Fluctuations in an ordered $c(2\times2)$ two-dimensional lattice-gas system with repulsive interactions

P. Argyrakis,[1,*] A. A. Chumak,[2] and M. Maragakis[1]
[1]*Department of Physics, University of Thessaloniki, 54124 Thessaloniki, Greece*
[2]*Institute of Physics of the National Academy of Sciences, Prospekt Nauki 46, Kiev-28, MSP 03028, Ukraine*
(Received 16 December 2004; published 21 June 2005)

Fluctuations of the particle density in an ordered $c(2\times2)$ two-dimensional lattice-gas system are studied both analytically and by means of Monte Carlo simulations. The ordering is caused by a strong interparticle repulsive interaction resulting in the second order phase transition. The lattice of adsorption sites is divided into two sublattices (almost filled and almost empty sublattices) each of which contains a small number of structural "defects," i.e., vacancies and excess particles. The relaxation of the correlation function of fluctuations turns out to be governed by two different functions. This peculiarity is to be contrasted with the traditional fluctuation theory which predicts the existence of a single damping constant, determined by the collective diffusion coefficient. A specific thesis of the proposed approach is that transport phenomena in ordered systems may be described in terms of both displacements and generation-recombination of structural defects. Accordingly, the correlation function of fluctuations depends on diffusion coefficients of two defect species as well as on the generation-recombination frequency. Our theory reduces to the usual one when fluctuations occur under local equilibrium conditions, i.e., for a sufficiently large size of probe areas and not too great values of interaction parameter. The analytical results agree well with those obtained in the Monte Carlo framework.

DOI: 10.1103/PhysRevB.71.224304 PACS number(s): 63.70.+h, 68.35.Fx, 64.60.Cn, 05.10.Ln

I. INTRODUCTION

This paper is concerned with the theoretical description of a complex phenomenon, namely, fluctuations in ensembles of particles adsorbed on a crystal surface. A regular particle flow is realized as a sequence of random displacements of individual particles. As a result, fluctuation characteristics in adsorbate layers and kinetic coefficients, which describe macroscopic transport of the adsorbate, are interconnected as having the same origin. The fluctuations (i.e., spontaneous deviations of physical quantities from their average values) cause microscopic forces, which return the system to equilibrium. It is evident that the corresponding relaxation process does not depend on the nature of the initial disturbance (whether it is thermally generated or caused by external forces). Hence studies of fluctuations may be used for obtaining kinetic coefficients.

In the presence of external electric fields, adsorbate fluctuations generate electric noises [for example, noises of emission current in field emission microscopy (FEM) or tunnel current in scanning tunnel microscopy (STM)]. Hence experimental measurements of the current-current correlation function may provide valuable information about the adsorbate fluctuations. Usually, it is assumed that the collective diffusion coefficient is a unique physical quantity, which governs the decay of these fluctuations. Such consideration looks quite reasonable in the case of a spatially homogeneous adatom system when the characteristic size of the probe area is much greater than the correlation length determined by adatom-adatom interaction.

A simple method of obtaining collective diffusion coefficient based on measurements of the correlation function of emission-current fluctuations was developed and widely used in practice (see, for example, surveys of Gomer[1] and Barth[2]). Its theoretical foundation has been given in Ref. 3. Later on, a real-time technique employing ST microscopy has been used to measure the diffusion coefficient by means of monitoring the current fluctuations on the tip.[8] Similar to the FE microscopy, the STM technique is based on the expectation that any changes in particle density under the tip should induce fluctuations in the measured tunneling current.

Additionally, numerical investigations of fluctuations in probe areas can be used for obtaining diffusion coefficients by computer simulations of the adsorbate migration. All methods described above deal with microscopically small probe areas [of the order of 100 Å in the case of FE microscopy, 10 Å or less in the case of ST microscopy, and of the order of ten lattice constants in the case of Monte Carlo (MC) simulations]. Thus the question about the validity of the diffusion equation for such small sizes may arise.

Another aspect of the problem is connected with the particle-particle interactions. In the case of large interaction parameters (or low temperature) and suitable adsorbate concentration, the adatom system undergoes a phase transition. In what follows, we consider the case of second order phase transition when a lattice of adsorption sites is divided into two sublattices with different average occupation numbers. Macroscopically, this system may be considered as homogeneous. At the same time, the relaxation of concentration fluctuations behaves in a somewhat different way compared to the disordered case. During the fluctuation relaxation two distinct physical processes take place. Any local fluctuation of concentration is redistributed between two sublattices, thus forming a local equilibrium. The characteristic time of local equilibration is equal to that of the ordering (disordering) time of the adsorbate structure. Along with the local ordering, the adatom flux induced by the concentration gradient occurs. The flux intensity depends essentially on whether or not local equilibrium has been established. When the ordering-disordering process is fast enough, the mass transport is governed by the usual diffusion equation, which is determined only by the collective diffusion coefficient D_c

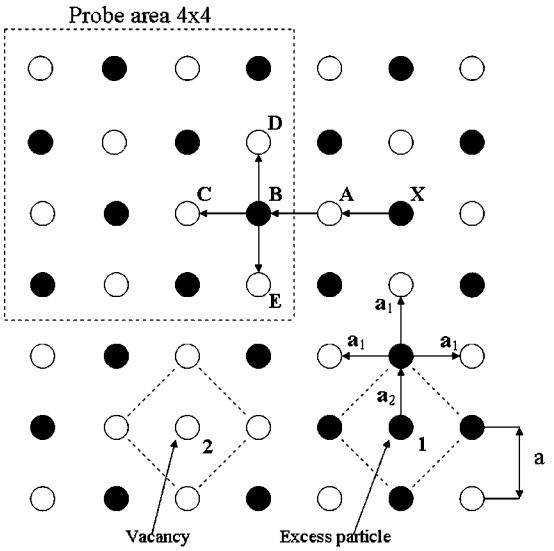

FIG. 1. Representation of 2D square lattice-gas model in the vicinity of half coverage. Black and white circles indicate occupied and unoccupied lattice sites. The ideal ordering is distorted by the presence of two types of defects (an excess particle and a vacancy are shown by arrows in sites 1 and 2, respectively).

(see Refs. 4–7). In the opposite case (slow ordering process), the characteristic time of the ordering enters evolution equations explicitly, thus bringing additional complexity to the analytical description of the system. The dissipation rate is described by a set of kinetic coefficients. The crossover between the two regimes is determined by the probe area size (for a given value of the interaction parameter). The collective diffusion controls the decay of fluctuations only in the case of sufficiently large probe areas.

Our paper presents an analysis of the particle density fluctuations for a specifically ordered lattice-gas system. It is shown that in the general case the fluctuation method cannot be employed directly for obtaining a collective diffusion coefficient. In what follows we show limiting cases when our approach is reduced to the traditional one.

II. MASS TRANSPORT CONTROLLED BY JUMPS OF DEFECTS OF THE ORDERED STRUCTURE AND THE LANGEVIN SOURCES OF FLUCTUATIONS

Our model deals with a square lattice-gas system. As an example, we consider a case of the ordered lattice-gas with square symmetry and repulsive nearest-neighbor (NN) interactions. The ordering is caused by second order phase transition, when the lattice of equivalent adsorption sites is divided into two sublattices. The ordering takes place in the vicinity of half-coverage ($\theta \approx 1/2$). Figure 1 shows schematically this system. Two types of defects, i.e., vacancies in the almost filled sublattice and "excess" particles in the almost empty sublattice, are responsible for transport phenomena. Average concentrations (per site) $n^{v,e}$ of both defect species were calculated in Refs. 5 and 6. They are given by

$$n^{v,e} = \mp\left(\theta - \tfrac{1}{2}\right) + \sqrt{\left(\theta - \tfrac{1}{2}\right)^2 + e^{-4\varphi}}, \tag{1}$$

where φ is the interaction energy between two nearest neighbors. Equation (1) together with the defect jump probabilities determines the state of the system and particle migration in it. It was shown previously[5–7] that any defect jump occurs as a pair of strongly correlated jumps of individual adatoms to elementary distances $\mathbf{a}_1$ and $\mathbf{a}_2$, where vectors $\mathbf{a}_{1,2}$ connect NN sites (see Fig. 1). The probability of individual particle jump (elementary jump) from filled site i to NN empty site j is assumed to be given by a jump frequency

$$\nu_{ij} = \nu_0 \exp[\epsilon_i], \tag{2}$$

where ν_0 is a constant, and ϵ_i is the interaction energy of the ith particle with NN particles. It is given by $\epsilon_i = \varphi \Sigma_{NN} n_m$, where φ is determined in units of kT, and $n_m = (1,0)$ is the occupancy number of the mth site, which is a NN of the ith site.

Thus the jump probability is assumed to be independent on the energy of the arrival state j. This practice is commonly used in modern Monte Carlo simulations (instead of the traditionally used METROPOLIS algorithm which uses the difference in the energy between the initial and the final state). It has been shown[8] that similar results for the domain size evolution are obtained for the two types of algorithms, but the single site energy algorithm has been suggested[9] to describe the kinetics more faithfully (it is believed to be a more realistic representation of the diffusive dynamics in experimental systems, although it is slower than the METROPOLIS algorithm). Also, Refs. 10–12 should be mentioned here in which the effect of a saddle point displacement (due to adatom-adatom interaction) on the diffusion coefficient was studied.

The probabilities per unit time of the vacancy and excess particle to jump to distance $\mathbf{s} = \mathbf{a}_1 + \mathbf{a}_2$ are given by $\frac{1}{2}\nu_0$ and $\frac{1}{2}\nu_0 e^{\varphi} \equiv \frac{1}{2}\nu_1$, respectively. Hence the changes of the occupancy numbers of both defect types for small time interval Δt may be written in the form of balance conditions as

$$\frac{n^e_{\mathbf{i}}(t+\Delta t) - n^e_{\mathbf{i}}(t)}{\Delta t} = -\frac{1}{2}\nu_1 \sum_{\{\mathbf{s}\}} (n^e_{\mathbf{i}} - n^e_{\mathbf{i}+\mathbf{s}}),$$

$$\frac{n^v_{\mathbf{i}}(t+\Delta t) - n^v_{\mathbf{i}}(t)}{\Delta t} = -\frac{1}{2}\nu_0 \sum_{\{\mathbf{s}\}} (n^v_{\mathbf{i}} - n^v_{\mathbf{i}+\mathbf{s}}). \tag{3}$$

As previously, 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 $\mathbf{a}_1 = -\mathbf{a}_2$.

Equations (3) describe the average probability for a set of variables $\{n^{e,v}_{\mathbf{i}}\}$ to be changed during time Δt. Fluctuations of the number of jumps between any two sites are ignored in Eqs. (3). At the same time, we intend to study fluctuations. Hence we should complement these equations with the corresponding fluctuation terms, i.e., with the Langevin sources. To do this, it is useful to represent the exact number of defect jumps $K^{e,v}_{\mathbf{i},\mathbf{i}+\mathbf{s}}$ from site $\mathbf{i}$ to site $\mathbf{i}+\mathbf{s}$ for time Δt as

$$\frac{1}{\Delta t} K^{e,v}_{\mathbf{i},\mathbf{i}+\mathbf{s}} = \frac{1}{2}\nu_{1,0} n^{e,v}_{\mathbf{i}} + \frac{1}{\Delta t}\delta K^{e,v}_{\mathbf{i},\mathbf{i}+\mathbf{s}}, \tag{4}$$

where δK is a fluctuation of the number of jumps by definition. The employing of Eq. (4) modifies the balance conditions for occupation of a given site by defects to a form

which is similar to Eqs. (3) but with the difference that the Langevin sources, $J_i^{ex,v}(t)$, appear in the right side parts

$$\frac{n_{\mathbf{i}}^{e}(t+\Delta t)-n_{\mathbf{i}}^{e}(t)}{\Delta t}=-\frac{1}{2}\nu_1\sum_{\{\mathbf{s}\}}(n_{\mathbf{i}}^{e}-n_{\mathbf{i}+\mathbf{s}}^{e})+J_i^{ex}(t),$$

$$\frac{n_{\mathbf{i}}^{v}(t+\Delta t)-n_{\mathbf{i}}^{v}(t)}{\Delta t}=-\frac{1}{2}\nu_0\sum_{\{\mathbf{s}\}}(n_{\mathbf{i}}^{v}-n_{\mathbf{i}+\mathbf{s}}^{v})+J_i^{v}(t); \qquad (5)$$

Eqs. (5) give a more general form of the balance equations suitable for studying fluctuations in the system.

The sources are defined in terms of fluctuations of the number of jumps as

$$J_{\mathbf{i}}^{e,v}(t)=-\frac{1}{\Delta t}\sum_{\{\mathbf{s}\}}[\delta K_{\mathbf{i},\mathbf{i}+\mathbf{s}}^{e,v}-\delta K_{\mathbf{i}+\mathbf{s},\mathbf{i}}^{e,v}], \qquad (6)$$

where the first term in square brackets is due to jumps from the $\mathbf{i}$th site to site $\mathbf{i}+\mathbf{s}$ and the second term describes the fluctuations of the backward jumps.

To study fluctuations it is sufficient to know the correlation function of the Langevin sources. The analysis is facilitated considerably in view of the fact that defect jumps may be considered as statistically independent (uncorrelated) in the case of a rarefied defect gas. In this case, a procedure described in Ref. 13 is applicable. The absence of correlation between different jumps means that only correlation of the same jumps takes place, i.e.,

$$(\Delta t)^{-2}\langle\delta K_{\mathbf{i},\mathbf{i}+\mathbf{s}}^{e,v}(t)\,\delta K_{\mathbf{i}',\mathbf{i}'+\mathbf{s}'}^{e,v}(t')\rangle\propto\delta(t-t')\,\delta_{\mathbf{i},\mathbf{i}'}\,\delta_{\mathbf{s},\mathbf{s}'}. \qquad (7)$$

The proportionality coefficient in the right-hand part of Eq. (7) may be easily calculated in view of the fact that the number of jumps between two sites for a small time interval Δt is equal to 0 or 1. The probability of two jumps is negligible. This results in

$$\langle(K_{\mathbf{i},\mathbf{i}+\mathbf{s}}^{e,v})^2\rangle\approx\langle K_{\mathbf{i},\mathbf{i}+\mathbf{s}}^{e,v}\rangle=\Delta t\frac{1}{2}\nu_{1,0}n^{e,v}. \qquad (8)$$

Making use of Eqs. (6)–(8) results in the following expression for the Langevin correlator:

$$\langle J_{\mathbf{i}}^{e,v}(t)J_{\mathbf{i}'}^{e,v}(t')\rangle=\nu_{1,0}n^{e,v}\delta(t-t')\sum_{\{\mathbf{s}\}}(\delta_{\mathbf{i},\mathbf{i}'}-\delta_{\mathbf{i},\mathbf{i}'-\mathbf{s}}). \qquad (9)$$

In the wave-vector domain, Eq. (9) is transformed to

$$\langle J^{e,v}(t)J^{e,v}(t')\rangle_{\mathbf{k}}=2n^{e,v}D^{e,v}k^2\delta(t-t'), \qquad (10)$$

where Fourier transformation with respect to variable $\mathbf{i}-\mathbf{i}'$ is defined by

$$f_{\mathbf{k}}=\sum_{\mathbf{i}-\mathbf{i}'}e^{i\mathbf{k}(\mathbf{i}-\mathbf{i}')}f(\mathbf{i}-\mathbf{i}'), \qquad (11)$$

and summing up is over all sites of the corresponding sublattice.

Equation (10) is derived considering $k\mathsf{a}$ to be a small quantity. Also, we have introduced the new quantity $D^{e,v}=4\nu_{1,0}\mathsf{a}^2$, which stands for diffusion coefficient of excess particles (e) and vacancies (v). Here a is the lattice constant shown in Fig. 1.

In the $\mathbf{k}$-representation, balance equations for fluctuations of the occupancies in both sublattices are given by

$$\partial_t\delta n_{\mathbf{k}}^{e,v}=-D^{e,v}k^2\delta n_{\mathbf{k}}^{e,v}+J_{\mathbf{k}}^{e,v}(t), \qquad (12)$$

where $\delta n_{\mathbf{k}}^{e,v}$ is a Fourier transform of the fluctuation of the defect occupancy number $n_{\mathbf{i}}^{e,v}-n^{e,v}$. For the sake of brevity, we have employed a symbol of derivative ∂_t in the left part of Eq. (12). Besides that, similarly to Eq. (10), we have retained the terms only quadratic in $k\mathsf{a}$.

As we see, the problem of fluctuations is reduced to the solution of two diffusion equations with statistically independent source terms. Hence, even in this simple case, fluctuations of the adsorbate density are characterized by two very different quantitatively diffusion coefficients D^e and D^v. This is in contrast to the case of disordered lattice gas.

The physical picture described above is not complete. It does not include effects of defect recombination and thermal generation. It is evident that the encountering of a vacancy and an excess particle results in their annihilation. Also, a pair of the defects (excess particle-vacancy) may be generated in the course of three strongly correlated adatom jumps. Three possible paths are shown schematically by arrows in Fig. 1. Initially, a particle occupying site X is displaced to empty site A. In this new configuration, a particle occupying site B may be displaced with small probability to one of the free sites C, D, or E. Then the $A\rightarrow B$ jump accomplishes the formation of the defect pair when a vacancy is in site X and an excess particle is in one of the sites C,D,E. The probability of each path was calculated in Refs. 5–7 for two- and three-dimensional lattices.

Hence Eqs. (12) should be complemented with the generation-recombination term $G-R$ and with the corresponding $g-r$ Langevin source term. The linearized $G-R$ term is given by[6,7]

$$G-R=28\nu_1(n^e\delta n_{\mathbf{k}}^{v}+n^v\delta n_{\mathbf{k}}^{e}). \qquad (13)$$

A system of equations for defect fluctuations, which takes into account the generation-recombination processes, is given by

$$i\omega\delta n^e=-D^ek^2\delta n^e-\Gamma(\delta n^en^v+\delta n^vn^e)+J^e+(g-r),$$

$$i\omega\delta n^v=-D^vk^2\delta n^v-\Gamma(\delta n^en^v+\delta n^vn^e)+J^v+(g-r), \qquad (14)$$

where $\Gamma=28\nu_1$. Fourier transform with respect to time variable is used in Eqs. (14). This results in changing $\partial_t\rightarrow i\omega$. Moreover, all fluctuating quantities in Eqs. (14) have to be considered as functions of the frequency ω and the wave vector $\mathbf{k}$. The correlation function of the Langevin sources may be expressed in terms of physical values, which enter Eq. (13). It is given by

$$\langle(g-r)_t(g-r)_{t'}\rangle_{\mathbf{k}}=56\nu_1\delta(t-t')n^en^v. \qquad (15)$$

As we see, in the presence of generation-recombination (GR) processes, fluctuations of different defect types become interconnected. The GR term takes into account the relaxation mechanism responsible for establishing local equilibrium in the defect system. Also, it can be interpreted as the

one determining the relaxation of the order parameter variations. When the GR term is dominating in Eqs. (14), a solution of Eqs. (14) must satisfy the condition of local equilibrium $\delta n^e n^v = -\delta n^v n^e$. The importance of the GR term depends on the value of the wave vector $\mathbf{k}$ and the average values of $n^{e,v}$. For estimation, let us consider the most important case when $\mathbf{k}$ is of the order of reverse size of the probe area, l^{-1}, and $n^e \approx n^v$. It is just the range of $\mathbf{k}$, which gives major contribution to fluctuations of the number of particles in the probe area. Hence the GR term is dominating when $\Gamma n^e > D^e k^2$. Taking into account the relation $n^e n^v = e^{-4\varphi}$, which follows from Eq. (1), we may easily see that the GR term is important when the characteristic distance between defects is of the order or less than the size of the probe area.

Concluding this section, our qualitative analysis includes size effect in the phenomenon of adsorbate fluctuations. In what follows, we analyze this point in more detail, both analytically and numerically.

III. FLUCTUATIONS IN PROBE AREA

A system of linear equations (14) may be easily solved with respect to functions $\delta n^{e,v}$. When these quantities are known, we may return to spatiotemporal variables and obtain fluctuations of the number of particles δN in a given probe area S, which includes $4l^2$ lattice sites. Thus we have

$$\delta N(t) = \frac{2}{N_T}\sum_{\mathbf{k}} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\omega t} \times \left[\sum_{\mathbf{i}\in S} e^{-i\mathbf{k}\mathbf{i}} \delta n^e(\mathbf{k},\omega) - \sum_{\mathbf{j}\in S} e^{-i\mathbf{k}\mathbf{j}} \delta n^v(\mathbf{k},\omega) \right], \quad (16)$$

where sites $\mathbf{i}$ and $\mathbf{j}$ belong to different sublattices, and N_T is the total number of lattice sites in the system.

As previously, the conditions of spatiotemporal uniformity of fluctuations are assumed. This imposes the following restriction on the correlation function of any fluctuating quantity $f(\mathbf{r},t)$[14]

$$\langle f_{\omega,\mathbf{k}} f_{\omega',\mathbf{k}'} \rangle = \pi N_T \delta_{\mathbf{k},-\mathbf{k}'} \delta(\omega+\omega') \langle f^2 \rangle_{\omega,\mathbf{k}}. \quad (17)$$

Taking into account Eqs. (10) and (14)–(17), we can easily obtain the analytical term for the particle number fluctuations in the probe area. It is given by

$$\langle \delta N(t)\, \delta N(0) \rangle \equiv \langle \delta N(t)^2 \rangle_t = \frac{2}{N_T}\sum_{\mathbf{k}} S_{k_x} S_{k_y} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\omega t} \langle (\delta n^e - \delta n^v)^2 \rangle_{\mathbf{k},\omega}, \quad (18)$$

where

$$S_{k_{x,y}} = 2\left[\frac{\sin(k_{x,y} l \mathrm{a})}{k_{x,y}\mathrm{a}} \right]^2 \quad (19)$$

and

$$\langle (\delta n^e - \delta n^v)^2 \rangle_{\mathbf{k},\omega} = 2k^2 \times \frac{\omega^2 (n^e D^e + n^v D^v) + k^2 (D^e - D^v)^2 \Gamma n^e n^v + n^e D^e (D^v k^2 + \Gamma n)^2 + n^v D^v (D^e k^2 + \Gamma n)^2}{\{\omega^2 - k^2 [D^e D^v k^2 + \Gamma (D^e n^e + D^v n^v)]\}^2 + \omega^2 [(D^e + D^v) k^2 + \Gamma n]^2}, \quad (20)$$

where $n = n^e + n^v$.

The intergrand has two pairs of symmetric poles in complex plane ω. These poles are located at the imaginary axis. It is straightforward to integrate analytically over ω by employing the residue theorem. The integration contour should be closed at infinity in the upper half plane in the case of $t > 0$ and in the lower half plane when $t < 0$. As a result, we will get two terms with different decay laws:

$$\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\omega t} \langle (\delta n^e - \delta n^v)^2 \rangle_{\mathbf{k},\omega} = e^{-\gamma_1 |t|} \left[\langle (\delta n^e - \delta n^v)^2 \rangle_{\mathbf{k},\omega} (\omega - i\gamma_1) \right]_{\omega \to i\gamma_1} + e^{-\gamma_2 |t|} \left[\langle (\delta n^e - \delta n^v)^2 \rangle_{\mathbf{k},\omega} (\omega - i\gamma_2) \right]_{\omega \to i\gamma_2}, \quad (21)$$

where $\gamma_{1,2}$ are positive functions of $\mathbf{k}$. The explicit form of these values may be easily obtained by employing Eq. (20). They are given by

$$\gamma_{1,2} = \frac{1}{2}(A \pm \sqrt{A^2 - B^2}), \quad (22)$$

where $A = [(D^e + D^v)k^2 + \Gamma(n^e + n^v)]$ and $B^2 = 4k^2 [D^e D^v k^2 + \Gamma (D^e n^e + D^v n^v)]$.

It follows from Eq. (21) that two different relaxation times govern the decay of fluctuations. The diffusion coefficients of both defect types as well as the recombination parameter Γ determine evolution of fluctuations. The relaxation times have very simple physical interpretation in the case of a small value of recombination rate Γn as compared to the diffusion rate: $D^e k^2 \gg \Gamma n$. Putting $n^e = n^v$, we have

$$\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\omega t} \langle (\delta n^{ex} - \delta n^v)^2 \rangle_{\mathbf{k},\omega} \approx n^e [e^{-D^e k^2 |t|} + e^{-(D^v k^2 + \Gamma n)|t|}]. \quad (23)$$

Equation (23) exhibits three different relaxation mechanisms. The first term in square brackets describes fast diffusion of the excess particles. The second term describes slow diffu-

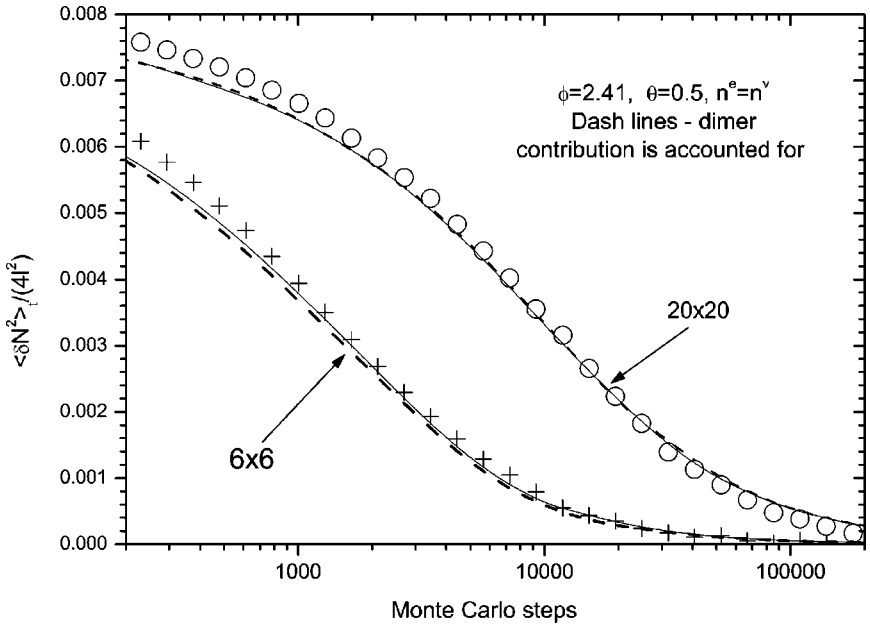

FIG. 2. Time dependence of the correlation function divided by the number of sites in probe area for $\theta=0.5$ and $\varphi=2.41$. Time is monitored in units of Monte Carlo steps. Symbols denote MC data, solid and dashed lines are obtained from Eq. (18). Dashed lines are obtained with the dimer jumps accounted for.

sion of vacancies accompanied with recombination of the defects. The traditional theory yields exponential dependence $e^{-D_c k^2|t|}$ only, where the collective diffusion coefficient D_c is given in our case by[5,6]

$$D_c = \frac{D^e n^e + D^v n^v}{n^e + n^v}. \tag{24}$$

As we see, neither γ_1 nor γ_2 are equal to $D_c k^2$.

In the opposite limit $D^e k^2 \ll \Gamma n$ we return to the traditional behavior of fluctuations. In this case the right-hand part of Eq. (21) is reduced to $(n^e+n^v)e^{-D_c k^2|t|}$, i.e., to the result followed from diffusion-controlled fluctuation theory. The reason is quite understandable. This limit corresponds to the physical picture where a local equilibrium is established due to fast generation-recombination processes.

It is evident that the relative contribution of fluctuations with a given wave vector $\mathbf{k}$ to the correlation function of Eq. (18) depends on time difference t and the size of the probe area l. With the increase of l or $|t|$ the actual range of wave vectors (centered at $\mathbf{k}=0$) is decreased and the traditional theory becomes applicable for the description of fluctuations.

IV. COMPARISON OF ANALYTICAL WITH MONTE CARLO DATA

Simulations of the particle migration were executed in a lattice-gas system of 200×200 sites. Probe areas imbedded in the whole lattice are oriented as shown in Fig. 1. We studied two sizes of probe areas, 20×20 and 6×6. We simulate random jumps of individual particles. The dependence of jump probabilities on the occupancy of the adjacent sites was determined by Eq. (2). Time was monitored in units of MC steps (MCS). In the course of one MCS each lattice site is interrogated once (on average) for the probability of a particle jump out of it. One MCS was chosen to correspond to $[4\nu_0(e^{2\varphi}+1)(e^{\varphi}+1)]^{-1}\approx 1/4\nu_0 e^{-3\varphi}$ of time.

The preparation of the initial state of the system consisted of three important points. We started from an ordered, checkboard, arrangement of the particles. Then we introduced randomly the defects (vacancies and excess particles), the number of which was calculated according to Eq. (1). After that, the particles were allowed to move randomly for 50 000 MC steps. This procedure ensures the lack of forming of domain walls in the system and allows it to reach a state of equilibrium, where there is essentially a homogeneous distribution of the defects. We have verified this visually, through snapshots of the system taken in various periods of time, from the initial state and for every 1000 MCS, for all the interaction parameters we have used. The study of fluctuations due to particle migration was started only after 50 000 MC steps. To get a correlation function, we have averaged over many independent runs (200 000 runs for the case of the 6×6 probe area and 50 000 runs for the case of the 20×20 probe area).

Figure 2 shows the dependence of the correlation function on time. The case of half coverage ($\theta=0.5$) is considered. MC and analytical data given by Eqs. (18) and (20) are shown in symbols and solid lines, respectively. In general, we see a good quantitative agreement of both approaches. A noticeable discrepancy in the range of small times may be easily understood. It is the time interval where the value $\nu_{0,1}t$ is not large ($\nu_{0,1}t\leqslant1$) and fluctuation phenomena should be described through kinetic theory but not by means of hydrodynamic equations (14). In other words, the applicability of Eqs. (14) is doubtful in this range.

Also, we consider fluctuations at θ somewhat higher than 0.5. It is the coverage where $n^e/n^v=e^{\varphi}$. In its explicit form it is given by $\theta=0.5+e^{-2\varphi}\sinh\varphi/2$. The results are shown in Figs. 3 and 4. The discrepancy between the theoretical and MC data is of the order of 10%–20%. But the difference between the two becomes much less evident when we take into account the contribution of dimer configurations of excess particles to mass transport. Each dimer consists of a pair of corresponding defects, which are occasionally NN or next NN in the almost empty sublattice (see more details in Refs.

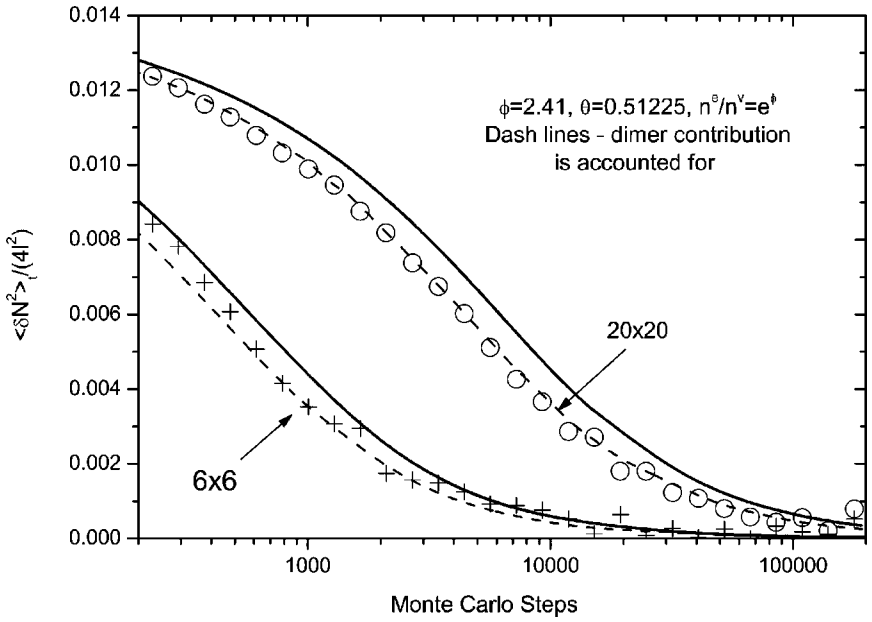

FIG. 3. The same as in Fig. 2 for $\theta = \frac{1}{2} + e^{-2\varphi} \sinh \varphi/2$ and $\varphi = 2.41$.

6, 7, and 15). The modification of our theory in order to take into account the contribution of dimer configurations is reduced to changing the diffusion coefficient of excess particles D^e by the form $D^e(1+\frac{4}{3}e^{\varphi}n^e)$. The increase of D^e due to dimer contribution in cases of $\varphi = 2.41$ (Fig. 3) and $\varphi = 3$ (Fig. 4) amounts to 40% and 30%, respectively. The corresponding analytical data for fluctuations shown in Figs. 3 and 4 are also different. A good agreement between the theory and computer simulations is observed only in the case where dimer jumps are accounted for (dashed lines). (Similarly to the case of $\theta = 0.5$, a noticeable disagreement of analytical and MC curves for areas of 6×6 sites in the early time domain can be seen.)

The contribution of dimer displacements to fluctuations is not significant at $\theta = 0.5$. We see in Fig. 2 that the dashed line is almost merged with the solid one for large size areas of 20×20 sites and is very close to the solid lines for the probe area of 6×6. It is because the dimer concentration is very low at this specific coverage (of the order of $e^{-4\varphi}$ per site), which corresponds to maximum ordering of the lattice-gas system.

Up to here, we have considered the contribution of high-probability defect jumps to diffusion. The corresponding jump frequencies were given by $\frac{1}{2}\nu_0$ for vacancy jumps, $\frac{1}{2}\nu_1$ for excess particle jumps, and $\frac{1}{3}\nu_2$ for dimer jumps. The mass transfer in the course of GR jumps was tacitly ignored in spite of the fact that any GR jump is undertaken as a result of adparticle displacements in three lattice constants. The effect of adparticle displacements in the course of recombination jumps may be considered by introducing additional diffusion terms to the equations for fluctuations, Eqs. (14). The scheme of derivation of the additional terms is outlined in Ref. 7 for the three-dimensional lattice and will not be repeated here. The modified equations are given by

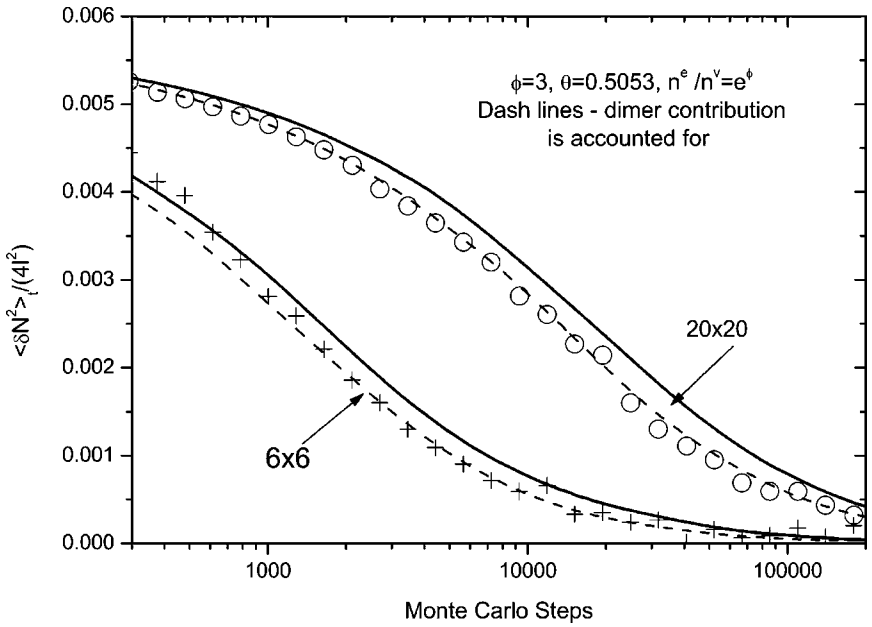

FIG. 4. The same as in Fig. 3 for $\varphi = 3$.

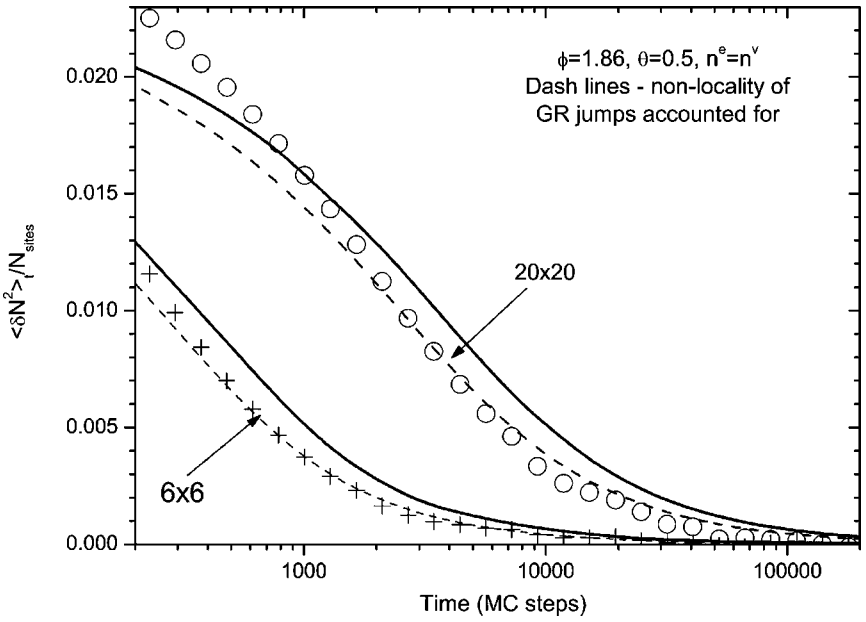

FIG. 5. The same as in Fig. 2 for coverage $\theta=0.5$ and $\varphi=1.86$. Dashed lines show theoretical results with account for particle displacements in the course of GR jumps.

$$i\omega\delta n^e = -D^e k^2 \delta n^e + \frac{39}{28}\Gamma a^2 k^2 n^e \delta n^v - \Gamma(\delta n^e n^v + \delta n^v n^e) + J^e + (g-r)^e,$$

$$i\omega\delta n^v = -D^v k^2 \delta n^v + \frac{39}{28}\Gamma a^2 k^2 n^v \delta n^e - \Gamma(\delta n^e n^v + \delta n^v n^e) + J^v + (g-r)^v. \tag{25}$$

The additional terms in the right-hand parts of Eqs. (25) are of no importance at large values of the interaction parameter φ. For example, at $\theta=0.5$ and $\varphi=2.41$ these terms being proportional to $e^{-\varphi}\ll 1$ may be disregarded. At the same time, they become competitive at comparatively small values of φ (but still greater than φ_c) due to the large numerical coefficient. A large value of the coefficient arises from the many possible paths, by which the recombination of a given defect may occur.

GR jumps modify the collective diffusion coefficient D^c, which is no longer determined by Eq. (24). The collective diffusion coefficient may be obtained from Eqs. (25) by the method described in Ref. 7. It is given by

$$D^c = \frac{D^e n^e + D^v n^v + 78\nu_{-3}a^2}{n^e + n^v}, \tag{26}$$

where $\nu_{-3}=\nu_0 e^{-3\varphi}$. Besides that, the GR source of fluctuations in the first of Eqs. (25) is different from that in the second equation. This is in contrast to Eqs. (14), where the same GR sources are involved in both equations. The difference is explained by the nonlocality of each GR event. The nonlocality means that the defects in any generated or recombined pair are spaced in three lattice constants (see explanations to Fig. 1). Therefore the corresponding sources are not δ-correlated in a spatial domain. Hence the correlators differ from those given by Eq. (15). Repeating the arguments employed for derivation of Eq. (10), we find

$$\langle (g-r)_t^{e,v}(g-r)_{t'}^{e,v}\rangle_{\mathbf{k}} = 2\Gamma n^e n^v \delta(t-t'),$$

$$\langle (g-r)_t^{e}(g-r)_{t'}^{v}\rangle_{\mathbf{k}} = 2\Gamma n^e n^v \delta(t-t')\left(1-\frac{39}{28}a^2k^2\right). \tag{27}$$

The right-side term in the second Eq. (27), which is dependent on k, arises from the small nonlocality described above.

The solution of the system of Eqs. (25) is similar to the solution of Eqs. (14). The complication of equations for fluctuations and modification of the GR Langevin sources given by Eqs. (27) does not introduce principal difficulties in calculations of the correlation function $\langle \delta N^2\rangle_t$. The results are shown in Fig. 5 for $\theta=0.5$. A distinct effect of the nonlocality of GR jumps on fluctuations for a small value of the interaction parameter ($\varphi=1.86$) can be seen. A good agreement of the theory and MC simulations is reached within the theory of nonlocal GR processes only. Thus it may be concluded that MC simulations help in pointing out the necessary modifications of the theory. Also, Fig. 5 shows that our analytical calculations are sufficiently accurate even close to the phase transition (the interaction parameter used in Fig. 5 is only 5.5% greater than the critical value, $\varphi_c\approx 1.76$). This is because the defect concentration is still low, in spite of the proximity of φ to the critical value. It follows from Eq. (1) that the defect number amounts for only 2.4% from the total number of lattice sites in this case.

We have also considered fluctuations at a specific coverage, $\theta=0.5-e^{-2\varphi}\sinh\varphi/2$, where $(n^e/n^v)=e^{-\varphi}$. It is the coverage (symmetric to the case shown in Figs. 3 and 4) where the adatom mobility has a deep minimum.[16] Hence the influence of nonlocality on the collective diffusion [i.e., the contribution of the third term in the numerator of Eq. (26)] is the most significant. A similar strong effect on fluctuations may be expected. We see in Fig. 6 that the difference between data obtained from the two versions of the theory reaches 30% in some regions. Figure 6 shows a good agreement of

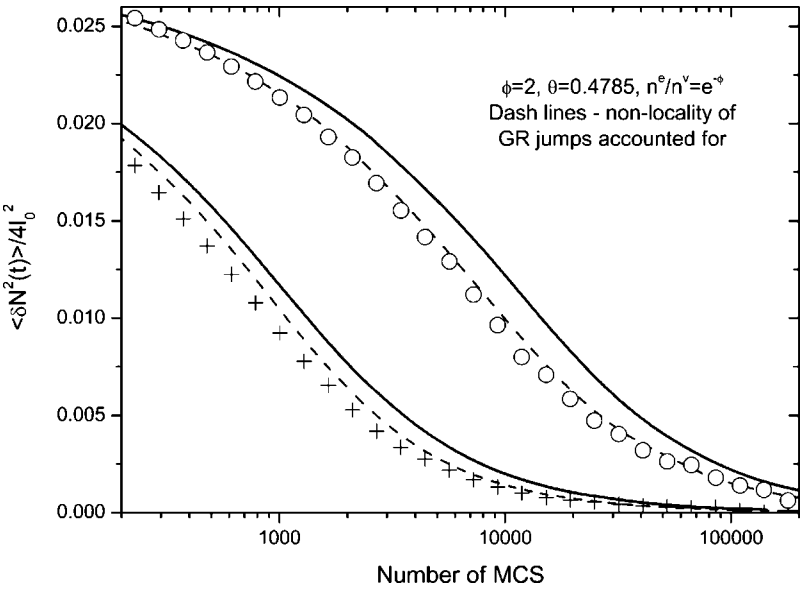

FIG. 6. The same as in Fig. 5 for coverage $\theta=\frac{1}{2}-e^{-2\varphi}\sinh\varphi/2$ and $\varphi=2$.

MC simulations with the version of the theory accounting for the nonlocal nature of GR events.

Figures 2–6 explain the details of adatom kinetics, which may be studied by the comparison of MC and analytical data. At the same time it is not clear how these results compare to the ones given by the traditional approach, which is based on the diffusion equation. For practical purposes, it is important to know the range of the validity of the traditional method. To compare the two, we will express the correlation function obtained by the traditional theory in a form, which is similar to Eq. (18). It is given by

$$\langle \delta N^2\rangle_t = \langle \delta N^2\rangle_{t=0}\frac{a^2}{4\pi^2 l^2}\int dk_x dk_y S_{k_x} S_{k_y} e^{-D_c k^2|t|}$$

$$= \langle \delta N^2\rangle_{t=0} I^2(\tau), \tag{28}$$

where $\tau=|t|D_c(la)^{-2}$,

$$I(\tau)=\frac{2}{\pi}\int_0^\infty dx\left(\frac{\sin x}{x}\right)^2 e^{-\tau x^2}.$$

We can see from Eq. (28) that the normalized correlation function of fluctuations $\langle \delta N^2\rangle_t/\langle \delta N^2\rangle_{t=0}\equiv I^2(\tau)$ is a universal function of dimensionless time τ only. In other words, this function depends on the size of the probe area and the collective diffusion coefficient not separately, but via the combination defining τ. The asymptotic value of $I^2(\tau)$ is given by $1/(\pi\tau)$ for $\tau\gg 1$; when $\tau=0$ we get $I^2=1$.

It is straightforward to obtain the ratio $\eta(t)\equiv\langle \delta N^2\rangle_t/\langle \delta N^2\rangle_{t=0}$ for our model of the ordered lattice-gas. A value of

$$\langle \delta N^2\rangle_{t=0}=2l^2(n^e+n^v) \tag{29}$$

should be substituted there. In the case of noninteracting lattice-gas $\langle \delta N^2\rangle_{t=0}=4l^2\theta(1-\theta)$. The ratio η may be plotted as a function of τ, thus providing direct comparison with the universal function $I^2(\tau)$. Figure 7 illustrates the ratio $\eta(\tau)$ for a set of interaction parameters and sizes of probe areas. The case where $\theta=0.5$ is considered. The curve $I^2(\tau)$ almost coincides with that for $\varphi=2$ and a probe area of 20×20 sites. At the same time, we see that the increase of φ or decrease of l results in significant discrepancy between our theory and the traditional approach.

Similar graphs for MC data are shown in Fig. 8. $\langle \delta N^2\rangle_{t=0}$ was determined by Eq. (29). To obtain τ, we have used the theoretical value of the collective diffusion coefficient given by Eq. (24). Similarly to the previous figure, we see considerable deviations of MC data from the universal curve. Moreover, MC graphs have no tendency of merging at $\tau\to 0$. This is in accordance with the observation that hydrodynamic description of fluctuations is not applicable to the adatom system at small times.

The asymptotic values of η $(\tau\to\infty)$ coincide with the ones given by the traditional approach. This can be easily explained. It is the case where only small-value wave vectors contribute to the correlation function of Eq. (18). Hence the diffusion terms in Eqs. (14) and (25) are small when compared to GR terms. Thus the local equilibrium is established in the defect system and the decay of fluctuations is governed by the diffusion equation, which contains a collective diffusion coefficient as the unique relaxation parameter.

It should be emphasized that the correlation function is very small just at large values of τ. Hence, in the case of highly ordered lattice-gas, obtaining D_c from asymptotic MC data is very problematic, if possible at all.

Figures 7 and 8 show that the traditional fluctuation method is not applicable to the ordered lattice-gas, where transport phenomena are controlled by the migration of structural defects of different types. A similar conclusion follows from the paper of Gomer and Uebing.[17] They have simulated migration in a lattice-gas system undergoing $p(2\times 1)$ ordering. It was shown that in the range of ordering, the diffusion coefficients obtained within the Cubo-Green approach are very different from those obtained by the fluctuation method (see Figs. 13–15 in Ref. 17).

Also, Refs. 18 and 19 should be mentioned. The traditional version of fluctuation method was employed there for obtaining the collective diffusion coefficient. We find a dras-

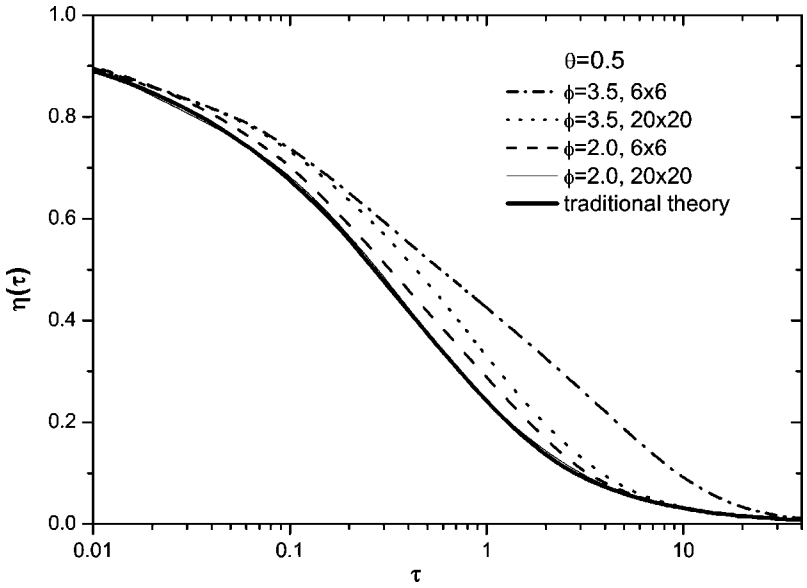

FIG. 7. Theoretical dependence of normalized correlation function on the dimensionless time τ [$\tau=|t|D_c(la)^{-2}$]. The plot $I^2(\tau)$ (thick solid line) is almost merged with the curve for $\varphi=2$, $2l=20$ (thin solid line).

tic disagreement of our data with the results of Refs. 18 and 19 in the range of high ordering. For example, when $\theta=0.5$ and the interaction parameter φ is nearby 3, the diffusion coefficient D_c given by Eq. (24) is smaller by an order of magnitude than the diffusion coefficient obtained in Refs. 18 and 19 (respectively, Figs. 6 and 8 there). The reason for this strong disagreement may be due to inadequate employing of the fluctuation method in the cited papers.

V. CONCLUSION

Concluding, we have studied density fluctuations in a system with strong particle-particle interactions, where kinetic coefficients and correlation functions may be obtained analytically with good accuracy. Thus it becomes possible to compare in detail the results of MC simulations with the corresponding theory. The agreement ensures the adequacy of the theoretical method we have used. We have analyzed the information about dissipative processes that is contained in the correlation function of fluctuations. This study may be useful for practical utilizing of the fluctuation method as an important tool of adsorbate diagnostics.

Our analysis shows the distinct peculiarities of fluctuation processes in the ordered system. The decay of fluctuations occurs in a more complicated manner than in the disordered case. It is shown that a direct use of the fluctuation method for the determination of diffusion coefficient from real experiments or MC simulations cannot be certain in the general case. On the other hand, the fluctuations contain information about any dissipation mechanism in the adatom system and it is possible to use the fluctuation studies for obtaining physical quantities describing relaxation. Our consideration explains how it can be done in specific cases. For example, the Fourier transform of the correlation function in Eq. (23) is represented by two terms with different relaxation parameters. It is a straightforward procedure to calculate this Fourier transform from computer simulations of particle migra-

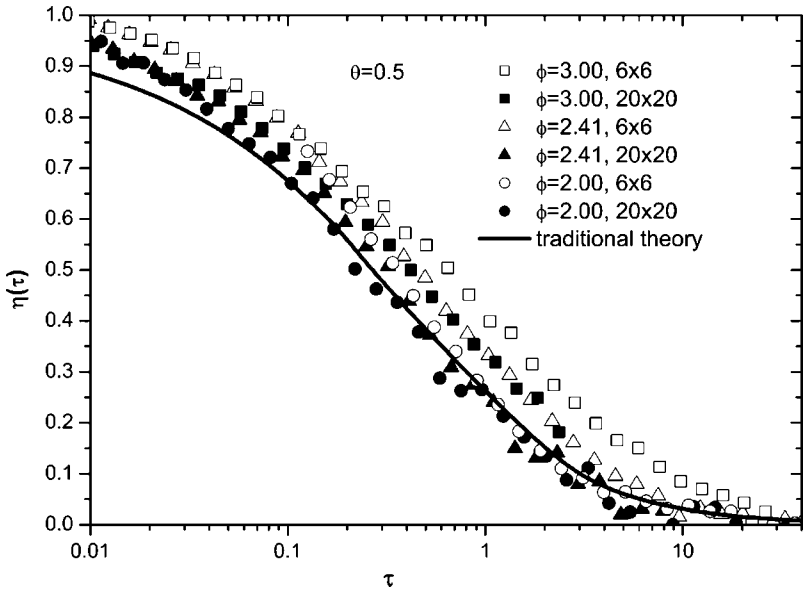

FIG. 8. MC data for normalized correlation function are denoted by symbols. The plot $I^2(\tau)$ is shown for comparison.

tion and get both functions. In such a way, any of the three quantities D^e, D^v, and Γ could be obtained by means of MC simulations only. The collective diffusion coefficient may be obtained in the usual way for sufficiently large probe areas and not too large an interaction parameter (see discussion of the results shown in Figs. 7 and 8).

The theoretical approach used here is not applicable in the range of very small times and very small probe areas, where hydrodynamic Eqs. (14) and (25) are not applicable. This case requires a more general consideration, which does not imply the value ka to be small. Our future work will cover this range, in order to attain the quantitative agreement between analytical and MC data at small times, which is still beyond our approach.

The model of particle jumps [see Eq. (2)] may be modified to take into account both the saddle-point effect and the energy of the final state. Such generalization may be done with ease as well as the consideration of lattice-gas systems with another symmetry.

ACKNOWLEDGMENT

This work was supported by NATO Collaborative Linkage Grant PST/CLG/979878.

*Corresponding author. Email address: panos@physics.auth.gr

[1] R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).
[2] J. V. Barth, Surf. Sci. Rep. **40**, 75 (2000).
[3] R. Gomer, Surf. Sci. **38**, 373 (1973).
[4] M. Lozano and M. Tringides, Europhys. Lett. **30**, 537 (1995).
[5] A. A. Chumak and C. Uebing, Ukr. J. Phys. **44**, 180 (1999).
[6] A. A. Chumak and C. Uebing, Eur. Phys. J. B **9**, 323 (1999).
[7] P. Argyrakis and A. A. Chumak, Phys. Rev. B **66**, 054303 (2002).
[8] M. C. Tringides, C. M. Soukoulis, and P. Levenberg, J. Phys.: Condens. Matter **5**, 4721 (1993).
[9] H. C. Kang and W. H. Weinberg, Phys. Rev. B **41**, 2234 (1990).
[10] A. A. Tarasenko, F. Nieto, L. Jastrabik, and C. Uebing, Phys. Rev. B **64**, 075413 (2001).
[11] A. Danani, R. Ferrando, E. Scalas, and M. Torri, Surf. Sci. **402–404**, 281 (1998).
[12] A. Danani, R. Ferrando, E. Scalas, and M. Torri, Surf. Sci. **409**, 117 (1998).
[13] A. A. Chumak and A. A. Tarasenko, Surf. Sci. **91**, 694 (1980).
[14] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1970).
[15] A. A. Chumak and C. Uebing, Eur. Phys. J. B **17**, 713 (2000).
[16] C. Uebing and R. Gomer, J. Chem. Phys. **95**, 7626 (1991). In this paper the minimum of particle mobility was obtained by means of MC simulations. Later on, it was interpreted as a crossover point from vacancy to excess particle transport mechanism. The corresponding theory was developed in Refs. 6 and 7 for two- and three-dimentional lattices, respectively.
[17] C. Uebing and R. Gomer, Surf. Sci. **381**, 33 (1997).
[18] A. A. Tarasenko, F. Nieto, L. Jastrabik, and C. Uebing, Eur. Phys. J. D **12**, 311 (2000).
[19] A. A. Tarasenko, L. Jastrabik, F. Nieto, and C. Uebing, Phys. Rev. B **59**, 8252 (1999).