PHYSICAL REVIEW B **66**, 054303 (2002)

Mass transport in an ordered three-dimensional lattice-gas system

Panos Argyrakis
Department of Physics, University of Thessaloniki, 54124 Thessaloniki, Greece

Alexander A. Chumak
Institute of Physics of the National Academy of Sciences, pr. Nauki 46, 252028 Kiev, Ukraine

(Received 20 December 2001; revised manuscript received 19 April 2002; published 29 August 2002)

Diffusion phenomena on a three-dimensional discrete lattice are studied both analytically and by means of computer simulations. The case of repulsive interaction between the particles occupying nearest-neighbor lattice sites is considered. It is shown that in the case of the disordered particle arrangement, transport phenomena can be described within a theory based on the assumption of uncorrelated particle jumps. In contrast, strong correlation in particle motion, which takes place in antiferromagnetically ordered systems results in considerably lowering the diffusion coefficients. Both random walks and generation-recombination processes of ''structural defects'' of the ordered state govern mass transport in this case. It is shown that jumps of individual defects (vacancies and excess particles of the almost filled and empty sublattices, respectively) and dimers contribute to mass flow. In the vicinity of stoichiometric concentration the defect jumps accompanied with their recombination may also contribute significantly. The jump and collective diffusion coefficients are derived analytically. Comparison of the analytical forms with Monte Carlo data shows a good agreement.

DOI: 10.1103/PhysRevB.66.054303 PACS number(s): 68.35.Fx, 64.60.Cn

I. INTRODUCTION

Lattice-gas (LG) models are widely employed to describe thermodynamic and kinetic properties of various physical systems. In general, two-dimensional (2D) models are useful for theoretical study of surface mass transport, while 3D models are appropriate to describe bulk phenomena, such as ionic conductivity, solid electrolyte transport, etc.

The general intention of early theories which concern LG transport (see, for example, Refs. 1–3) was to include the effect of strong particle-particle interaction in the mobility and in the diffusion coefficient. In these papers the kinetic problem was reduced to the calculation of the grand partition function and its derivatives with respect to chemical potential and interaction parameters. Unfortunately, these papers give a naive method for the analytical study of transport coefficients, since they ignore the effect of correlation in successive particle jumps. Sometimes such simplification is adequate, but not always. Thus, for example, the application of this approach to the problem of tracer transport gives a value for the tracer diffusion coefficient that is equal to the jump diffusion coefficient (i.e., the adatom mobility). But it is known that the tracer and the jump diffusion coefficients have different values, even in the simplest case of zero-value particle-particle interaction (see, for example, Refs. 4–6).

In the absence of particle-particle interactions, the importance of jump correlation (memory effect) for the tracer diffusion was explained in Refs. 4–6. Jump correlation is responsible for the prevailing tendency of a tagged particle to return to the previous residence site. It is just the site which is not occupied immediately after the tracer displacement. The other lattice sites are characterized with probabilities which correspond to the average concentration. Such ''back correlation'' lowers the effective jump frequency of the tracer while the collective and jump diffusion coefficients are not affected. Nevertheless, the analog of back correlation mechanism may arise and essentially lower the values of the above-mentioned diffusion coefficients when a strong interaction is present.

The effect of jump correlation on particle migration was studied in Refs. 7 and 8. A lattice with square symmetry and a strong repulsive interaction between particles in the nearest-neighbor (NN) positions was considered there. Due to strong repulsion, the lattice of equivalent sites is divided in two interpenetrating sublattices (almost filled and almost empty sublattices) when the particle concentration c is close to 1/2 per site [see Fig. 1(a)]. All sites of one sublattice have nearest neighbors (NN's) belonging to the other. The ordered $c(2\times2)$ structure is formed as a result of second-order phase transition. Particle jumps from the filled to the empty sublattice result in almost immediate backward jumps (back correlation). Such flip-flop displacements giving no contribution to mass transport are counted by uncorrelated jump theory as effective. It was shown[7] that only jumps of structural defects, i.e., vacancies (excess atoms) in filled (empty) sublattices are effective in diffusion and conductivity phenomena.

The results of the theory developed in Refs. 7 and 8 differ from those obtained within the assumption of uncorrelated particle motion.[1–3] The disagreement concerns mainly the range of the highly ordered state. The goal of the present paper is to generalize the theory of Ref. 7 to the 3D case and illustrate the importance of jump correlations. It follows from our consideration that the problem of mass transport in a well-ordered state of cubic lattice is reduced to the kinetics of rarefied gas of the defects. The present analysis shows that single defects as well as dimer configurations of defects give dominant contribution to mass transport, while trimers and more complex configurations are not effective. We obtain the range of parameters where correlation is important. Combined analytical and Monte Carlo (MC) simulation results make it possible to test and compare various theoretical approaches.

In addition to the works cited above, different approaches for mass transport in LG systems have appeared.[9–18] Most authors ignore the correlations, sometimes without sufficient reasons. Thus the second important goal of this paper is to emphasize the importance of correlation effects in the kinetics of lattice systems.

II. EQUILIBRIUM CONCENTRATIONS AND JUMP PROBABILITIES OF THE DEFECTS

We consider a cubic lattice-gas system with NN repulsive interactions. The corresponding Hamiltonian is given by

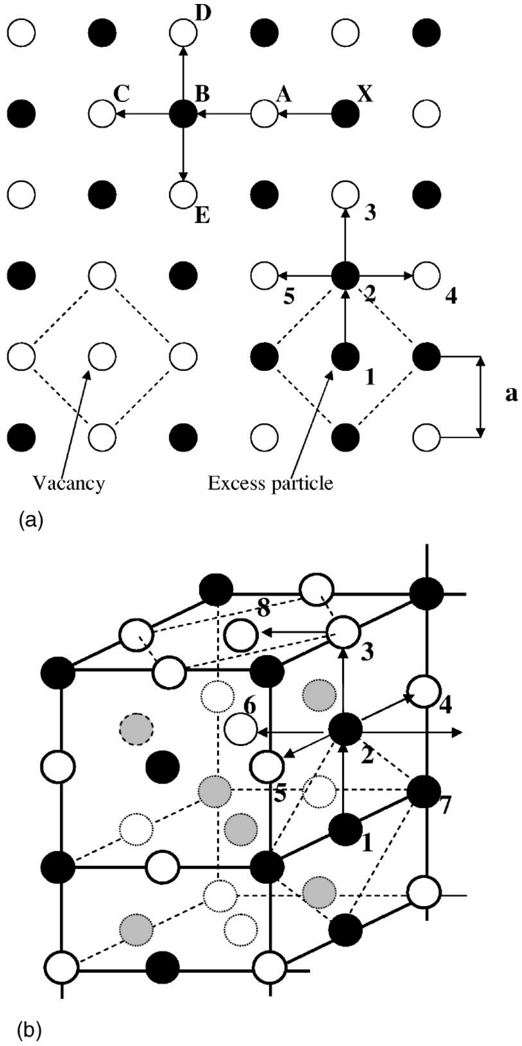

FIG. 1. Schematics of antiferromagnetic ordering in the vicinity of $c=1/2$. (a) Representation of 2D square lattice-gas model. Black and white circles indicate occupied and unoccupied lattice sites, respectively. The ideal ordering is distorted by the presence of two types of defects (a vacancy and excess particle are shown by arrows). (b) Schematic of cubic lattice-gas model. Black and gray circles show occupied, and white circles unoccupied sites. Two defects in sites 1 and 8 can be seen. The displacement of the defect in site 1 is possible only after a jump of one of the side particles. Jumps of side particle 2 to NN unoccupied sites are indicated by five arrows.

$$H=\sum_{\langle ij\rangle}\varphi n_i n_j, \tag{1}$$

where we use the variables of occupation numbers n_i with $n_i=1$ (0) for occupied (unoccupied) lattice site i; the notation $\langle ij\rangle$ implies the summation in Eq. (1) over NN sites and each pair enters the sum only once; φ is the interaction energy of the NN particles measured in units of kT.

The ideal zero-temperature $(\varphi\rightarrow\infty)$ structure for concentration $c=1/2$ is a sequence of empty and filled lattice sites. Filled sites form a face-centered-cubic lattice with a period of $2a$ [see Fig. 1(b)]. The lattice of empty sites having the same geometry is displaced by a with respect to the filled one. The ordering is formed spontaneously as a result of the strong repulsive interaction. The critical value of the interaction parameter φ is equal to 0.887. A filled site in the empty sublattice [site 1 in Fig. 1(b)] and an empty site in the filled sublattice [site 8 in Fig. 1(b)] represent two types of the "defects," i.e., the excessive particle and vacancy, respectively. Similar to the 2D case, defects of each type are away from one another by a distance of more than one lattice constant a, hence there is no direct interaction between them. Such favorable circumstance gives the possibility to obtain the defect concentrations in the case of equilibrium systems described by the statistical operator

$$\rho=Q^{-1}\exp\left\{\mu\sum_i n_i-H\right\}, \tag{2}$$

where μ is the dimensionless chemical potential, and the partition function Q is determined by the normalization condition $sp\{\rho\}=1$. Similarly as in Ref. 7 we can easily obtain the average occupancy of vacancies n^v and excess particles n^{ex} of each site of the filled and empty sublattices, respectively. They are given by

$$n^{v,ex}=e^{-3\varphi\mp(\mu-3\varphi)}=\mp\left(c-\frac{1}{2}\right)+\sqrt{\left(c-\frac{1}{2}\right)^2+e^{-6\varphi}}. \tag{3}$$

A simple way to derive Eq. (3) is as follows: When the defects are spaced a large distance apart, then the state of each of them can be described by its own statistical operator. For example, the state of the excess particle in site 1 [see Fig. 1(b)] is determined by ρ_1, which is given by

$$\rho_1=(Q_1)^{-1}\exp[\mu n_1-6\varphi n_1], \tag{4}$$

where the parameters μ and φ are the same as in Eq. (2). Then the average occupancy of site 1 is given by

$$n^{ex}=\langle n_1\rangle\simeq sp(\rho_1 n_1)\simeq e^{\mu-6\varphi}, \tag{5}$$

where the condition $n^{ex}\ll 1$ is used. A similar consideration for a vacancy results in

$$n^v=e^{-\mu}. \tag{6}$$

Combining Eqs. (5) and (6) with the "neutrality" condition $n^{ex}-n^v\equiv 2(c-\frac{1}{2})$ results in the defect concentrations as given in Eq. (3).

It can be easily seen from Eq. (3) that the total number of both defect types is minimum at half filling, i.e., at $c=\frac{1}{2}$. In this case it is given by $\frac{1}{2}N(n^v+n^{ex})=Ne^{-3\varphi}$, where N is the total number of lattice sites. We can see that the system tends to ideal ordering exponentially when $\varphi\rightarrow\infty$ (with decreasing temperature).

It is evident that the number of defects fluctuates in time. The encounter of two defects of different types results in their annihilation. In contrast, the process of pair creation increases the defect concentration. At equilibrium both processes have equal rates. The generation-recombination balance condition can also be used for obtaining equilibrium defect concentrations. In the following we will derive the generation-recombination terms. Their explicit form is used for the complete description of the defect kinetics.

To study the generation and recombination of the defects, the mechanism of particle jumps should be specified. We restrict ourselves to the model in which only jumps to the NN unoccupied sites are allowed. The probability of the displacements from filled site i to one of the nearest-neighbor empty sites j per unit time can be taken in the form

$$\nu_{ij}=\nu_0\exp\{\varepsilon_i\}, \tag{7}$$

where $\varepsilon_i=\varphi\Sigma_k n_k$, sites i and k are the nearest neighbors. Such dependence of the jump frequency on φ and n_k means that NN repulsive interaction ($\varphi>0$) facilitates overcoming the potential barrier by the jumping particle. This is not a unique choice of the jump frequency. Sometimes, an alternate model of particle jumps is used (see, for example, Refs. 13–15 and 19–21). Our formalism can be generalized to accommodate different jump frequencies. Within our approach, the effect of "saddle point"[9] can also easily be considered.

Each generation event is a result of a series of low probability elementary jumps. Some successions of jumps resulting in pair formation are shown schematically in Fig. 1(a) for the 2D case. A series of three jumps $X\rightarrow A, B\rightarrow C, A\rightarrow B$ results in creation of the vacancy and excess particle in sites X and C, respectively. This series of jumps we name path. Alternate paths resulting in pair creation (for example $X\rightarrow A$, $B\rightarrow D$, and $A\rightarrow B$) occur with probabilities exactly the same as the first one. It is shown in the Appendix that the rate P of each path in the 3D case is given by $\nu_0 e^{-5\varphi}$. The derivation employs the inequality $e^{-\varphi}\ll 1$. This inequality does not introduce strong restriction on the range of applicability of the theory. Thus, for example, the exponent $e^{-\varphi}$ is equal to 0.4 for the critical value of φ. Our theory is concerned only with the region below the critical point ($\varphi>\varphi_c$).

The overall probability of the vacancy (excess particle) generation in a given site is equal to the product of path probability times the number of paths. To obtain the number of paths, we use an observation that the excess particle position (with respect to vacancy position) is determined by a vector $\mathbf{r}=\mathbf{a_1}+\mathbf{a_2}+\mathbf{a_3}$, where $|\mathbf{a_i}|=a$. Each vector $\mathbf{a_i}$ may be oriented along positive and negative directions of any of three principal axes of the cubic lattice. A choice of three vectors $\mathbf{a_i}$ is restricted by the obvious conditions: $\mathbf{a_1}\neq-\mathbf{a_2},-\mathbf{a_3}$, and $\mathbf{a_2}\neq-\mathbf{a_3}$. All of these are satisfied when the following order of summing up in $\Sigma_{\mathbf{r}}$ is used: (i) $\mathbf{a_1}$ runs over six values; (ii) $\mathbf{a_2}$ runs over five values; (iii) $\mathbf{a_3}$ runs over five values when $\mathbf{a_1}=\mathbf{a_2}$ and only four values when $\mathbf{a_1}\neq\mathbf{a_2}$. As a result, we have $\Sigma_{\mathbf{r}}=126$. Hence the generation term is given by

$$G=126\nu_0 e^{-5\varphi}. \tag{8}$$

The recombination occurs through the same paths as the generation, but in the reverse order. Hence arguments similar to previous ones may be repeated to obtain the recombination term. It is given by

$$R=\nu_0 e^{\varphi}\sum_{\{\mathbf{r}\}} n_{\mathbf{i}}^{v} n_{\mathbf{i+r}}^{ex}. \tag{9}$$

For convenience, the stochastic variables $n_{\mathbf{i}}^{v}$ and $n_{\mathbf{j}}^{ex}$ of vacancies and excess particles are introduced in analogy with the occupation numbers of particles n_i. After averaging Eq. (9) over the ensemble and replacing $\langle n_{\mathbf{i}}^{v} n_{\mathbf{i+r}}^{ex}\rangle$ by the product of average values $n^v n^{ex}$, the balance condition $G=R$ is reduced to the form

$$n^v n^{ex}=e^{-6\varphi}. \tag{10}$$

As we see from Eq. (10), the product of vacancy and excess particle concentrations depends only on the interaction parameter φ but not on the jump mechanism. Such a situation is typical for equilibrium thermodynamic systems. A jump mechanism governs the time for attaining equilibrium but does not affect the equilibrium defect concentrations. Combining Eq. (10) with the "neutrality" condition results in the defect concentrations coinciding with Eq. (3).

To study the defect kinetics, not only the concentrations, but also the defect jump frequency should be obtained. Let us consider the displacements of isolated defects. Again, we use Figs. 1(a) and (b) for explanations. The displacement of the particle in site 1 is possible only if one of the adjacent sites becomes vacant. Hence the first stage of the defect displacement involves jump of side atom 2 to one of the free sites 3,4, etc. The probability of the first jump $2\rightarrow3$ per small time interval Δt is given by $\Delta t\nu_1$ ($\nu_k\equiv\nu_0 e^{k\varphi}$). The new particle arrangement has a very short lifetime (of the order of ν_5^{-1}) because each particle in sites 1 and 3 has five NN filled sites. For this time, any of them undertakes a jump to site 2 with probability equal to 1/2. The jump $3\rightarrow2$ returns the system to the initial state while the other jump $1\rightarrow2$ completes the defect displacement $1\rightarrow3$ to two lattice constants. The jump $1\rightarrow2$ represents the second stage of the defect displacement. The product of the probabilities of both stages is given by $\Delta t\nu_1\times\frac{1}{2}$.

As we see, the probability of the excess particle jump $1\rightarrow3$ (i.e., the jump to the next-NN site of the empty sublattice) per unit time is given by $\frac{1}{2}\nu_1$. The defect jump to the NN site of the empty sublattice (for example, $1\rightarrow4$) has a probability twice as high because two equivalent paths $1\rightarrow2\rightarrow4$ and $1\rightarrow7\rightarrow4$ contribute. The corresponding jump probabilities of the vacancies are given by $\frac{1}{2}\nu_0$ and ν_0.

III. DIFFUSION DUE TO JUMPS OF ISOLATED DEFECTS AND RECOMBINATION JUMPS

If we know the dependence of the defect concentrations and jump frequencies, we can easily now derive the collective and jump diffusion coefficients. Master equations for both species of defects are given by

$$\partial_t n_{\mathbf{i}}^{ex} = -\frac{1}{2}\nu_1 \sum_{\{\mathbf{s}\}} (n_{\mathbf{i}}^{ex} - n_{\mathbf{i+s}}^{ex}) + G - R,$$

$$\partial_t n_{\mathbf{i}}^{v} = -\frac{1}{2}\nu_0 \sum_{\{\mathbf{s}\}} (n_{\mathbf{i}}^{v} - n_{\mathbf{i+s}}^{v}) + G - R, \tag{11}$$

where vector $\mathbf{s}$ is given by $\mathbf{s} = \mathbf{a_1} + \mathbf{a_2}$ and the summation is over all possible orientations of $\mathbf{a}_{1,2}$ excluding $\mathbf{a_1} = -\mathbf{a_2}$.

After statistical averaging over equilibrium distribution ρ, Eqs. (11) are reduced to the trivial condition $G = R$. Let us now suppose that a small concentration inhomogeneity is imposed on the system $[n^{v,ex} \rightarrow n^{v,ex} + \delta n^{v,ex}(\mathbf{i},\mathbf{t})]$. Then the quantities $n_{\mathbf{i}}^{v,ex}$ can be changed by $\delta n^{v,ex}(\mathbf{i},\mathbf{t})$ in Eq. (11) and the $G-R$ terms, linearized in $\delta n^{v,ex}(\mathbf{i},t)$, are given by

$$\delta(G-R)^{ex} = -\nu_1 \sum_{\{\mathbf{r}\}} [\delta n^{ex}(\mathbf{i}) n^v + \delta n^v(\mathbf{i}+\mathbf{r}) n^{ex}] \tag{12}$$

for the first of Eqs. (11) and

$$\delta(G-R)^{v} = -\nu_1 \sum_{\{\mathbf{r}\}} [\delta n^{v}(\mathbf{i}) n^{ex} + \delta n^{ex}(\mathbf{i}+\mathbf{r}) n^{v}] \tag{13}$$

for the second one. When the perturbation $\delta n^{v,ex}$ is slowly varying in space (i.e., the characteristic length of inhomogeneity l is much greater than a), Eqs. (11) can be rewritten in a differential form as

$$\partial_t \delta n^{v,ex}(\mathbf{i},t) = D^{v,ex} \Delta \, \delta n^{v,ex}(\mathbf{i},t) + \delta(G-R)^{v,ex}, \tag{14}$$

where $\Delta \equiv (\partial/\partial \mathbf{i})^2$, and the diffusion coefficients of single vacancies D^v and excess particles D^{ex} are given by

$$D^{v(ex)} = 6a^2 \nu_{0(1)} . \tag{15}$$

The term $\delta(G-R)^{ex}$ in Eq. (14) is given by

$$\delta(G-R)^{ex} = -126\nu_1[\delta n^{ex}(\mathbf{i}) n^v + \delta n^v(\mathbf{i}) n^{ex}] - 85\nu_1 a^2 n^{ex} \Delta \, \delta n^v(\mathbf{i}), \tag{16}$$

and an explicit form for $\delta(G-R)^v$ can be obtained from Eq. (16) by formal changing indices $ex \rightarrow v$ and $v \rightarrow ex$. When the spatial gradients are small enough, i.e., $D^{v,ex} l^{-2} \ll 126\nu_1 n^{v,ex}$ the generation-recombination terms become dominant in Eq. (14) and the solutions $\delta n^{v,ex}$ must satisfy the condition

$$126\nu_1[n^v \, \delta n^{ex}(\mathbf{i}) + n^{ex} \, \delta n^v(\mathbf{i})] = 0. \tag{17}$$

Equation (17) describes the local equilibrium in the defect system. It relates perturbations of the defect densities when their space-time evolution is a slow process.

Subtracting the equation for vacancy evolution from the one for excess particles evolution given by Eq. (14) and using relation (17) we get the diffusion equation for concentration disturbance. It is given by

$$\partial_t c(\mathbf{r},t) = D_c \Delta c(\mathbf{r},t), \tag{18}$$

where the collective diffusion coefficient D_c is given by

$$D_c = 6D_0 \frac{n^v + e^{\varphi} n^{ex} + (85/3)e^{-5\varphi}}{n^v + n^{ex}}, \tag{19}$$

where $D_0 = \nu_0 a^2$. As we see, there are no thermodynamic relations (like the Kubo-Green formula) that are required to obtain the diffusion coefficient D_c. We have derived it considering migration and recombination of individual defects only.

If one knows D_c, the jump diffusion coefficient can be obtained using a Kubo-Green relation. It is given by $D_J = D_c[\partial \mu / \partial \ln(c)]^{-1}$. It follows from Eqs. (19) and (3) that

$$D_J = \frac{3}{c} D_0 [n^v + e^{\varphi} n^{ex} + (85/3)e^{-5\varphi}]. \tag{20}$$

It can be seen from Eqs. (19) and (3) that $D_c(c)$ is a nearly monotonic function. A maximum at $c = \frac{1}{2} + \frac{3}{85}(1 - e^{-\varphi})$ is noticeable only at comparatively low values of φ. In contrast, the jump diffusion coefficient has a deep minimum close to $c = 0.5$. More precisely, the minimum is at $c_{min} \approx \frac{1}{2}(1 - e^{-2.5\varphi})$ and $D_J(c_{min}) \approx 12 D_0 e^{-2.5\varphi}(1 + \frac{85}{6} e^{-2.5\varphi})$. The concentration c_{min} corresponds to a crossover in the transport mechanism from a vacancy to excess particle. The exponentially low value of $D_J(c_{min})$ is due to the low defect concentration at this point. We should add here that a similar minimum was obtained theoretically by Sato and Kikuchi[22] for 2D honeycomb ordered lattice.

There is an alternative procedure for the derivation of D_J. It is based on obtaining the response of the system on an external homogeneous field (see details in Ref. 7). The alternative formalism results in the expression for D_J exactly coinciding with Eq. (20). In this case the derivation employs only a kinetic approach but not a Kubo-Green relation.

Analytical formulas (19) and (20) describe diffusion coefficients in a short range of c close to 1/2. In the following we consider also the motion of more complex defect configurations. This will give the possibility to generalize the theory far beyond $c = 0.5$.

IV. CONTRIBUTION OF THE DIMER MOTION

It follows from Eq. (3) that the defect concentration is increased with increasing deviation of c from the stoichiometric value 1/2. Also, the probability of two or more defects to be NN or next NN of the corresponding sublattice is increased. Figure 2 illustrates the particle arrangement where two defects (excess particles in sites 1 and 2) are NN's of the empty sublattice. These two defects increase the jump probabilities of two adjacent particles in sites 3 and 8 considerably (to values ν_2). The arrows indicate four possible displacements of particle 3. After any of these jumps, the new configuration of the system is highly unstable because each of the three particles (two defects and the displaced

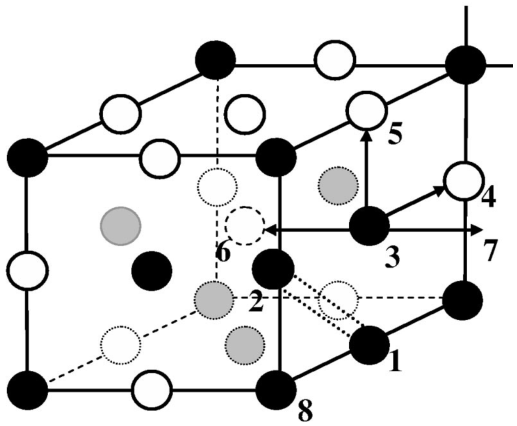

FIG. 2. Two defects in sites 1 and 2 are nearest neighbors in the empty sublattice. They form a NN dimer. Particles in sites 3 and 8 have high probability (equal to ν_2) to be displaced. Any jump of particle 3 shown by the arrow results in the dimer displacement with probability $\nu_2/3$.

particle) has five nearest neighbors. Thus three particles have equal probabilities per unit time (ν_5) to be displaced to site 3. The displacement of one of the particles at sites 1 or 2 results in the dimer displacement. A series of two particle jumps, which results in the dimer displacement, can be considered as a single dimer jump with the total probability equal to $\frac{1}{3}\nu_2$. The dimers bring to the kinetic coefficients a contribution comparable to or higher than that of single excess particles when the number of defects is sufficiently large, i.e.,

$$n^{ex}e^{\varphi}\geqslant 1. \tag{21}$$

Thus the contribution of the dimers is important when their small concentration is compensated by high mobility.

When condition (21) is fulfilled it is conceivabe to think that more complex defect configurations (for example, trimers and compact clusters of four and five defects) might also be effective in mass transport. Nevertheless, the present simple analysis shows that the motion of complex defects is rather rotational than translational. The following explanation elucidates this important point. Let us consider the most probable jumps of the trimer formed by excess particles in sites 1, 2, and 6. In contrast to the dimer case, we see here only one site (site 3) where a particle has the highest jump probability given by ν_3. After any of trimer jumps (with probabilities $\frac{1}{4}\nu_3$), a particle in site 3 has again the highest probability of jump. The site in which a particle has the highest jump probability does not change its position in the course of trimer displacements. The trimer performs many jumps involving the immobile site 3 before the disintegration. These strongly correlated jumps are not effective in mass transport similar to the case of flip-flop jumps. The above explanation also concerns the correlated motion of clusters formed by four and five defects.

We do not consider the contribution of complex configurations of the vacancies. The effect of their motion is negligible because of low mobility and small concentration. Thus, for example, the jump frequency of the dimer configuration of vacancies is somewhat lower than that of single vacancy while the concentration of dimers is much smaller. This is in contrast to the case of excess particles where the dimer high mobility make them competitive in mass transport.

As we see the motion of single defects and dimers of the excess particles prevails in mass transport in the range of low defect concentration. In fact, our consideration applies to that part of the phase diagram where ordering occurs (excluding only the boundary regions).

The theory developed in Sec. III can be easily generalized to take into account the effect of dimer motion. The derivation of the diffusion coefficients can be facilitated if we take into account two important factors. First of all, we should consider only the most probable jumps of the dimers, i.e., the jumps with the probability given by $\frac{1}{3}\nu_2$. Second, the positions of different defects are not correlated and their local concentration is determined by the local concentration of the particles as given by Eq. (3). A straightforward calculation employing the scheme outlined in Sec. III results in the diffusion coefficient given by

$$D_c=6D_0\frac{n^v+e^{\varphi}n^{ex}+\frac{8}{3}(e^{\varphi}n^{ex})^2+\frac{85}{3}e^{-5\varphi}}{n^v+n^{ex}}. \tag{22}$$

The terms in the numerator determine contributions of (i) isolated vacancies, (ii) isolated excess particles, (iii) dimers, and (iv) recombination jumps, respectively. The corresponding value of the jump diffusion coefficient is given by

$$D_J=\frac{3}{c}D_0\left\{n^v+e^{\varphi}n^{ex}+\frac{8}{3}(e^{\varphi}n^{ex})^2+\frac{85}{3}e^{-5\varphi}\right\}. \tag{23}$$

V. APPROXIMATION OF UNCORRELATED JUMPS

The theoretical schemes developed in Refs. 1–3 are based on the approximation of uncorrelated jumps (UJ's). It is assumed that a local particle flux can be described by small local perturbations in the statistical operator. The modified statistical operator $\tilde{\rho}$ is similar to the one given by Eq. (2) with the only difference that the chemical potential is no more constant, but a function slowly varying in space and time. The explicit form of $\tilde{\rho}$ is assumed to be given by

$$\tilde{\rho}=\tilde{Q}^{-1}\exp\left\{\sum_i \mu_i n_i-\sum_{\langle ij\rangle}\varphi n_i n_j\right\}, \tag{24}$$

and a local flux between NN sites i and j is determined by $\tilde{\rho}$ as

$$sp\{\tilde{\rho}[n_i h_j \nu_{ij}-n_j h_i \nu_{ji}]\}=\nu_0\langle h_i h_j\rangle e^{\mu}\frac{\partial\mu}{\partial\mathbf{i}}(\mathbf{i}-\mathbf{j}), \tag{25}$$

where $h_i=1-n_i$, the jump frequency ν_{ij} is given by Eq. (7). The expansion $\mu(\mathbf{j})=\mu(\mathbf{i})+(\partial\mu/\partial\mathbf{i})(\mathbf{j}-\mathbf{i})$ is employed in the course of derivation of Eq. (25).

The local flux density can be easily calculated using Eq. (25). It can be written in a form of Fick's law as $\mathbf{J}=-D_c\vec{\nabla}c$, where the collective diffusion coefficient is given by

$$D_c=D_0\langle h_i h_j\rangle \frac{e^{\mu}}{c}\frac{\partial\mu}{\partial(\ln c)}\equiv D_J\frac{\partial\mu}{\partial(\ln c)}. \tag{26}$$

Equation (26) is obtained under the assumption that the local relationship between μ and c $\{\mu(\mathbf{i})\equiv\mu[c(\mathbf{i})]\}$ is valid. At first, formula (26) was derived in Ref. 3. It connects explicitly the diffusion coefficients (D_c and D_J) with μ, $\partial\mu/\partial(\ln c)$, and $\langle h_i h_j\rangle$. The last quantity is the equilibrium probability of two NN sites to be vacant. To get an explicit dependence of the diffusion coefficients on c and φ, one needs only to calculate the partition function and its derivatives with respect to c and φ.

The diffusion coefficients in Eq. (26) obtained within the UJ theory can be calculated analytically in the range of highly ordered state, i.e., in the range where the defect concentrations are given by Eq. (3). To simplify calculations, it is convenient to rewrite Eq. (26) in an alternate form as

$$\begin{aligned} D_J&=D_0\langle h_i h_j\rangle\frac{e^{\mu}}{c}\\ &\equiv D_0\frac{1}{c}\langle e^{\varepsilon_i}n_i h_j\rangle\\ &\approx D_0\frac{1}{c}(1-n^{v})(1-n^{ex})[1+n^{ex}(e^{\varphi}-1)]^5. \end{aligned} \tag{27}$$

It follows from Eq. (27) that $D_J\approx 2D_0$ when $c=1/2, e^{\varphi}\gg 1$. At the same time, the value of the jump diffusion coefficient defined by Eq. (23) is equal to $6D_0e^{-2\varphi}$ at $c=0.5$. Thus the theory based on the assumption of uncorrelated jumps gives a value of D_j which is by a factor of $e^{2\varphi}/3$ higher than ours. The large disagreement between the different approaches can be easily explained. The UJ theory does not distinguish between effective and ineffective jumps. It deals with the average jump frequency which is much higher than the frequency of the effective jumps in the range of $0.5\geqslant c$. The difference between the results of both theories is not so pronounced when $c>0.5$, because the jumps of excess particles (effective jumps) prevail in that region.

Figure 3 illustrates the dependence of the jump diffusion coefficients given by Eqs. (23) and (27) on the concentration c. The difference between the two theories is larger for higher values of the interaction parameter φ. The corresponding data can differ by more than an order of magnitude. The difference, however, decreases for values of c which are away from the central point $c=0.5$. This is an obvious trend caused by the weakening of the correlation in a low-ordered state. Also, the significance of recombination mechanism can be seen in Fig. 3. The contribution of recombination jumps to D_J is noticable mainly in the vicinity of $c=0.5$ for $\varphi=1.5$. Comparison of theoretical and computer simulation data is given in the next section.

VI. COMPARISON WITH COMPUTER SIMULATIONS

To obtain the jump diffusion coefficient we use a computer simulation method described in Refs. 23 and 24.

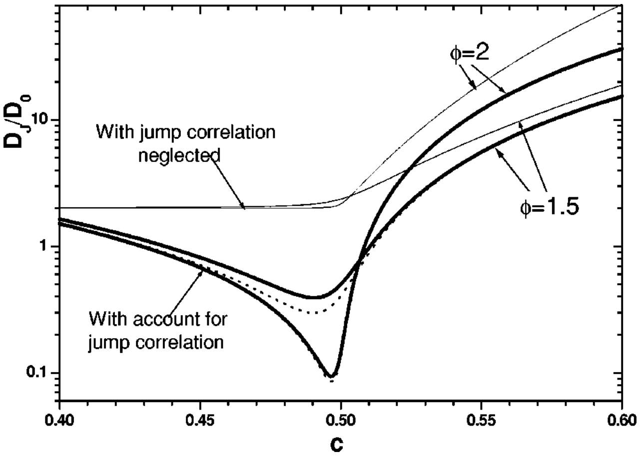

FIG. 3. Theoretical dependence of $D_J(c)/D_0$.Thick lines show results of the present paper approach [see Eq. (23)]. Dotted lines show the same but with recombination transport mechanism neglected. Thin solid lines show the dependence of Eq. (27), obtained within the uncorrelated jump theory.

Briefly, we add a few remarks. This scheme employs the probabilities of particle jumps given by Eq. (7). Both computer simulations and theory are based on the same model of random particle jumps, therefore a direct meaningful comparison is possible.

Initially particles are distributed randomly on the lattice. Then they are allowed to diffuse. Each particle is allowed to jump to one of its neighbor sites with a probability determined by the occupancy of the adjacent sites. Time is monitored in terms of MC steps. One MC step corresponds to N random interrogations of lattice sites (on average, one per site). The probability of each jump P_j cannot exceed 1. We define P_j as $P_j=e^{\varepsilon_i-5\varphi}$, where the interaction energy of jumping particle, ε_i, is always less or equal to 5φ. This choice of P_j ensures that $1\geqslant P_j$, and each MC step corresponds to an interval of real time equal to $t_S=e^{-5\varphi}/6\nu_0$.

The explicit form of t_S may be used to estimate the required number of MC steps (N_S) for various kinetic processes. For example, the jump of a given particle from a filled site to any NN site of the empty sublattice occurs with a duration of $(6\nu_0)^{-1}$. The corresponding value of N_S is given by $N_S=(6\nu_0 t_S)^{-1}=e^{5\varphi}$. This is just the number of MC steps required for the elementary displacement of a vacancy. As we see, the value of N_S grows exponentially (as $e^{5\varphi}$) when the interaction parameter is increased (the same is also true for the required computer time to carry out the calculation). Thus, for example, N_S is equal to 2.5×10^4 when $\varphi=2$. To study the diffusion motion of particles in the range of vacancy-controlled transport, this number should be taken much higher (at least by several orders).

A slow process of defect generation introduces another restriction on the minimum value of N_S. It follows from our previous consideration that the thermal generation governs the establishment of the equilibrium defect concentration in the vicinity of $c=0.5$, while outside this region the concentration of the defect majority is given by $2|c-0.5|$. The defect system can attain equilibrium when the number of defects generated during the simulation process is much higher

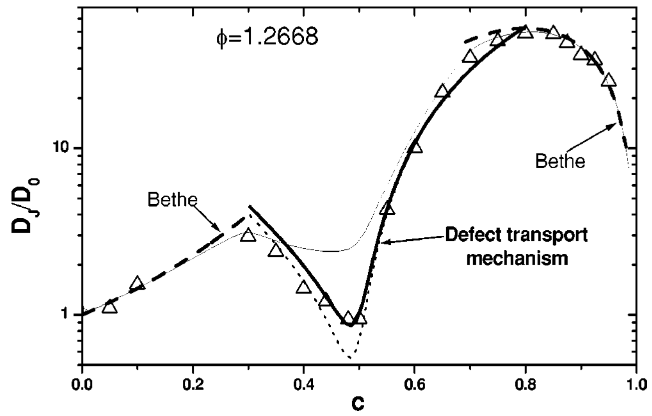

FIG. 4. The dependence of $D_J(c)/D_0$ for $\varphi = 1.2668$ ($T = 0.7T_c$). Symbols show results of MC simulations of particle migration on a lattice of size $N = 30\times 30\times 30$. A total of 1000 different realizations were averaged. The thin solid line shows the results of uncorrelated jump theory [computer calculations employing Eq. (26)]. Dash lines in regions $c<0.3$ and $c>0.7$ show the results of approximate calculations (Bethe approximation) using Eq. (26). The rest of the notation is the same as in Fig. 3.

than their equilibrium number. As a rough estimate, the defect concentration can be taken equal to $e^{-3\varphi}$ in the vicinity of $c=0.5$. Hence the corresponding criterion is given by $N_S t_S G \gg e^{-3\varphi}$. More explicitly, it is given by

$$N_S \gg e^{7\varphi}/21. \tag{28}$$

The exponential growth of N_S imposes restrictions on the range of interaction parameters which can be studied by means of computer simulation. We choose the maximum value of $\varphi = 1.2668$ that corresponds to $T = 0.7T_c$. This value of φ is sufficiently large to consider the particle arrangement (in the vicinity of $c=0.5$) as well-ordered since only 2% of lattice sites are occupied by defects. The simulation results for D_J/D_0 are shown in Fig. 4 by symbols. The results of the theory based on the defect transport mechanism are shown by solid line in the interval $0.3<c<0.8$. In general, a good agreement between the two is observed. To emphasize the effect of recombination jumps, we show the theoretical data with these jumps ignored (dotted line). As we see, the maximum contribution of this mechanism is of the order of 40% for $T=0.7T_c$. To our knowledge, the recombination mechanism of transport has not been previously considered in the literature.

The thin solid line in Fig. 4 represents the results of the UJ theory [see Eq. (26)]. The dependence of both chemical potential and average $\langle h_i h_j\rangle$ on c, which enter Eq. (26), were obtained by simulations in the grand canonical ensemble (absorption-desorption algorithm, see Refs. 23 and 24 for details). We see that the results given by the UJ theory disagree considerably with the MC modeling the particle jumps in the range of c close to 0.5. At the same time both approaches give almost identical results in the disordered region (far outside the middle part of the plot). The same conclusions follow from Ref. 25 where similar computer experiments were employed to study square lattice-gas transport.

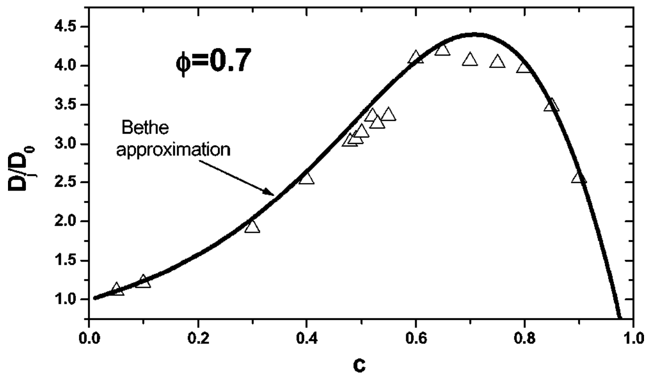

FIG. 5. The dependence of D_J/D_0 on the concentration c in the high-temperature (disordered) phase. The notation is the same as in Fig. 4.

Finally, we present the results of analytical calculations of D_J as defined in Eq. (26). The Bethe (quasichemical) approximation is employed to obtain the partition function (see details in Ref. 26). The result is shown by the dash lines in the side regions $c<0.3$ and $c>0.7$. As we see, this simple approximation is sufficient to reproduce with a good accuracy the dependence of $D_J(c)$ in the disordered region. At the same time, it should be emphasized that the Bethe approximation as well as defect transport theory are not applicable for the description of boundary regions of concentrations where the order-disorder transitions occur. The former is not good here because of insufficient accounting of the correlations, while the latter fails to describe high-density gas of the defects. The boundary regions require alternative approaches that is beyond our study.

To illustrate the accuracy of the Bethe approach for the study of disordered systems, we consider the case of low value of the interaction parameter $\varphi = 0.7 < \varphi_c$. This value of φ corresponds to the disordered state in the entire interval of c. Figure 5 illustrate a good agreement between the analytical and MC data.

VII. CONCLUSIONS

This work deals with the peculiarities of mass transport in the ordered 3D lattice-gas model under a repulsive potential. As in the case of 2D systems, we observe that the system goes into a well-ordered state when it reaches equilibrium. This is the outcome of a second-order phase transition, which is caused by strong particle-particle repulsion. Any changes of the ordered state induce microscopic forces, which restore the initial order. These forces give rise to correlation in particle motion in an ordered lattice.

The underlying idea of the theory employed here is to consider the motion of structural defects rather than that of individual particles. The defects can be considered as rarified gas of long-living quasiparticles, whose movement over the lattice entirely determines the mass transport. Elementary displacements of the defects being a result of two or three strongly correlated jumps of individual particles are not correlated. This factor facilitates the analytical derivation of the diffusion coefficients. Equations (22) and (23) show an explicit dependence of D_c and D_J on the concentrations and jump probabilities of the defects. The comparison between the analytical and the simulation data (see Fig. 4) shows that the model is quite adequate. At the same time we see that a theory that ignores jump correlations fails to describe mass transport in the ordered state.

ACKNOWLEDGMENTS

This work has been supported by the Greek-Ukrainian Bilateral Collaboration grant 8362/7.6.2001.

APPENDIX

For explanations, we employ Fig. 1(a) considering it a section of a 3D lattice. In the following we keep in mind that similar planes are present below and above the one shown in here. Let us consider a small time interval $\delta t \ll (\nu_0)^{-1}$. During this time the probability of jump $X \rightarrow A$ is equal to $\delta t \nu_0$. Further evolution of the particle arrangement where sites A and B are initially occupied is governed by a kinetic equation, which takes into account strong particle-particle interactions through the dependence of jump frequency $\nu_{i,j}$ on ε_i, i.e., on the filling of sites adjacent to the ith one. One can easily see that the particle in site A, which has five nearest neighbors, will jump to its previous position X for a small time interval δt_1 $[(\nu_0)^{-1} e^{-5\varphi} < \delta t_1 \ll \delta t]$ with a probability close to 1. Two flip-flop jumps $X \rightarrow A$ and $A \rightarrow X$ do not change the state of the system. Nevertheless, there is a small probability for a particle jump from site B to any of free sites (C,D,E, and to two free sites in perpendicular direction), while site A is occupied. After any of the last jumps, a particle in site A has a low probability to be displaced to site B and to complete the creation of a pair. Each series of jumps, which results in pair defect creation in sites X and C, X and D, etc., has very low probability when $e^{-\varphi} \ll 1$. Therefore the probability of each path can be calculated independently of the others.

It follows from the above that a system of coupled equations for the occupancy of sites A,B,C can be written as

$$\partial_t n_C = \nu_1 n_A n_B - \nu_5 n_C (1 - n_B),$$

$$\partial_t n_B = \nu_5 n_C (1 - n_B) - \nu_1 n_A n_B + \nu_4 n_A n_C,$$

$$\partial_t n_A = -2\nu_4 n_A n_C - \nu_5 n_A n_B, \tag{A1}$$

where $\nu_k \equiv \nu_0 e^{k\varphi}$, the derivatives for discontinuous functions n_A, n_B, and n_C are determined in a usual manner as

$$\partial_t n_i \equiv \lim_{\Delta t \rightarrow \infty} \frac{n_i(t+\Delta t) - n_i(t)}{\Delta t}. \tag{A2}$$

Equations (A1) connect the evolution of stochastic variables n_A, n_B, and n_C, which can take the value of either 1 or 0. It is convenient to describe the evolution of particle arrangement in terms of the corresponding probabilities. A simple algebraic manipulation and statistical averaging makes it possible to derive from Eqs. (A1) a closed system of two equations, which is sufficient for our purpose. It is given by

$$\partial_t \langle n_A n_B \rangle = -(\nu_1 + \nu_5) \langle n_A n_B \rangle + (\nu_4 + \nu_5) \langle n_A n_C \rangle,$$

$$\partial_t \langle n_A n_C \rangle = -(2\nu_4 + \nu_5) \langle n_A n_C \rangle + \nu_1 \langle n_A n_B \rangle. \tag{A3}$$

The initial conditions for the two Eqs. (A3) are given by $\langle n_A n_B \rangle (t=0) = 1$ and $\langle n_A n_C \rangle (t=0) = 0$. This choice corresponds to $n_C = 0$ and $n_A = n_B = 1$ when $t = 0$.

Solution of Eqs. (A3) is given by

$$\langle n_A n_C \rangle = \frac{\nu_1}{\lambda_1 - \lambda_2} (e^{\lambda_1 t} - e^{\lambda_2 t}),$$

$$\langle n_A n_B \rangle = \frac{1}{\nu_1} [\partial_t + (2\nu_4 + \nu_5)] \langle n_A n_C \rangle, \tag{A4}$$

where

$$\lambda_{1,2} = -\frac{\nu_1}{2} - \nu_4 - \nu_5 \pm \left[\left(\frac{\nu_1}{2} + \nu_4 + \nu_5 \right)^2 + \nu_1(\nu_4 + \nu_5) - (\nu_1 + \nu_5)(2\nu_4 + \nu_5) \right]^{1/2}.$$

The function $\langle n_A n_C \rangle (t)$, which is the probability of two sites (A and C) to be occupied, can be used to calculate the probability of pair generation. This probability per unit time (P) is given by the product of the probabilities of the first jump (equal to ν_0) and jump from site A to site B during the time when site C is filled. Thus we have

$$P = \nu_0 \nu_4 \int_0^\infty dt \langle n_A n_C \rangle (t).$$

A straightforward calculation employing inequality $e^{-\varphi} \ll 1$ results in

$$P = \nu_0 e^{-5\varphi}.$$

---

[1] A.A. Chumak and A.A. Tarasenko, Surf. Sci. **91**, 694 (1980).
[2] D.A. Reed and G. Ehrlich, Surf. Sci. **105**, 603 (1981).
[3] V.P. Zhdanov, Surf. Sci. Lett. **149**, L13 (1985).
[4] G.L. Montet, Phys. Rev. B **7**, 650 (1973).
[5] R.A. Takhir-Kelly and R.J. Elliott, Phys. Rev. B **27**, 844 (1983).
[6] J.W. Haus and K.W. Kehr, Phys. Rep. **150**, 263 (1987).
[7] A.A. Chumak and C. Uebing, Eur. Phys. J. B **9**, 323 (1999).
[8] A.A. Chumak and C. Uebing, Eur. Phys. J. B **17**, 713 (2000).

[9] A. Danani, R. Ferrando, E. Scalas, and M. Torri, Surf. Sci. **402-404**, 281 (1998).

[10] A. Danani, R. Ferrando, E. Scalas, and M. Torri, Surf. Sci. **409**, 117 (1998).

[11] T. Hjelt, I. Vattulainen, J. Merikoski, T. Ala-Nissila, and S.C. Ying, Surf. Sci. **300**, L501 (1997).

[12] T. Hjelt, I. Vattulainen, J. Merikoski, T. Ala-Nissila, and S.C. Ying, Surf. Sci. **402-404**, L253 (1998).

[13] I. Vattulainen, Surf. Sci. **412/413**, L911 (1998).

[14] I. Vattulainen, J. Merikoski, T. Ala-Nissila, and S.C. Ying, Phys. Rev. B **57**, 1896 (1998).

[15] I. Vattulainen, S.C. Ying, T. Ala-Nissila, and J. Merikoski, Phys. Rev. B **59**, 7697 (1999).

[16] A.A. Tarasenko, F. Nieto, L. Jastrabik, and C. Uebing, Eur. Phys. J. D **12**, 311 (2000).

[17] A.A. Tarasenko, L. Jastrabik, F. Nieto, and C. Uebing, Phys. Rev. B **59**, 8252 (1999).

[18] A.A. Tarasenko, F. Nieto, L. Jastrabik, and C. Uebing, Phys. Rev. B **64**, 075413 (2001).

[19] A.A. Chumak and C. Uebing, Surf. Sci. **476**, 129 (2001).

[20] R. Kutner, K. Binder, and K.W. Kehr, Phys. Rev. B **28**, 1846 (1983).

[21] A. Sadiq and K. Binder, Surf. Sci. **128**, 350 (1983).

[22] H. Sato and R. Kikuchi, J. Chem. Phys. **55**, 677 (1971). In this paper the path probability approach was employed. Since this approach is an approximate one, it is of interest to see how accurate it is. It is possible to compare directly the results of Ref. 22 and the theory based on the concept of defect transport. Following the approach developed in Ref. 7 and in the present paper we can easily obtain the value of D_J for the case of highly ordered honeycomb lattice in the vicinity of $c=0.5$. It is given by $D_J=(3/2c)D_0(n^v+e^{\varphi}n^{ex}+\frac{44}{3}e^{-2\varphi})$. The values of $n^{v,ex}$ are given by Eq. (3) with the only exception that 6φ in Eq. (3) should be changed by the factor 3φ. In Fig. 10(a) of Ref. 22 the quantities σT and ρ correspond to $(D_J/D_0)c$ and c, respectively. The curve $T=0.3$ corresponds to the value of $\varphi=10/3$ in the notation of our paper. This value of φ ensures a high ordering of the honeycomb lattice in the vicinity of $c=0.5$. A simple calculation for $c\approx0.5$ gives a value of σT that is by several times lower than that in Fig. 10(a) of Ref. 22. In our opinion, the version of path probability method employed in Ref. 22 is not sufficient to describe adequately the migration in a highly ordered state when a strong jump correlation occurs.

[23] R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).

[24] C. Uebing and R. Gomer, J. Chem. Phys. **95**, 7626 (1991).

[25] G.S. Bokun, Ya.G. Groda, C. Uebing, and V.S. Vikhrenko, Physica A **296**, 83 (2001).

[26] A. A. Tarasenko, P. M. Tomchuk, and A. A. Chumak, *Fluctuations in the bulk and on the surface of solids* (Naukova Dumka, Kiev, 1992), p. 252 (in Russian).