$ (0 and 1) in Eq. (A1) and to rewrite the latter in the form

$$\begin{aligned} \langle w_{ji}\hat{n}_i(1-\hat{n}_j)\rangle &= w_0(Q_{n-1}/Q_n)\sum_{\alpha}(1-\hat{n}_j) \\ &\quad \times[\exp(-\beta U_{n-1,\alpha})/Q_{n-1}] \end{aligned} \tag{A4}$$

because the energy $U_{n-1,\alpha}$ does not depend on the state of site i. The expression in the square brackets in Eq. (A4) can be interpreted as a normalized distribution function of the system of $n-1$ particles over N sites under the condition that site i is vacant. Having in mind that

$$Q_{n-1}/Q_n=\exp(\beta\mu) \tag{A5}$$

and that site j is a NN of site i Eq. (A4) leads to the final form of Eq. (32).

APPENDIX B

It is convenient to simplify notations introducing quantities

$$X_i^{(k)}=\exp[-\beta\varphi_{(k)}(\hat{n}_i)], \tag{B1}$$

where i designates the state of the lattice site [occupied ($i=1$) or vacant ($i=0$)] while the superscript k refers to the mean potentials to the nearest ($k=1$) or next nearest ($k=2$) neighbors. Then, the variational condition leads to an algebraic set of equations (in more detail the calculations for a square lattice are described in Ref. [42])

$$X_i^{(k)}=\sum_{j=0}^{1}\frac{W_{ij}^{(k)}c_j}{X_j^{(k)}}, \quad i=0,1, \quad k=1,2 \tag{B2}$$

with the kernels

$$W_{11}^{(1)}=\exp(-\beta J), \quad W_{10}^{(1)}=W_{01}^{(1)}=W_{00}^{(1)}=1, \tag{B3}$$

$$W_{ij}^{(2)}=B_{ij}^2, \quad B_{ij}=\sum_{k=0}^{1}\frac{c_k W_{ik}^{(1)}W_{jk}^{(1)}}{X_i^{(1)}X_j^{(1)}(X_k^{(1)})^2}. \tag{B4}$$

The solution of Eq. (B2) can be written in a closed form

$$X_1^{(k)}=X_0^{(k)}\eta_k, \tag{B5}$$

where

$$X_0^{(1)}=\sqrt{c_0+c_1/\eta_1}, \quad X_0^{(2)}=\sqrt{V_{00}c_0+(V_{01}c_1/\eta_2)}, \tag{B6}$$

$$\eta_1=-\frac{c_1-c_0}{2c_0}+\sqrt{\left(\frac{c_1-c_0}{2c_0}\right)^2+\frac{c_1}{c_0}W_{11}^{(1)}}, \tag{B7}$$

$$\eta_2=\frac{-V_{01}(c_1-c_0)+\sqrt{V_{01}^2(c_1-c_0)^2+4V_{00}V_{11}c_0c_1}}{2V_{00}c_0},$$

$$V_{ij}=W_{ij}^{(2)}. \tag{B8}$$

Although NN interactions are only taken into account the mean potential for the next nearest (second) neighbors is different from zero due to statistical effects, which manifest themselves through the kernel $W_{ij}^{(2)}$ in Eq. (B2).

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