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# Microscopic approach to the collective diffusion in the interacting lattice gas

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## Abstract

A variational approach to collective diffusion in the interacting lattice gas, based on kinetics of microscopic states of the system, is presented. The approach accounts for equilibrium correlations and is capable of predicting the coverage dependence of the diffusion coefficient  $D(\theta)$  in an analytic form. It provides a viable alternative to approaches based on a hierarchy of kinetic equations for correlation functions and in contrast to them is free of uncertainties often introduced by various truncation schemes. Applications to one-dimensional lattice gas models with increasing degree of complexity are presented. A two-dimensional gas with strong interparticle repulsive interactions is chosen to illustrate the application to a system with structural ordering. In each case, analytic predictions agree very well with the results of the Monte Carlo simulations. In particular, rapid changes/discontinuities of  $D(\theta)$ , discovered in numerical simulations, are confirmed and their origin understood.

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## 1. Introduction

Collective or chemical diffusion in systems consisting of interacting particles jumping from one binding site to another depends on the particle density. The

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interactions which affect the jump rates of particles between neighboring binding sites may also influence diffusion in systems in higher than one-dimension by inducing structural phase transformations which favor different geometrical configurations of the ensemble of particles at different densities. In two dimensions (2D), the effectiveness of the surface mobility of the adsorbed species in relation to that of other processes (adsorption, desorption, chemical reactions, etc.) determines the catalytic activity [1,2]. In nanostructuring [3], growth of nanostructures from beam deposited clusters is controlled by the cluster surface diffusion enabling them to aggregate into islands. The relevant experimental progress is reviewed in Refs. [4–6]. Collective diffusion in one-dimensional (1D) systems, once of rather academic interest only, has recently become practically relevant. Recent investigations of Au [7] (or Si [8]) adsorbed on top of a Si(1 1 1) $\sqrt{3} \times \sqrt{3}$ -Au chain structure show that the adatoms' diffusion is 1D, that the interaction between the adsorbed Au atoms is strongly repulsive (inhibiting simultaneous occupation of the adjacent sites by Au atoms), and that the atomic migration is affected by the density of the diffusing Au atoms. Helium atoms confined within a narrow interstitial channel within a triangular lattice of carbon nanotube bundles present another example of a strictly 1D “adsorbate” [9]. Equilibrium properties of a similar 1D gas of C<sub>60</sub> molecules encapsulated within carbon nanotubes were investigated within the lattice gas model [10].

Theoretical investigation of the rate of decay of long-wavelength particle density fluctuations in an interacting lattice gas—parametrized in terms of the chemical diffusion coefficient—is a challenging many-body problem encountering many difficulties, largely mathematical in nature. Analytic results are rare and the investigative tool of choice are Monte Carlo simulations. A work by Reed and Ehrlich [11], an early Gomer's review [12], and two more recent ones by Danani et al. [13] and Ala-Nissila et al. [14] summarize some of the efforts. Other relevant contributions are due to Kreuzer [15], who investigates the diffusion, adsorption, and desorption kinetics within the kinetic lattice gas model using a hierarchy of kinetic equations for many-site correlation functions and solving it by designing various, not always well controlled, truncation schemes.

In this review we report on another recently developed approach [16a] also based on the kinetic lattice gas model which allows to derive an analytic expression for the density dependence of the diffusion coefficient in interacting lattice gases with nearest neighbor interactions. In this approach, not tried before, the diffusion coefficient is extracted directly from equations describing kinetics of *microscopic* states of the system. We present in this short paper only the theoretical background, justify approximations used, signal some technical issues, and confront the analytic results obtained for selected 1D and 2D systems with the results of Monte Carlo simulations of diffusion in these systems. In 1D we progress from a relatively simple case applicable for high temperatures ( $k_B T \gg |J|$ , where  $J$  is a typical interaction energy between nearest neighbors), through a case of strong repulsive interactions ( $J \gg k_B T$ ) to the most complicated case of repulsive or attractive interactions of arbitrary magnitude. In 2D we concentrate on strong repulsive interactions for densities (coverages) around which the system is expected to be

structurally ordered. Technical details of the calculations involved are presented in Refs. [16a–c].

## 2. Theoretical background

Our approach is based on the kinetic lattice gas model. Specifically, we assume that the kinetics of the microscopic states of the lattice gas is due to a stochastic hopping of particles to neighboring sites, that no more than one particle can occupy simultaneously the same site, that only one particle in the gas hops at a time, and that the rates of the hops depend only on the instantaneous local environment of the hopping particle.

For example, in 1D with only the nearest neighbor interactions affecting the jumps, there are only four different jump rates: (i)  $W$  for a jump of an isolated particle:  $[\circ \bullet \rightarrow \circ \circ]$ ; (ii)  $\Gamma$  for a pair breaking hopping:  $[\bullet \bullet \rightarrow \circ \circ]$ ; (iii)  $R$  for a pair formation:  $[\circ \bullet \rightarrow \circ \bullet]$ ; and (iv)  $T$  for hopping in which one pair is broken and the other one formed:  $[\bullet \bullet \rightarrow \circ \bullet]$ . In Kreuzer's [15] approach  $\Gamma$  and  $R$  are the results of the initial and the target state interactions, respectively, and  $\Gamma R = TW$ . In 2D the number of possible rates is, of course, larger.

What differs our approach from all earlier approaches is that we extract the diffusion coefficient directly from the set of *microscopic* Master rate equations for the time-dependent probabilities  $P(c, t)$  that a *microstate*  $c$  of the lattice gas occurs at time  $t$

$$\dot{P}(c, t) = \sum_{c'} \{W_{c,c'} P(c', t) - W_{c',c} P(c, t)\}, \quad (1)$$

rather than from a hierarchy of kinetic equations for ensemble averaged quantities like particle density and many-site correlation functions. Consequently, we are free of uncertainties introduced by various truncation and expansion schemes necessary to deal with such equations. In Eq. (1),  $W_{c,c'}$ —the probability rate of a transition from a microstate  $c'$  to  $c$ —is either zero or equal to one of the four rates listed above.

For a lattice gas in 1D ( $N$  particles/atoms distributed among  $L$  sites) we identify a microstate as  $c \equiv [X, \mathbf{m}] = [X, m_1, m_2, \dots, m_{N-1}]$ , where  $X = \ell a$  specifies a lattice position of the “reference” particle and  $m_i a$  is a distance from it to the  $i$ th particle ( $i = 1, 2, \dots, N - 1$ ). The influence of the boundaries is avoided by letting  $\ell = 0, \pm 1, \dots, \pm \infty$  and imposing the periodic boundary conditions with periodicity  $La$ . The set of integers  $\mathbf{m} = [m_1, m_2, \dots, m_{N-1}]$ , referred to as a “configuration”, satisfies in 1D an ordering condition  $1 \leq m_1 < m_2 < \dots < m_{N-1} \leq L - 1$  (the first of the  $N$  particles is chosen as the reference particle). For example, for  $N = 3$ , the microstate  $\circ \circ \bullet \bullet \circ \circ \bullet \circ \circ \dots$  is identified as  $[X, m_1, m_2] = [2a, 1, 4]$  and the configuration is  $\mathbf{m} = [1, 4]$ . Similar scheme can be designed in 2D, with a slightly more complicated combinatorics [16a, 16b] due to the absence of any ordering condition.

Taking a lattice Fourier transform with respect to the position of the reference particle,  $X$ , allows to tie  $P_{\mathbf{m}}(k, T)$ —the transforms of the probabilities  $P(c, t)$ —to the

particle density fluctuations corresponding to a wavelength  $2\pi/k$ . The master equations can be written as  $\dot{P}_{\mathbf{m}}(k, t) = \sum_{\mathbf{m}'} M_{\mathbf{m},\mathbf{m}'}(k) P_{\mathbf{m}'}(k, t)$ , in which the  $k$ -space rate matrix  $M(k)$  (with elements  $M_{\mathbf{m},\mathbf{m}'}(k)$ ) has macroscopically large dimension, it is not Hermitian (because the jump rates in opposite directions may be different, like for  $\Gamma$  and  $R$  above) and its off-diagonal matrix elements corresponding to jumps of the reference particle depend on  $k$  through a factor  $\exp(\pm ika)$ . Diagonal matrix elements are negative,  $M_{\mathbf{m},\mathbf{m}} = -\sum_{\mathbf{m}'} W_{\mathbf{m}',\mathbf{m}}$ , and one can show [16,17] that all eigenvalues of  $M(k)$  are negative. The diffusion coefficient is evaluated as  $D(\theta) = \lim_{k \rightarrow 0} [\lambda(k)/k^2]$ , where  $-\lambda(k)$  is the diffusive eigenvalue of  $M(k)$ , i.e., the eigenvalue which vanishes in this limit. The density is defined as  $\theta = N/L$  so the eigenvalue must be evaluated for fixed  $L$  and  $N$ , before the thermodynamic limit is taken.

If  $\tilde{z}(k)$  is a left eigenvector of a non-Hermitian matrix  $M(k)$  then [16a,17], due to the detailed balance conditions, components of the corresponding right eigenvector are  $e_{\mathbf{m}}(k) = P_{\mathbf{m}} \tilde{z}_{\mathbf{m}}^*(k)$  where  $P_{\mathbf{m}}$  is the probability of a configuration  $\mathbf{m}$  in equilibrium (i.e.,  $P$  is the right eigenvector of  $M(k=0)$  corresponding to its vanishing eigenvalue). Therefore, the diffusive eigenvalue, in particular, can be written as  $-\lambda(k) = X(k)/Y(k)$  with

$$X(k) = \sum_{\mathbf{m}',\mathbf{m}} \tilde{z}_{\mathbf{m}'}(k) M_{\mathbf{m}',\mathbf{m}}(k) P_{\mathbf{m}} \tilde{z}_{\mathbf{m}}^*(k), \quad (2a)$$

$$Y(k) = \sum_{\mathbf{m}} P_{\mathbf{m}} |\tilde{z}_{\mathbf{m}}(k)|^2, \quad (2b)$$

and  $\tilde{z}(k)$  denoting, from now on, the diffusive left eigenvector of  $M(k)$ . Note that the presence of the denominator  $Y(k)$  assures that the overall normalization of  $P_{\mathbf{m}}$ 's and  $\tilde{z}_{\mathbf{m}}(k)$ 's is irrelevant.

To use Eq. (2) in practice “variational” candidates for  $\tilde{z}_{\mathbf{m}}k$ 's as well as for  $P_{\mathbf{m}}$ 's have to be proposed. In all 1D applications so far [16a, 16c] we have selected

$$\tilde{z}_{m_1, m_2, \dots, m_{N-1}}(k) \approx 1 + e^{iakm_1} + e^{iakm_2} + \dots + e^{iakm_{N-1}}. \quad (3)$$

It is, in fact, the exact diffusive eigenvector of  $M(k)$  for a system without interactions i.e., when all allowed transitions occur at the same rate  $W$  (in such case all configurations are equally probable in equilibrium:  $P_{\mathbf{m}} \equiv 1$  for all  $\mathbf{m}$ 's). Some other choices are possible but to approximate the diffusive eigenvector all components of  $\tilde{z}(k)$  should be equal to each other in the limit  $ka \rightarrow 1$ . In fact, designing different variational eigenvectors and confronting the obtained results with either experiment or numerical simulations seems to be a good way of gaining a deeper insight into the diffusion process, the task which is far from over. For a 2D system to be considered in Section 3.2 a slight modification away from the form given in Eq. (3) was necessary to describe the diffusion process correctly.

The choice of  $\tilde{z}(k)$  given in Eq. (3) allows to formulate simple combinatoric rules [16] to evaluate sums over configurations in  $X$  and  $Y$ . The key consideration is that each term in the denominator is proportional to a sum of all exponential terms  $\exp[ika(m_i - m_j)]$  involving relative positions of every two particles within a

configuration  $m$ . Using detailed balance, the numerator  $X(k)$  is cast into a form of a sum over pairs of configurations in which positions of all particles in a given pair are the same except for that of the hopping particle. Each of the two configurations involved is then divided into: (i) an active cell determining the actual  $k$ -dependence of the contribution and (ii) an environment. The active cell consists of two sites occupied by a hopping particle before and after the jump and the sites surrounding them whose occupation state determines the jump rate. The environment consists of all remaining sites occupied by particles not included in the active cell. In our 1D case there are only four possible types of active cells, shown at the beginning of Section 2, corresponding to the jump rates  $W, \Gamma, R$ , and  $T$  containing 1, 2, 2, and 3 particles, respectively. For each type of the active cell there is a macroscopically large number of possible environments but when contributions due to all configuration pairs  $\mathbf{m}, \mathbf{m}'$  are added in Eq. (2a) the  $k$ -dependence of the result is solely due to the particles within the active cells. For the choice of  $\tilde{z}$  given in Eq. (4) a set of rules can be worked out [16a] according to which terms  $\exp(-iak\ell)$  for occupied sites a cell must be combined in a prescribed way to give the  $k$ -dependent contribution due to such cell. It is then multiplied by a number of all possible environments consistent with this particular cell. This factor can be evaluated using arguments based on combinatorics. It depends on  $L$  and  $N$  which, together with such dependence in the denominator  $Y(k)$ , provides ultimately dependence on coverage  $\theta = N/L$  in the thermodynamic limit. In 2D the number of possible active cells is larger than in 1D, their actual number and types depend on the structural phase of the system for coverages of interest, but the evaluation procedure of  $X$  and  $Y$  is essentially the same.

### 3. Special cases and results

#### 3.1. Selected results for 1D

We consider the 1D lattice gas first. For the non-interacting system all  $P_{\mathbf{m}}$ 's are equal to 1, so such a choice can be tried at high enough temperatures at which the modifications of the rates by interactions are moderate (on a scale of  $k_B T$ ). Note that such a choice, in particular, violates the detailed balance condition between configurations related to each other by  $\Gamma$  and  $R$  transitions: ratio of their equilibrium probabilities is  $\Gamma/R$  rather than 1. The result is [16a]

$$D(\theta)/a^2 = W(1 - \theta)^2 + T\theta^2 + 2(2\Gamma - R)\theta(1 - \theta). \quad (4)$$

This simple dependence has expected limits:  $D = Wa^2$  for  $\theta \ll 1$  and  $D = Ta^2$  for  $\theta \approx 1$ . In the latter case diffusion is due to a random walk of isolated holes (unoccupied sites) jumping at a rate  $T$ .

Selecting more accurate candidates for  $P_{\mathbf{m}}$ 's, one should be guided by the detailed balance. A particularly simple case is the one in which particles at neighboring sites repel each other very strongly, i.e., when  $R \ll W$ . For simplicity, we assume that  $R = W$  and  $T = \Gamma$  (i.e., that the rates do not depend on the postjump environment

of the hopping particle). At  $\theta = 0.5$ , when the number of particles and holes is the same, the energy is minimized when particles and holes occupy alternating sites. Referring to two particles (holes) occupying neighboring sites as a particle (hole) pair, we have no pairs of either type in equilibrium. For  $\theta > 0.5$ , when the number of particles is larger than that of holes, the most probable configurations are those in which there are no pairs of holes but there are pairs of particles which break at the fast rate  $T$  causing a pair to migrate by  $2a$ . The diffusion coefficient, due to the random walk of particle pairs, is  $T(2a)^2 = 4Ta^2$  because any other jumps (leading to a creation of a hole pair and an extra particle pair) occur at a much slower rate  $R$ . Setting  $P_{\mathbf{m}} = 1$  for configurations  $\mathbf{m}$  with no hole pairs we get  $P_{\mathbf{m}} \propto (R/\Gamma)^n \ll 1$  for configurations with  $n$  hole pairs. Consequently, in both  $X$  and  $Y$  we sum only over configurations with no hole pairs (but allow for pairs and larger clusters of particles). For  $\theta < 0.5$ , however, it is not sufficient to merely use the particle-hole symmetry and modify the result obtained for  $\theta > 0.5$ . Although it is still true that configurations with no pairs of particles (this time) are most probable (and  $P_{\mathbf{m}} = 1$  for them) and that  $P_{\mathbf{m}} \propto (R/\Gamma)^n \ll 1$  for configurations with  $n$  pairs of particles, we must account in the numerator  $X$  also for configurations with one pair of particles ( $n = 1$ ) because they are converted into a no-particle-pair configuration at a fast rate  $\Gamma$  or into another one-particle-pair configuration at an equally fast rate  $T$ . These rates, present in  $M_{\mathbf{m},\mathbf{m}}$  in Eq. (2a), multiply  $P_{\mathbf{m}} \propto R/\Gamma$  resulting in contributions of order of  $R$ , comparable to the contributions of the order of  $W$  due to the no-particle-pair configurations. Taken together, the result for the diffusion coefficient is [16a]

$$D(\theta)/a^2 = \begin{cases} W/(1 - 2\theta)^2 & \text{for } \theta < 0.5, \\ T/\theta^2 & \text{for } \theta > 0.5. \end{cases} \quad (5)$$

Divergence at  $\theta$  approaching 0.5 from below is due to the fact that diffusion there is controlled by  $T$  which effectively was set equal to  $\infty$  when for  $\theta < 0.5$  we keep finite  $W$  together with  $W \ll T$ .

The model can be further refined to account for interactions of any strength and sign [16c]. In a given configuration each particle forms a bond with its neighbor to the right, say, (so there are  $N$  bonds in the system) which is either saturated when the nearest site is occupied or, otherwise, it is broken. If a saturated bond energy is  $J$  ( $J > 0$  for repulsive interactions and  $J < 0$  otherwise) then a configuration  $\mathbf{m}$  with  $s_{\mathbf{m}}$  broken bonds has energy  $(N - s_{\mathbf{m}})J$  with respect to the energy of the system with  $N$  independent particles. Consequently, we can set  $P_{\mathbf{m}} = p^{s_{\mathbf{m}}}$ , where  $p = \Gamma/R = \exp(J/k_B T)$ . This allows to reorganize the sum over configurations in  $X$  and  $Y$  in such a way that one sums over all configurations with a given number of broken bonds first. Still, exact summation is not feasible and a procedure can be applied analogous to that known in standard statistical mechanics where canonical ensemble approach is often replaced with a grand canonical one. Namely, one can open the system by injecting extra holes (and lattice sites) into any existing cluster of holes. This does not change the number of broken bonds (and the total interaction energy) in the system, i.e., the extra configurations created have the same probability

factors  $P_m$  as that into which a hole is injected (recall that the overall normalization of probability factors is irrelevant). At the same time one introduces a Legendre multiplier  $r$ , playing a role analogous to that of a fugacity (activity) parameter. Its validity is fixed by requiring that a mean number of holes in the open system is equal to their actual number  $H = (1 - \theta)N$ . One gets

$$\frac{pr}{[1 + r(p - 1)](1 - r)} = \frac{1 - \theta}{\theta}, \tag{6}$$

resulting in  $r = r(\theta)$ . The sums over configurations in the “grand canonical” counterparts of  $X$  and  $Y$  (having now an extra factor  $r^H$  under the sums) can be evaluated analytically because, by letting  $H$  free, the number of configurations is no longer restricted. Evaluating  $X$  one encounters the same structure of the sums as before which allows to divide the system into an active cell (determined by the transition and contributing the entire  $k$ -dependence to  $X$ ) and the environment (providing a combinatoric weight factor to each active cell contribution). The ratio  $X/Y$  leads in the  $ka \ll 1$  limit to the diffusion coefficient

$$D(p, r(\theta)) = \frac{[1 + r(2 - r)(p - 1)]^2}{p[1 + r^2(p - 1)][1 + r(p - 1)]^2} \times \{W(pr)^2 + (1 - r)[Tp(1 - r) + 2\Gamma r\{p + r(1 - r)(1 - p)\}]\}, \tag{7}$$

depending on  $\theta$  through  $r$ , as determined by Eq. (6). The rate  $R$  was eliminated using  $p = \Gamma/R$ . Eqs. (6) and (7) provide an approximation to  $D$  which is expected to work better for  $\theta < 0.5$ . For  $\theta > 0.5$  a more accurate approximation would be in which the system is opened by injecting particles into clusters of particles (which, similarly as before, does not change the total interaction energy in the system). One can show that in this case one has to replace  $\theta \leftrightarrow (1 - \theta)$  in Eq. (6) and then  $D$  is obtained from Eq. (7) after replacing  $W \leftrightarrow \Gamma$  and  $\Gamma \rightarrow R$  in it. Both approximations lead to the same value but not the same slope of  $D(\theta)$  at  $\theta = 0.5$ . In practice, for repulsive interactions both approximations give almost the same result for the entire interval of  $\theta$ .

The results of all theoretical versions of the model are compared in Figs. 1 and 2 with the results of Monte Carlo simulations for repulsive and attractive, respectively, interactions between particles at neighboring sites. In the simulations the diffusion coefficient is extracted from the time evolution of an initial step-like density profile [18]. For the full model (Eqs. (6) and (7)) the agreement ranges from almost perfect for the repulsive interactions to good for the attractive ones. For the latter, the largest deviations occur near  $\theta = 0.5$  where the simulation results are also least accurate due to the tendency of the system to cluster into densely and weakly populated regions. In fact, it is quite surprising that for such a non-homogeneous case our analytic approach works as well as it does. The slope discontinuity at  $\theta = 0.5$  in Fig. 1 is due to the use of different system opening scenarios below and above  $\theta = 0.5$ , as explained below in Eq. (7). The simplified models represented by Eq. (4) (high temperatures and/or weak interactions) and Eq. (5) (strong repulsion) work surprisingly well for parameters where they are expected to be valid.

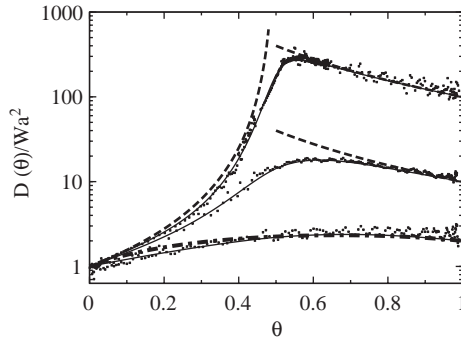


Fig. 1.  $D(\theta)/Wa^2$  as a function of coverage  $\theta$  for  $R = W$ ,  $T = \Gamma$  and, counting from top to bottom, for  $p \equiv \Gamma/R = 100, 10$  and  $2$  (repulsive interactions). Points: results of Monte Carlo simulations; continuous: from Eq. (7) for  $\theta < 0.5$  and from its modification explained below Eq. (7) for  $\theta > 0.5$ ; dots and dashes (along the lowest set of data): from Eq. (4); dashes: from Eq. (5).

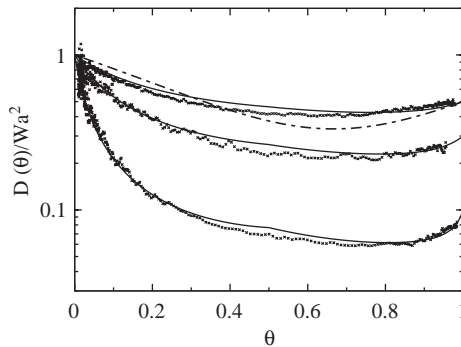


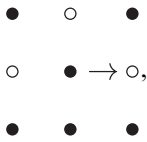
Fig. 2. The same as in Fig. 1 but, counting from top to bottom, for  $p = 0.5, 0.3$ , and  $0.1$  (repulsive interactions). Designations of the curves as in Fig. 1.

### 3.2. Selected results for 2D

The method can be applied to 2D cases. An example is an adsorbate with strong repulsive interactions on a square  $L \times L$  lattice of adsorption sites treated in detail in Ref. [16]. Let  $J$  and  $J'$  be modifications of the potential energy of a particle at an adsorption site and at a bridge site between two adsorption sites, respectively, due to the interactions with particles adsorbed at nearest sites. With  $W$  being a jump rate between two adsorption sites over the bridge for an isolated particle, all possible jump rates in a dense interacting system can be written as  $W_{n_A}^{m_B} = W \sigma^{m_B} / \gamma^{n_A}$ , where  $\sigma = \exp(-J'/k_B T)$ ,  $\gamma = \exp(-J/k_B T)$ , while  $n_A = 0, 1, 2, 3$  and  $m_B = 0, 1, 2, 3, 4$  is a number of occupied adsorption sites nearest, respectively, to the adsorption site at which the jump originates and to the barrier site over which the particle jumps. In this model the rates are not affected by the local environment of the target



adsorption site. For example, for



the rate is  $W_1^3$ —the particles in the upper and lower left corners are already too far to influence the rate. We further assume that  $J, J' > 0$  (repulsive interactions) and consider temperatures low enough so  $\gamma \ll 1$  (no assumption on  $\sigma$  is necessary). In such case, at coverages  $\theta = 0.5$  the lattice gas is organized into a staggered “checkerboard” order in which the filled and the empty sites form two interpenetrating  $(\sqrt{2} \times \sqrt{2})45^\circ$  sublattices, referred to as  $F$  and  $E$ , respectively, with  $L^2/2$  sites each. For  $\theta > 0.5$  (but close enough to it for the system to preserve the staggered order) the extra particles are added throughout the  $E$  sublattice. These extra particles cannot jump themselves but may affect a jump rate of the particles of the  $F$  sublattice. The diagram above shows one of the active cells (a jumping particle plus four sites of the  $E$  sublattice surrounding it with one extra particle in the center of the lowest row) considered in a calculation of the numerator  $X(\mathbf{k})$ . Two other active cells with one extra particle have to be considered (the one with an extra particle at the center of the leftmost column is associated with the rate  $W_1^2$ ) and there are three possible types of the active cells with two extra particles and one with extra three particles.

All possible configurations can be classified into the primary, secondary and marginal ones. In the primary configurations all sites in the  $F$  sublattice are filled and the extra particles (above  $\theta = 0.5$ ) reside at the  $E$  sites. When one of the particles at an  $F$  site jumps to a neighboring unoccupied  $E$  site, we get a secondary configuration “linked” by the jump to the particular primary configuration. All other configurations are marginal. For strongly repulsive interactions the secondary configurations are short lived so, according to the detailed balance condition, their probability factors  $P_{\mathbf{m}}$  are much smaller than those for the primary ones. The probability factors of the marginal configurations are even smaller. Therefore, only primary configurations contribute significantly to  $Y(\mathbf{k})$  while both the primary and the secondary configurations contribute in equal measure to  $X(\mathbf{k})$  (c.f. discussion leading to Eq. (5)).

Furthermore, exactly like in 1D, the entire  $\mathbf{k}$  dependence of  $X(\mathbf{k})$  is due to the distribution of particles within the active cells while the number of possible environments for each active cell provides a dependence on  $N$  and  $L^2$  resulting in the dependence of  $D$  on  $\theta \equiv N/L^2$ . Detailed rules for calculating the  $\mathbf{k}$ -dependent active cell contributions are the same as in 1D with possible modifications depending on particulars of a variational choice for  $\tilde{z}_{\mathbf{m}}(\mathbf{k})$ . In fact, for each primary configuration the choice being a direct generalization to 2D of Eq. (3) is adequate. For each secondary one, say  $\mathbf{m}$ , an average of all  $\tilde{z}'_{\mathbf{m}}$ ’s corresponding to all primary configurations  $\mathbf{m}'$  linked to  $\mathbf{m}$ , weighted by the jump rates  $W_{\mathbf{m},\mathbf{m}'}$ , is more appropriate. Detailed justification is given in Ref. [16b]. It is based on a structure of a diffusive eigenvector for a particle migrating over periodic lattice of alternating

deep and shallow adsorption sites. The results for  $\theta < 0.5$  can be obtained from the ones for  $\theta > 0.5$  using a particle–hole transformation together with the appropriate modification of all the jump rates involved. The result for the diffusion coefficient is

$$\frac{D}{Wa^2} = \begin{cases} 2[4\sigma(1 + \sigma)\theta^2 + 8\frac{(1 + \sigma)\sigma}{2\sigma + 1}\theta(1 - 2\theta) + (1 - 2\theta)^2], \\ 8\frac{\sigma^2}{\gamma} \left[ (1 + \sigma)(1 - \theta)^2 + 2\frac{(1 + \sigma)\sigma}{(2 + \sigma)\gamma}(1 - \theta)(2\theta - 1) \right. \\ \left. + \left(\frac{\sigma}{2\gamma}(2\theta - 1)\right)^2 \right], \end{cases} \quad (8)$$

for  $\theta < 0.5$  (upper line) and  $\theta > 0.5$  (lower line). In fact, this result is valid only within the coverage interval, approximately  $0.35 < \theta < 0.65$ , in which the gas is structurally ordered. Furthermore, the fact that for three extra particles/holes in an active cell the configuration obtained after the particle jump is not, strictly speaking, secondary one (its probability factor  $P_m$  is not small), is expected to be a major source of error in terms proportional to  $(1 - 2\theta)^2$  for densities near the ends of this interval where configurations with such triads become dominant. Interactions do not modify the potential energy of particles at adsorption sites for  $\theta < 0.5$  so  $D$  does not depend on  $\gamma$  there.

Theoretical results are compared in Fig. 3 with the results of the simulations. The agreement is very good with deviations which are due to an oversimplified treatment of extra particle/hole triads. A striking feature is a presence of discontinuities of the diffusion coefficient at  $\theta = 0.5$  which were, in fact, noticed already by Chumak and Uebing [19]. Their persistent presence in unpublished numerical simulations by one of the authors (M.Z.K.) was, in fact, the primary motivation for developing the

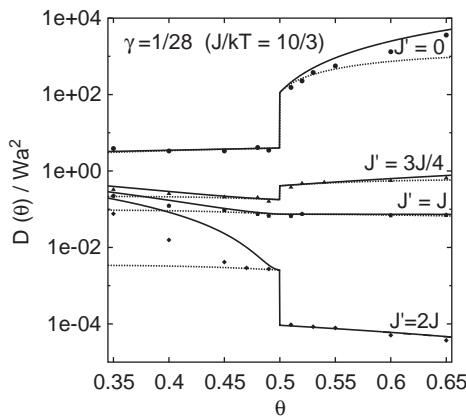


Fig. 3.  $D(\theta)/Wa^2$  as a function of coverage  $\theta$  for  $\gamma = \frac{1}{28}$  and, counting from top to bottom,  $\sigma = 1, 0.082, \frac{1}{784}$  and  $\frac{1}{784}$  for the  $\theta$  interval in which the gas is structurally ordered. Points: results of MC simulations; continuous: from Eq. (8); dashes: from Eq. (8) without the contribution from the  $(1 - 2\theta)^2$  terms.

present analytic approach. Here, the discontinuity is understood as a result of different effective hopping rates for extra particles than those for holes in an ordered system at half coverage. In fact, an exact discontinuity should not be expected because thermal fluctuations assure that even precisely at  $\theta = 0.5$  there exists a possibility of creating a hole in the  $F$  as well as creating a particle in the  $E$  sublattice. For  $\theta$  slightly above 0.5, say, the extra particles in the  $E$  sublattice dominate and control the diffusive behavior. The opposite is true for  $\theta < 0.5$ .

#### 4. Concluding remarks

We have reviewed here a recently designed method of treating collective diffusion in an interacting lattice gas. The relevant examples are provided by one-[7–10] or two-dimensional adsorbates [1–6]. In this approach the density/coverage dependence in an algebraic form is extracted directly from equations describing kinetics of microstates of the system. The approach bears some similarity to the variational approach in quantum mechanics—eigenvectors of the rate matrix must be postulated—except that there does not exist the “lowest bound” principle because the rate matrix is not Hermitian and both, left and right eigenvectors must be postulated at the same time. We have demonstrated on several examples that the method is viable. The work is in progress on extending its applicability. The treatment of the 2D system must be improved to deal correctly with particle/hole triads for the case of strong repulsive interactions and arbitrary sign and strength of the interactions have to be dealt with.

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