

**Chemical diffusion in an interacting lattice gas: Analytic theory and simple applications**

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A variational approach to microscopic kinetics of an interacting lattice gas is presented. It accounts for the equilibrium correlations in the system and allows one to derive an algebraic expression for the particle density (coverage) dependent chemical diffusion coefficient for a wide variety of interaction models. Detailed derivation is presented for a one dimensional case for which the results are compared with the results of Monte Carlo simulations. Generalization and an application to the simplest case of the two dimensional lattice gas is briefly described.

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**I. INTRODUCTION**

The collective or chemical diffusion of surface species involves jumps of the adsorbed interacting particles from one binding site to another. The rates of these jumps depend on the interactions between the neighboring particles resulting in the coverage (adsorbate density) dependent diffusion coefficient. The interactions affect the coverage dependence of diffusion also through the structural transformations within the adsorbate layer which favor different geometrical configurations within the adsorbate at different coverages. The effectiveness of the surface mobility in relation to that of other surface processes, like adsorption, desorption, chemical reactions, etc., determines the catalytic activity of the surface.<sup>1,2</sup> Growth of nanostructures from beam deposited clusters is controlled by the cluster surface diffusion enabling them to grow into islands making surface diffusion a subject of interest in nanostructuring.<sup>3</sup> The experimental progress in this field has been recently reviewed in Refs. 4–7.

Collective diffusion in one dimensional systems, the main subject of this work, has recently become practically relevant too. Recent investigations of Au or Si adsorbed on top of a Si(111)5 × 2-Au chain structure<sup>8,9</sup> show that the diffusion of adatoms is one dimensional (1D), that the interaction between adsorbed the Au/Si atoms is strongly repulsive (inhibiting simultaneous adsorption at the adjacent sites), and that the atomic migration is affected by the density of the diffusing adatoms. Helium atoms confined within a narrow interstitial channel within the triangular lattice of carbon nanotube bundles present another example of a strictly 1D “adsorbate.”<sup>10</sup> Equilibrium properties of a similar 1D gas of C<sub>60</sub> molecules encapsulated within carbon nanotubes were already investigated within the lattice gas model.<sup>11</sup>

From the perspective of a theorist the chemical or collective diffusion in the presence of interactions between adsorbed atoms is a complicated many-body problem encountering many difficulties, largely mathematical in nature. Analytic results are rare and usually the method of choice to study chemical diffusion are Monte Carlo simulations. An important work by Reed and Ehrlich,<sup>12</sup> an early Gomer’s

review<sup>13</sup> and two more recent ones by Danani *et al.*<sup>14</sup> and Ala-Nissila *et al.*<sup>15</sup> summarize some of the efforts. Other efforts relevant in this context are due to Kreuzer<sup>16–18</sup> who investigates the diffusion, adsorption, and desorption kinetics within the kinetic lattice gas model by deriving a hierarchy of kinetic equations for many-site correlation functions and solving it by designing appropriate truncation schemes (see also references to earlier works quoted in Ref. 16).

The mathematical difficulties motivate efforts to design and investigate very simple models which, although oversimplifying the situation occurring in nature, show some resemblance to them and can be solved exactly in a mathematically transparent way. Deeper insights gained due to the possibility of exact treatment should compensate for unrealistic simplifications present in such description. It is a goal of the present paper to investigate a model often invoked in the context of the surface diffusion, that of the kinetic lattice gas model, but approach it in a way different than it was done in the past. We devote this work mainly to the interacting lattice gas in one dimension which we treat in considerable detail. Generalization to the two dimensional lattice gas is not very demanding once the results of the analysis in one dimension are understood well at an intuitive level. We include in this paper preliminary only results for the simplest case of the interacting lattice gas in two dimensions. Other two dimensional cases in which structural phase transformations have to be accounted for will be considered in future publications.

Our goal is to develop an approximate analytic method allowing to derive the coverage dependent diffusion coefficient in the lattice gas in which the effects of the particle-particle interactions go beyond simple site blocking. The basic assumptions are standard: we assume that the kinetics of the microstates of the lattice gas can be described as a stochastic hopping of particles to neighboring sites, that the rates of these hops depend only on the instantaneous local environment of a given atom (Markovian process), and that at any given time only one atom in the gas hops. In our approach we start from the set of the Markovian master rate equations for the probabilities  $P(\{c\}, t)$  that a microscopic configuration (a microstate)  $\{c\}$  of a lattice gas occurs at time  $t$ .  $\{c\}$  is understood as a set of variables specifying which

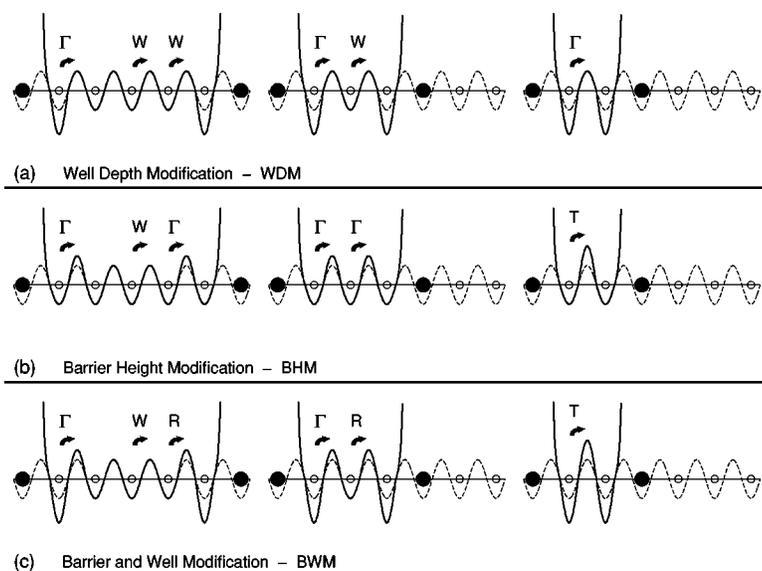


FIG. 1. Three interaction models for diffusion in a one dimensional lattice gas: (a) the well depth modification (WDM) model, (b) the barrier height modification (BHM) model, and (c) the barrier and well modification (BWM) model. The potential experienced by an atom placed between two neighbors (continuous line, black full circles, respectively)—considered here to be fixed—is superimposed on the potential experienced by an isolated atom (dashes). The infinite barriers prevent an atom from jumping to sites already occupied. The arrows symbolize selected transitions and the corresponding transition rates are shown above the arrows. Three panels (counting from the left) in each row show the transition rates appropriate for progressively smaller distance between the “fixed” atoms.

particular sites in the lattice are occupied and which are not. The rate equations account for the transitions between the microstate  $\{c\}$  and all microstates  $\{c'\}$  differing from  $\{c\}$  in the occupation numbers of the two sites between which the atomic jump occurs.<sup>17–19</sup> Our approach, however, differs from all other approaches based on the kinetic lattice gas model in this respect that we extract the coverage dependent diffusion coefficient directly from the *microscopic* rate equations rather than from the hierarchy of kinetic equations for the ensemble averaged quantities like the local particle density and many-site correlation functions. To our best knowledge, such an approach was never tried before. The advantage, beside being able to derive algebraic relations for the coverage dependence of the diffusion coefficient, is that we are free of uncertainties introduced by various truncation schemes necessary to deal with the ensemble averaged equations.

The paper is organized as follows. In Sec. II we define the details of the model and describe the theoretical method used to extract the diffusion coefficient from it. We also consider there the noninteracting system showing that the method predicts the expected density independent diffusion coefficient in this case. In Sec. III we apply the theory to the simplest case in which the modifications of the hopping rates by the interactions are rather modest. This part of the paper is fairly detailed, culminating in Sec. III C with the formulation of simple and physically appealing rules of evaluating the coverage (or density) dependent diffusion coefficient  $D(\theta)$  in a large class of kinetic lattice gas models. Section IV is devoted to another one dimensional case, that of very strong repulsive interactions between nearest neighbor atoms. This is a highly nontrivial case in which we take an advantage of the possibility of building into the considerations the equilibrium correlations in the system. Our analytical results for  $D(\theta)$  agree perfectly with the results of the Monte Carlo simulations. Although the work on two dimensional systems is still in progress we present, in Sec. V, the application of the method to the simplest two dimensional case of a lattice gas in which the interactions influence the hopping rates

moderately so no structural phase transformations are expected. Section VI is devoted to a final summary. Certain lengthy calculations, not required for understanding the method and not requiring any approximations, are presented in several Appendixes. Appendix A which, while not being technical in nature, summarizes a mathematical material essential for understanding the method presented in this work.

## II. THEORY

### A. Models for diffusion along a chain

We consider a one dimensional lattice with  $L$  sites which can be occupied by particles referred to as atoms. The total length of the chain is  $La$  where  $a$  is a distance between the neighboring sites. If only one atom is present we can think about it as moving in a periodic force field described by a potential having minima at positions  $X=\ell a$ ,  $\ell=1,2,\dots,L$ , with barriers in-between. If  $W$  is a jump probability per unit time between the nearest sites then the atomic migration along the chain is described by a diffusion coefficient<sup>20</sup>

$$D_0 = Wa^2. \quad (1)$$

If there are  $N$  atoms present on the lattice then, in general, the chemical diffusion coefficient depends on the average particle density (coverage)  $\theta=N/L$  and this dependence is determined by the details of the interactions between the atoms. It is well known,<sup>16,21</sup> however, that if only the site blocking interaction is present, i.e., the atom cannot jump into the site already occupied but the jump rates for all allowed transitions remain  $W$ , then the diffusion coefficient is equal to  $D_0$ , given in Eq. (1), for all coverages. Diffusion which does depend on coverage is due to the interactions between atoms going beyond a simple site blocking.

In Fig. 1 three simplest interaction models are shown. Let the jump rate of an isolated atom be  $W$ . An atom at a site adjacent to another site already occupied is subjected to forces different than those experienced by an isolated atom. We consider three models with progressively more compli-

cated interaction induced modifications of the jump rates. In the WDM model [Fig. 1(a)] the atom at a site adjacent to an occupied site is either attracted to (as shown) or repelled from it—the atom at such site experiences the potential with the well depth different than it would otherwise be, leading to the transition rate  $\Gamma$ , different than  $W$ , for the atom to leave the site. All the remaining jump rates are still  $W$ . Alternatively, in the BHM model [Fig. 1(b)] it is the barrier height for an atom at a site adjacent to an occupied one which is modified. Here, not only breaking a pair but also creating it occurs at a rate  $\Gamma$  different than  $W$ . Moreover, when the jumping atom is between two other atoms separated only by  $3a$  (the “tight configuration”)—so any jump simultaneously breaks and creates a pair—the barrier for such jump is affected by both neighbors leading to a still different jump rate  $T$ . Finally, in the BWM model, both effects considered in the preceding two models are present. Here, the rates of pair breaking and creation are different ( $\Gamma$  and  $R$ , respectively) except in the tight configuration in which the jump rate is denoted  $T$  again. For  $\Gamma=R=T=W$  we have only the site blocking interaction.

The models listed here can be classified according to the scheme used by Kreuzer in Refs. 17 and 18. For example, the WDM model is termed there the initial state interaction model, while the final state interaction model would correspond to  $\Gamma=W$  and  $T=R \neq W$ , which we do not show in Fig. 1. In the WDM and BHM models, both initial and final state interactions are involved and using Eq. (35) in Ref. 17 one can show that the rates  $W$ ,  $\Gamma$ ,  $R$ , and  $T$  are related to each other

$$TW = \Gamma R. \quad (2)$$

This condition is not necessarily valid in the interaction models in which interactions of an atom momentarily at a barrier site between its initial and final positions are accounted for.<sup>24</sup>

### B. Methodology

The starting point is a Markovian Master equation<sup>17–19</sup> for the probability  $P(\{c\}, t)$  that a microstate  $\{c\}$  of a lattice gas occurs at time  $t$ :

$$\frac{d}{dt}P(\{c\}, t) = \sum_{\{c'\}} [W(\{c\}, \{c'\})P(\{c'\}, t) - W(\{c'\}, \{c\})P(\{c\}, t)], \quad (3)$$

where  $W(\{c\}, \{c'\})$  is a transition probability per unit time that the microstate  $\{c'\}$  changes into  $\{c\}$  due to an atomic jump of an atom from an occupied site to an unoccupied neighboring site. The sum over  $\{c'\}$  runs over all such microstates from which the microstate  $\{c\}$  can be reached [the first term at the right hand side of Eq. (3)] or which can be reached from  $\{c\}$  (the second term). Conventionally,<sup>17–19</sup> a microstate is specified by a string of occupation numbers,  $\{c\} = [n_1, n_2, \dots, n_L]$ , such that  $n_\ell = 0$  or 1 when the  $\ell$ th site is either empty or occupied, respectively, by an atom. Such a method of identifying the microstates is, however, unsuitable for our purposes because it does not allow to express the

long wavelength density fluctuations in the lattice gas in terms of  $P(\{c\}, t)$ 's.

For a system of  $N$  particles distributed among  $L$  sites we propose to identify a microstate  $\{c\}$  by a set of  $N$  numbers

$$\{c\} = [X; m_1, m_2, \dots, m_{N-1}] \equiv [X; \{m\}], \quad (4)$$

where  $X = \ell a$  ( $\ell$  being an integer of any sign) is a position of one of the atoms, referred to as the reference atom, and  $m_i$  is an integer indicating how far, in units of the lattice constant  $a$ , the  $i$ th atom is away from the reference atom. The set  $\{m\} = [m_1, m_2, \dots, m_{N-1}]$  is referred to as a configuration—it accounts for the relative arrangement of atoms in a given microstate. In order to avoid the influence of the boundaries we let  $\ell = 0, \pm 1, \pm 2, \dots, \pm \infty$  and impose the periodic boundary conditions treating as equivalent positions  $X$  and  $X + nLa$  ( $n$ —an integer of any sign). It is convenient to consider all  $L$  sites to be arranged along a circumference of a circle of length  $La$ . Two possible directions along the line will be referred to either as clockwise (from left to right) or counterclockwise (from right to left). We choose the reference atom to be the leftmost one in the microstate and label the remaining atoms with integers  $i = 1, 2, \dots, N-1$  in the order in which they are encountered going from the reference atom in the clockwise (right) direction. Consequently all  $m_i$ 's are positive and with the shortest and the longest distance between any two atoms being  $a$  and  $(L-1)a$ , respectively,  $m_i$  differs at least by 1 from  $m_{i-1}$  and  $m_{i+1}$ . Therefore, we have

$$1 \leq m_1 < m_2 < \dots < m_i < \dots < m_{N-1} \leq L-1. \quad (5)$$

For example, if  $N=3$  then the microstate  $\circ\circ\bullet\circ\circ\bullet\circ\circ\dots$  is identified as  $[X; m_1, m_2] = [2a; 1, 4]$  and the corresponding configuration is  $\{m\} = [1, 4]$ .

An important advantage of identifying the microstates of the system as specified in Eq. (4) is that, by tying each microstate to a particular lattice location  $X$  through the reference atom, it is possible to relate the time dependent microstate probabilities  $P(\{c\}, t)$ , now denoted  $P_{m_1, m_2, \dots, m_{N-1}}(X, t)$ , to the probability  $\mathcal{P}(X, t)$  of finding an atom at a position  $X$  (which, in turn, is directly proportional to the local density/coverage). Namely, in each of the following microstates there is an atom at a position  $X$ :  $[X; m_1, m_2, \dots, m_{N-1}]$ —the leftmost atom (the reference) is at  $X$ ,  $[X - m_1 a; m_1, m_2, \dots, m_{N-1}]$ —the second atom, counting from the left, is at  $X$ ,  $[X - m_2 a; m_1, m_2, \dots, m_{N-1}]$ —the third atom is at  $X$ , etc. In general, in a microstate  $[X - m_i a; m_1, m_2, \dots, m_i, \dots, m_{N-1}]$  the  $(i+1)$ th atom counting clockwise from the reference atom (considered as the first one in the count) is precisely at  $X$ . Consequently, the probability of finding an atom at  $X$  at time  $t$  is the following sum over all configurations:

$$P(X, t) = \frac{1}{N} \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ \text{ord}}}^{L-1} [P_{m_1, m_2, \dots, m_{N-1}}(X, t) + P_{m_1, m_2, \dots, m_{N-1}}(X - m_1 a, t) + P_{m_1, m_2, \dots, m_{N-1}}(X - m_2 a, t) + \dots + P_{m_1, m_2, \dots, m_{N-1}}(X - m_{N-1} a, t)]. \quad (6)$$

Here,  $\sum_{m_1, \dots, m_{N-1}=1}^{L-1}$  denotes the sum over  $N-1$  indices

$[m_1, m_2, \dots, m_{N-1}] \equiv \{m\}$  in the limits specified by Eq. (5). We will refer to such a sum as an “ordered” one.

Returning to Master Eq. (3), it is easy to see that at the right hand side of a rate equation for  $P_{\{m\}}(X, t)$  the microstate probabilities  $P_{\{m'\}}(X, t)$  and  $P_{\{m'\}}(X \pm a, t)$  appear with appropriately chosen configurations  $\{m'\} = [m_1, \dots, m_{N-1}]$  (cf. Appendix A for more details). The transition rates  $W(\{c\}, \{c'\})$  depend only on the local environment of the hopping atom (fully specified by configurations  $\{m\}$  and  $\{m'\}$ ) but do not depend on the positions  $X$  and  $X'$  of the reference atom. Consequently,  $W(\{c\}, \{c'\}) \equiv W_{\{m\}, \{m'\}}$ . This allows to take an advantage of the lattice periodicity and take a lattice Fourier transform

$$P_{\{m\}}(k, t) = \sum_X e^{ikX} P_{\{m\}}(X, t), \quad (7)$$

of both sides of Eq. (3). Treating  $P_{\{m\}}(k, t)$ 's as components of a one-column array  $\mathbf{P}(k, t)$  one arrives at the set of the  $k$ -space rate equations written conveniently in the matrix form

$$\frac{d}{dt} \mathbf{P}(k, t) = \mathbb{M}(k) \cdot \mathbf{P}(k, t). \quad (8)$$

The number of elements in  $\mathbf{P}(k, t)$  and the dimension of the  $k$ -space rate matrix  $\mathbb{M}(k)$  (to be referred to simply as a rate matrix) is equal to the number of all possible configurations, as determined by condition (5). Most of the matrix elements  $M_{\{m\}, \{m'\}}(k)$  of  $\mathbb{M}(k)$  are zero. The nonvanishing matrix elements are proportional to  $W$ ,  $\Gamma$ ,  $T$ , or  $R$ . Some of them contain also a  $k$ -dependent phase factor  $\exp(\mp ika)$  accounting for the fact that some transitions convert the configuration tied to a lattice position  $X$  into the one tied to  $X \pm a$ . More details and some essential properties of the rate matrix  $\mathbb{M}(k)$  are provided in Appendix A. The reader not familiar with the properties of nonhermitian matrices is advised to read this appendix now.

The chemical diffusion coefficient can be extracted directly from rate Eq. (8) without going through the diffusion equation. For a long range density fluctuation,  $ka \ll 1$ , the return to equilibrium is due to diffusion proceeding at a rate  $\lambda(k)$  equal to that eigenvalue of  $-\mathbb{M}(k)$  which for  $ka \ll 1$  is proportional to  $(ka)^2$ .  $\lambda(k)$  will be referred to as a diffusive eigenvalue of the rate matrix and the diffusion coefficient is obtained as a  $ka \ll 1$  limit of  $\lambda(k)/k^2$ . There is a delicate point in this procedure because this limit must be taken while both  $N$  and  $L$  are kept finite because our goal is to obtain the diffusion coefficient as a function of an equilibrium (average) coverage  $\theta = N/L$  for both  $L$  and  $N$  being much larger than 1. Consequently,  $ka \ll 1$  does not mean setting  $k=0$  because performing all calculations one has to account for the restrictions imposed on  $k$  due to the periodic boundary condition

$$e^{ikaL} = 1 \quad (9)$$

and keep  $ka$  finite until one lets  $L$  and  $N$  to  $\infty$ . The procedure described here, straightforward in principle, is difficult to implement due to a huge dimension of the matrix  $\mathbb{M}(k)$ .

Formal expression for the diffusive eigenvalue of  $\mathbb{M}(k)$  is given in Eq. (A7). This matrix is not, in general, hermitian so a distinction must be made between its left and right eigenvectors. They are related to each other through the equilibrium probabilities  $P_{\{m\}}^{\text{eq}}$  appropriate to  $\mathbb{M}(0)$  [cf. Appendix A and Eq. (A5)]. Unfortunately, the left eigenvector  $\tilde{\mathbf{e}}^{(0)}(k)$  of  $\mathbb{M}(k)$  cannot be found analytically and the equilibrium probabilities  $P_{\{m\}}^{\text{eq}}$  determined by  $\mathbb{M}(0)$  are usually too complicated for any analytic approach. In this work, guided by the exact expression (A7) for  $\lambda(k)$ , the following variational expression for it will be used as a starting point:

$$-\lambda(k) \approx \frac{\Phi_{\text{var}}^\dagger(k) \cdot \mathbb{M}(k) \cdot [\mathbf{P}^{\text{var}} \Phi_{\text{var}}(k)]}{\Phi_{\text{var}}^\dagger(k) \cdot [\mathbf{P}^{\text{var}} \Phi_{\text{var}}(k)]}. \quad (10)$$

Here  $[\mathbf{P}\Phi]$  denotes a one-column array with components  $[\mathbf{P}\Phi]_{\{m\}} = P_{\{m\}} \Phi_{\{m\}}$  and  $\Phi_{\text{var}}^\dagger(k)$  is a variational candidate for  $\tilde{\mathbf{e}}^{(0)}(k)$  and  $\mathbf{P}^{\text{var}}$  approximates  $\mathbf{P}^{\text{eq}}$ . Their choice is dictated by physical considerations and the only formal restriction is that all components of  $\Phi_{\text{var}}^\dagger(k)$  are equal to each other for  $k=0$  [cf. discussion below Eq. (A6)]. This assures that  $\lambda(k)$  is proportional to  $(ka)^2$  for  $ka \ll 1$ . Into the candidate for  $\mathbf{P}^{\text{var}}$  one can build, at least in principle, any information one possesses about the *equilibrium* correlations present in the system.

We complete this discussion by considering the density fluctuation  $\mathcal{P}(k, t)$  defined as a lattice Fourier transform of the probability  $\mathcal{P}(X, t)$  [defined in Eq. (6)] of finding an atom at a position  $X$ . Using Eq. (7) it can be written in a form of a dot product involving  $\mathbf{P}(k, t)$ :

$$\begin{aligned} \mathcal{P}(k, t) &= \frac{1}{N} \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ \text{ord}}}^{L-1} \Phi_{m_1, m_2, \dots, m_{N-1}}^*(k) P_{m_1, m_2, \dots, m_{N-1}}(k, t) \\ &= \frac{1}{N} \Phi^\dagger(k) \cdot \mathbf{P}(k, t), \end{aligned} \quad (11)$$

where  $\Phi^\dagger(k)$  is a one-row array—a hermitian conjugate of a one-column array  $\Phi(k)$  whose  $[m_1, m_2, \dots, m_{N-1}]$ th component is

$$\begin{aligned} \Phi_{m_1, m_2, \dots, m_{N-1}}(k) &\equiv \Phi_{\{m\}}(k) = 1 + \sum_{i=1}^{N-1} e^{-ikam_i} \\ &= 1 + e^{-ikam_1} + e^{-ikam_2} + \dots + e^{-ikam_{N-1}}. \end{aligned} \quad (12)$$

Note that all components of  $\Phi(k=0)$  are equal to each other (equal to  $N$ ).

### C. Noninteracting case

The choice of  $\Phi_{\text{var}}^\dagger(k)$  and  $\mathbf{P}_{\text{var}}$  can only be dictated by physical intuition so it is important to consider a case for

which the left eigenvector and the equilibrium probabilities can be found exactly. The natural candidate is the “noninteracting” case in which the rates  $\Gamma$ ,  $R$ , and  $T$  are equal to  $W$ , i.e., when the only effect of the atom-atom interactions is the site blocking. The  $k$ -space rate matrix, denoted  $\mathring{M}(k)$ , is in this case hermitian. One can show that  $-\lambda_0(k)$ , given in

$$\lambda_0(k) = 4W \sin^2\left(\frac{ka}{2}\right), \quad (13)$$

is the *exact* eigenvalue of  $\mathring{M}(k)$  and that  $\Phi(k)$  defined in Eq. (12) is the corresponding exact (right) eigenvector

$$\mathring{M}(k) \cdot \Phi(k) = -\lambda_0(k)\Phi(k) \quad (14)$$

[the left eigenvector is  $\Phi^\dagger(k)$ ]. The resulting diffusion coefficient does not depend on coverage and is given in Eq. (1). The proof of Eq. (14), interesting in its own right, is given in Appendix B.

From this perspective, the last line of Eq. (11) means that the density fluctuation  $\mathcal{P}(k, t)$  is a projection of the solution  $\mathbf{P}(k, t)$  of rate Eq. (8)—for any interaction model—onto the “diffusive eigenspace” of  $\mathring{M}(k)$  for the noninteracting lattice gas. It implies that the density fluctuation for the noninteracting system, denoted  $\mathring{\mathcal{P}}(k, t)$ , decays in time at a *unique* rate being precisely  $\lambda_0(k)$ :

$$\mathring{\mathcal{P}}(k, t) = \mathring{\mathcal{P}}(k, 0)e^{-\lambda_0(k)t}. \quad (15)$$

This is the expected and *necessary* result: chemical diffusion in the system with no other interactions than the site blocking must be governed by the rate derived within the random walk model for a single particle.<sup>16,21</sup> In the case with interactions, however, the decay of the density fluctuation  $\mathcal{P}(k, t)$ —still being a projection of the exact solution  $\mathbf{P}(k, t)$  onto the diffusive eigenspace of its noninteracting counterpart—cannot be described by a single rate but rather by a linear combination of exponentially decaying terms—the rates are the eigenvalues of  $\mathbb{M}(k)$ . Diffusion corresponds to that eigenvalue which is proportional to  $(ka)^2$  in the long wavelength limit ( $ka \ll 1$ ).

### III. APPLICATION: MODERATE MODIFICATIONS OF THE RATES

We are ready now to apply the method developed in Sec. II. Our aim will be to evaluate  $\lambda(k)$  using Eq. (10). We postulate that  $\Phi_{\text{var}}(k)$  is adequately represented by  $\Phi(k)$  defined in Eq. (12)—the diffusive eigenvector of  $\mathring{M}(k)$ .<sup>22</sup> Depending on the relative magnitudes of the rates  $\Gamma$ ,  $R$ ,  $T$  with respect to  $W$  we propose different variational candidates for the equilibrium probabilities  $\mathbf{P}^{\text{var}}$ .

We start with the case in which the rates  $\Gamma$ ,  $R$ , and  $T$  differ moderately from the jump rates  $W$ . In this case we assume that each configuration  $\{m\} = [m_1, m_2, \dots, m_{N-1}]$  allowed by condition (5) is equally probable in equilibrium. In reality this is true only for the noninteracting lattice gas but the error made should be small for small enough interaction-induced

modifications of the hopping rates. Consequently, all components of  $\mathbf{P}^{\text{var}}$  are equal to each other [they can all be set to 1 because the denominator in Eq. (10) takes care of the normalization automatically]. It is convenient now to decompose the rate matrix  $\mathbb{M}(k)$  into  $\mathring{M}(k)$  and a correction

$$\delta\mathbb{M}(k) = \mathbb{M}(k) - \mathring{M}(k). \quad (16)$$

The rate matrix  $\mathring{M}(k)$  inserted into Eq. (10) results in  $-\lambda_0(k)$  with the present choice of  $\mathbf{P}^{\text{var}}$  and  $\Phi_{\text{var}}(k)$  so the result is

$$\begin{aligned} -\lambda(k) &\approx -\lambda_0(k) + \delta\lambda(k) = -\lambda_0(k) + \frac{\Phi^\dagger(k) \cdot \delta\mathbb{M}(k) \cdot \Phi(k)}{\Phi^\dagger(k) \cdot \Phi(k)} \\ &= -\lambda_0(k) + \frac{\delta\mathcal{M}(k; L, N)}{\mathcal{N}(L, N)}. \end{aligned} \quad (17)$$

The denominator  $\mathcal{N}(L, N)$  in the correction term accounts for the fact that  $\Phi(k)$ , defined in Eq. (12) is not normalized. In principle, it should depend on  $k$ . Evaluating, however, the numerator and the denominator one has to account for condition (9) and, as shown in Appendix C, this condition yields a  $k$ -independent  $\mathcal{N}(L, N)$  [cf. Eq. (C13)].

We note in passing that Eq. (17) is formally identical to that which would be obtained within the perturbation theory approach: the first order correction  $\delta\lambda(k)$  is the “expectation value” of the “perturbation”  $\delta\mathbb{M}(k)$  in the “unperturbed state”  $\Phi(k)$ . As such, the result is expected to be valid for relatively small interaction-induced modifications of the hopping rates. The starting expression, Eq. (10), is more general because, by a judicious choice of  $\mathbf{P}^{\text{var}}(k)$  and  $\Phi_{\text{var}}$  it allows, in principle, to incorporate effects which cannot be accounted for within the perturbation theory.

Both  $\mathcal{N}(L, N)$  and  $\delta\mathcal{M}(k; L, N)$  can be evaluated analytically but the details are complicated and tedious, particularly when  $\delta\mathcal{M}(k; L, N)$  is concerned. The result is, however, very simple, easy to interpret and easy to generalize to other models, including a lattice gas in more dimensions than one. For the purpose of illustrating the method we consider first the lattice gas consisting of  $N=3$  atoms and restrict considerations to the WDM interaction model (cf. Fig. 1) which we then generalize to the BWM model for general  $N$ .

#### A. Toward systematic approach, $N=3$

The lattice gas consisting of  $N=3$  atoms presents the simplest case in which all complications occurring for general  $N$  are already present. Considering it first allows for an almost immediate generalization. The microstates are identified as  $[X; m_1, m_2]$  with, cf. Eq. (5):

$$1 \leq m_1 < m_2 \leq L - 1. \quad (18)$$

Already in this case it is a rather tedious task to write down all possible types of the rate equations. The matrix index in Eq. (8) is  $\{m\} = [m_1, m_2]$  consisting of two ordered [cf. Eq. (18)] integers so the number of different components of  $P_{m_1, m_2}(k, t)$  and a dimension of the square matrix  $\mathbb{M}(k)$ , equal to the number of all possible configurations, is  $(L-1)(L-2)/2$ . The off diagonal matrix elements,  $M_{\{m\}, \{m'\}}(k)$

$\equiv M_{m_1, m_2; m'_1, m'_2}(k)$  are proportional to the transition rates  $W_{\{m\}, \{m'\}}$  from the microstate  $[X'; m'_1, m'_2]$  to  $[X; m_1, m_2]$  and depend on  $k$  through factors  $\exp(\mp ika)$  generated by the transitions for which  $X' = X \pm a$ . The diagonal terms  $M_{\{m\}, \{m\}}$  are negative, do not depend on  $k$ , and account for the total rate out of the configuration  $\{m\}$ . Majority of the off diagonal matrix elements of  $\mathbb{M}(k)$  [and of  $\dot{\mathbb{M}}(k)$ ] vanish and, typically, the nonvanishing matrix elements are  $M_{m_1, m_2; m_1 \pm 1, m_2 \pm 1}(k)$ ,  $M_{m_1, m_2; m_1 \pm 1, m_2}(k)$ ,  $M_{m_1, m_2; m_1, m_2 \pm 1}(k)$ , and  $M_{m_1, m_2; m_1, m_2}$ . Without interactions [i.e., when the rate matrix is  $\dot{\mathbb{M}}(k)$  with all nonvanishing matrix elements proportional to  $W$ ] the form of a typical (i.e., for  $m_1 \neq 1$ ,  $m_2 \neq L-1$ , and  $m_2 - m_1 > 1$ ) equation is

$$\begin{aligned}
 \dot{P}_{m_1, m_2}(k, t) = & -6WP_{m_1, m_2}(k, t) + W[e^{-ika}P_{m_1-1, m_2-1}(k, t) \\
 & + e^{ika}P_{m_1+1, m_2+1}(k, t) + P_{m_1-1, m_2}(k, t) \\
 & + P_{m_1+1, m_2}(k, t) + P_{m_1, m_2-1}(k, t) + P_{m_1, m_2+1}(k, t)].
 \end{aligned} \quad (19)$$

The first term at the right hand side is the ‘‘out’’ term which accounts for six ways in which a triad  $[X, m_1, m_2]$  can be destroyed: each of its three atoms can jump in one of two directions. The remaining ones are the ‘‘in’’ terms. Those proportional to  $\exp(-ika)$  and  $\exp(ika)$  account for a creation of a  $[X, m_1, m_2]$  triad due to the counterclockwise and clockwise jumps of the reference atom, respectively (because such jumps change the position  $X$  of the triad and both distances  $m_1 a$  and  $m_2 a$  by  $\pm a$ ). The terms without a phase factor account for jumps of the middle atom [two middle terms at the right hand side of Eq. (19)] or the remaining nonreference atom (the two last terms)—these jumps do not change  $X$ . The ‘‘special’’ equations, for which the site blocking must be accounted for, are only those for  $\dot{P}_{m_1, m_2}(k, t)$ 's with  $m_1 = 1$ ,  $m_2 = L-1$  and/or  $m_2 - m_1 = 1$ . For example, the equation for  $\dot{P}_{1, m_2}(k, t)$  would have an out term proportional to  $-4W$  unless  $m_2 = 2$  for which it would be proportional to  $-2W$ . In fact, the site blocking is accounted automatically for by not letting any pair of subscripts in Eq. (19) to violate condition (18).

With interactions beyond the site blocking, the rate matrix  $\mathbb{M}(k)$  differs from  $\dot{\mathbb{M}}(k)$  by having some  $W$  rates replaced with  $\Gamma$ ,  $T$ , or  $R$ . Consequently, certain rate equations contain  $\Gamma$ ,  $T$ , or  $R$  as well as  $W$ 's. As an example, for the WDM interaction model, the rate equations for  $\dot{P}_{m, m+1}(k, t)$  and  $\dot{P}_{m, m+2}(k, t)$  with  $m > 1$  corresponding to the configurations  $\bullet \circ \dots \circ \bullet \circ \bullet \circ \dots \circ$  and  $\bullet \circ \dots \circ \bullet \circ \bullet \circ \dots \circ$  (the leftmost  $\bullet$  is the reference atom having, due to the cyclic boundary conditions, the rightmost empty site  $\circ$  immediately to its left) are, respectively,

$$\begin{aligned}
 \dot{P}_{m, m+1}(k, t) = & -2(\Gamma + W)P_{m, m+1}(k, t) + W[e^{-ika}P_{m-1, m}(k, t) \\
 & + e^{ika}P_{m+1, m+2}(k, t) + P_{m-1, m+1}(k, t) \\
 & + P_{m, m+2}(k, t)],
 \end{aligned} \quad (20)$$

and

$$\begin{aligned}
 \dot{P}_{m, m+2}(k, t) = & -6WP_{m, m+2}(k, t) + W[e^{-ika}P_{m-1, m+1}(k, t) \\
 & + e^{ika}P_{m+1, m+3}(k, t)] + WP_{m-1, m+2}(k, t) \\
 & + \Gamma P_{m+1, m+2}(k, t) + \Gamma P_{m, m+1}(k, t) + WP_{m, m+3}(k, t).
 \end{aligned} \quad (21)$$

In Eq. (20) the number of terms is smaller than in either Eq. (19) or (21) on the account of the site blocking. In general, the rate equations for  $\dot{P}_{m_1, m_2}(k, t)$  which contain  $\Gamma$  are (i) those for which the  $m_1$  atom is paired with the reference atom (either tightly or with one empty site between them:  $m_1 = 1, 2$ , respectively); (ii) those for which the  $m_2$  atom is paired with the reference atom (either tightly or with one site between them:  $m_2 = L-1, L-2$ , respectively); (iii) those in which the  $m_1$  and  $m_2$  atoms are paired with each other [ $m_2 = m_1 + 1$ , or  $m_2 = m_1 + 2$ , exemplified in Eqs. (20) and (21), respectively]; and (iv) those in which the  $m_1$  and  $m_2$ , paired to each other tightly or with an empty site between them, are also paired with the reference atom through either of the ends. Out of the total of  $(L-1)(L-2)/2$  rate equations only  $6(L-3)$  are special:  $3(L-3)$  are like Eq. (20) and contain the rate  $\Gamma$  in the out terms and  $3(L-3)$  equations are similar to Eq. (21) with  $\Gamma$  in the in terms. In the remaining interaction models with special rates  $R$  and  $T$  the number of the special equations is larger.

The probability of finding an atom at a position  $X$  is defined in Eq. (6). Its lattice Fourier transform is given in Eqs. (11) and (12) which in this case read

$$P(k, t) = \frac{1}{3} \sum_{\substack{m_1, m_2 = 1 \\ \text{ord}}}^{L-1} \Phi_{m_1, m_2}^*(k) P_{m_1, m_2}(k, t), \quad (22)$$

and

$$\Phi_{m_1, m_2}(k) = 1 + e^{-ikam_1} + e^{-ikam_2}, \quad (23)$$

respectively. The ordered summation  $\sum_{m_1, m_2=1}^{L-1}$  is defined below Eq. (6) and here it could be written as  $\sum_{m_1=1}^{\text{ord}} \sum_{m_2=m_1+1}^{L-1}$  as well [cf. condition (18)].

$\Phi(k)$ , with components defined in Eq. (23) is an eigenvector of  $\dot{\mathbb{M}}(k)$  (cf. Appendix A). It can be now used in Eq. (17) to evaluate the correction  $\delta\lambda(k)$  to the diffusive eigenvalue. The evaluation of the denominator is straightforward leading to

$$N(L, N=3) = \sum_{\substack{m_1, m_2 = 1 \\ \text{ord}}}^{L-1} |\Phi_{m_1, m_2}|^2 = \frac{3}{2}(L-2)(L-3), \quad (24)$$

which agrees with the general result given in Eq. (C13).

The evaluation of the numerator,  $\delta\mathcal{M}(k; L, N) = \Phi^\dagger(k) \cdot \delta\mathbb{M}(k) \cdot \Phi(k)$ , is considerably more complicated and it should be organized in a way allowing for easy generalization for arbitrary  $N$  and an arbitrary interaction model. We concentrate on the WDM model. The matrix  $\delta\mathbb{M}(k)$  is then proportional to  $\Gamma - W$  and its only nonzero elements appear at such matrix positions at which the rate matrix  $\mathbb{M}(k)$  has  $\Gamma$

rather than  $W$  [compare Eq. (19) with Eqs. (20) and (21) as examples]. The dot product  $\delta\mathbb{M}(k) \cdot \Phi(k)$  has the same structure as  $\delta\mathbb{M}(k) \cdot \mathbf{P}(k, t)$  appearing in the rate equations which contain the rate  $\Gamma$ . Consequently, one can classify various contributions to  $\delta\lambda(k)$  as generated by various types of these rate equations of which Eqs. (20) and (21) are typical examples. A lengthy result of this rather tedious analysis is given here in full because the interpretation of each term is valid beyond  $N=3$ :

$$\frac{\delta\mathcal{M}(k; L, N=3)}{\Gamma - W} = -2(A_0 + B_0 + C_0) + (A_1 + A_2) + (B_1 + B_2) + (C_1 + C_2), \quad (25)$$

where

$$A_0 = \sum_{m_2=3}^{L-1} |\Phi_{1,m_2}|^2, \quad (26a)$$

$$B_0 = \sum_{m_1=2}^{L-2} |\Phi_{m_1, L-1}|^2, \quad (26b)$$

$$C_0 = \sum_{m_1=1}^{L-3} |\Phi_{m_1, m_1+1}|^2, \quad (26c)$$

and

$$A_1 = \sum_{m_2=3}^{L-1} \Phi_{2,m_2}^* \Phi_{1,m_2}, \quad (27a)$$

$$A_2 = e^{-ika} \sum_{m_2=3}^{L-1} \Phi_{2,m_2}^* \Phi_{1,m_2-1}, \quad (27b)$$

$$B_1 = \sum_{m_1=1}^{L-3} \Phi_{m_1, L-2}^* \Phi_{m_1, L-1}, \quad (27c)$$

$$B_2 = e^{ika} \sum_{m_1=1}^{L-3} \Phi_{m_1, L-2}^* \Phi_{m_1+1, L-1}, \quad (27d)$$

$$C_1 = \sum_{m_2=3}^{L-1} \Phi_{m_2-2, m_2}^* \Phi_{m_2-1, m_2}, \quad (27e)$$

$$C_2 = \sum_{m_1=1}^{L-3} \Phi_{m_1, m_1+2}^* \Phi_{m_1, m_1+1}. \quad (27f)$$

A simpler final expression will be obtained shortly but it is worthwhile to interpret the earlier results first. First of all, we note that each sum in Eqs. (26) and (27) has  $L-3$  terms.  $A_0$ ,  $B_0$ , and  $C_0$  are related together to  $3(L-3)$  rate equations similar to Eq. (20) with the rate  $\Gamma$  in the out terms while all terms in Eqs. (27) are related to the remaining  $3(L-3)$  equations with  $\Gamma$  in the in terms, like Eq. (21). Altogether, the matrix  $\delta\mathbb{M}(k)$  has  $6(L-3)$  nonvanishing matrix elements out of the total number  $[(L-1)(L-2)/2]^2$  of them.

In fact, each of the terms in Eq. (25) can be related to very specific processes breaking a bond between two atoms in a tight pair. Our goal is to provide such an interpretation of Eqs. (25), (26), and (27) which would allow to write all the expressions using simple diagrammatic rules.

The negative contributions in Eqs. (25) are due to the breaking of tight pairs of atoms contributing to the out terms in the rate equations.  $A_0$ , containing  $|\Phi_{1,m_2}|^2$ 's, accounts for the destructions of the configurations in which the  $m_1$  atom forms a tight pair with the reference atom [thus,  $m_1=1$  in Eq. (26a)]. The spectator atom which does not change its position can be at any position  $m_2$  between 3 and  $L-1$  (see, however, the end of this paragraph). The factor 2 in front is due to the fact that such a configuration can be destroyed when either the reference atom or the  $m_1=1$  atom jumps. In  $B_0$  the reference atom forms a tight pair with the  $m_2$  atom, i.e.,  $m_2=L-1$  in Eq. (26b). In  $C_0$  the tight pair does not involve the reference atom so  $m_2=m_1+1$  in Eq. (26c). One term in each sum ( $m_2=L-1$  in  $A_0$ ,  $m_1=L-2$  in  $B_0$ , and  $m_1=1$  in  $C_0$ ) corresponds to the destruction of a tight triad—each such configuration can also be destroyed in two ways so the factor 2 is appropriate for these contributions also. The tight triad terms could be distributed differently among  $A_0$ ,  $B_0$ , and  $C_0$ , e.g., the summation in  $A_0$  could start with  $m_2=2$  but then  $C_0$  would have to start with  $m_1=2$  to avoid overcounting, etc.

Similar assignments can be made for the remaining, defined in Eqs. (27), contributions to Eq. (25). They are best visualized in diagrams given in Fig. 2. These terms are due to the tight pair breaking processes which contribute to the in terms in the rate equations. In Fig. 2 the diagram associated with  $A_1$  shows the process in which the  $m_1=1$  atom tightly paired with the reference atom jumps out to site 2 creating a configuration with  $m_1=2$ . The spectator atom  $m_2$  can be anywhere except at site 2 which is needed to accept the jumping atom (i.e.,  $m_2$  runs in the sum from  $m_2=3$ ). In Eq. (27a) the factors  $\Phi_{2,m_2}^*$  and  $\Phi_{1,m_2}$  correspond to the final and the initial configurations, respectively. Similarly,  $A_2$  in Fig. 2 refers to the process in which the reference atom in the same initial configuration as for  $A_1$  jumps counterclockwise to the site  $L-1$ . The spectator atom, being at  $m_2-1$  in the initial configuration, can be anywhere except at the site  $L-1$  which accepts the jumping atom (i.e.,  $m_2$  runs up to and  $L-1$  inclusive). The initial configuration is represented by  $\Phi_{1,m_2-1}$  while the final one corresponds to  $\Phi_{2,m_2}^*$  because with the reference atom jumping counterclockwise the positions of both remaining atoms increase by 1. The phase factor  $\exp(-ika)$  is associated, as always in the in terms, with the counterclockwise jump of the reference atom. The  $B_1$ ,  $B_2$ ,  $C_1$ , and  $C_2$  are interpreted in a similar way. They correspond to the remaining two ways in which two out of  $N=3$  atoms can be paired in the initial configuration (in  $C_1$  and  $C_2$  the reference atom is a spectator which does not jump so these two terms do not have any phase factor).

The interpretation provided in the two earlier paragraphs would suffice but further simplifications are possible. Physically, the reference atom is not in any way privileged so several contributions listed in Eqs. (26) and (27) should be equal to each other. Indeed, using the periodic boundary con-

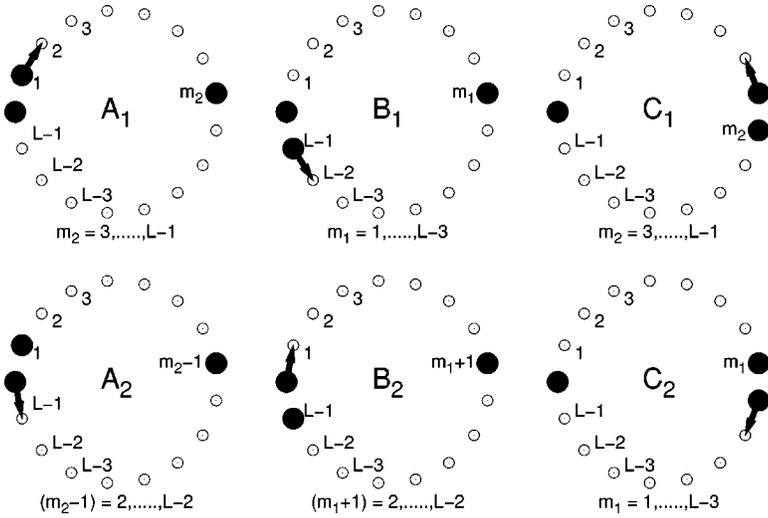


FIG. 2. Graphical representation of contributions to Eq. (25). See text for details.

dition in Eq. (9) and the fact that  $\Phi_{m_1, m_2} = \Phi_{m_2, m_1} = \Phi_{-m_1, -m_2}^* = \Phi_{L-m_1, L-m_2}^*$  (which requires to extend the definition of  $\Phi_{m_1, m_2}$  to include negative and/or not ordered indices—still keeping  $m_1 \neq m_2$ ) one can show that  $A_0 = B_0 = C_0$  and that among the remaining contributions the ones corresponding to the clockwise jumps are equal to each other and are equal to the complex conjugates of all contributions corresponding to the counterclockwise jumps:  $A_1 = B_2 = C_2 = A_2^* = B_1^* = C_1^*$ . We get

$$\frac{\delta \mathcal{M}(k; L, N=3)}{\Gamma - W} = 3[(A_1 - A_0) + (B_1 - B_0)]$$

$$= 3 \left[ \sum_{m_2=3}^{L-1} (\Phi_{2, m_2} - \Phi_{1, m_2})^* \Phi_{1, m_2} + \sum_{m_1=1}^{L-3} (\Phi_{m_1, L-2} - \Phi_{m_1, L-1})^* \Phi_{m_1, L-1} \right]. \quad (28)$$

To get this result we have noted that the summation over  $m_1$  in the definition of  $B_0$  in Eq. (26b) can run from  $m_1=1$  to  $m_1=L-3$  because  $|\Phi_{1, L-1}|^2 = |\Phi_{L-2, L-1}|^2$ . The important point is that the only contributions to be considered are  $A_1 - A_0$  and  $B_1 - B_0$  and we can ignore the contributions  $C_1$  and  $C_2$  and their diagrams from now on.

In fact, the diagrams in Fig. 2 originally intended to represent  $A_1$  and  $B_1$  may be reinterpreted now to represent, respectively,  $A_1 - A_0$  and  $B_1 - B_0$ , namely, with each of these two diagrams we associate the contributions of the type  $(\Phi_{\text{fin}} - \Phi_{\text{in}})^* \Phi_{\text{in}}$  where the subscripts in and “fin” represent, respectively, the initial and the final configuration in such a diagram. The contributions must be summed over all possible positions of the spectator atom. The diagram  $A_1$ , for example, takes care of all contributions due to jumps in the clockwise direction with the reference atom tightly paired with the  $m_1=1$  atom in all initial configurations. The third atom,  $m_2$ , is merely a spectator whose all possible positions contribute additively to the final result. Summing over its positions one must leave site 2 free (i.e., exclude  $m_2=2$  from

the sum) to allow for the jump of the  $m_1$  atom from  $m_1=1$  to  $m_1=2$ . The diagram labeled  $B_1$  in Fig. 2 accounts for all contributions due to jumps in the counterclockwise direction in a similar way. In fact,  $(B_1 - B_0)^* = A_1 - A_0$  but it is convenient for that what follows not to use this property yet. The overall factor 3 in Eq. (28) can be traced back to the number of ways two out of three atoms along the ring can be arranged into a tight pair.

In order to deal with the BHM and the BWM interaction models (cf. Fig. 1) for  $N=3$  we note that a special role is played in Eq. (28) by the terms  $m_2=3$  in the first sum and  $m_1=L-3$  in the second one. Referring to the diagrams  $A_1$  and  $B_1$  in Fig. 2 we see that these terms correspond to the processes in which a tight pair is broken and another one is simultaneously formed. The rate of such a process is  $\Gamma$  in the WDM interaction model but it is  $T$  in the remaining two models in Fig. 1. Consequently, in such models, these two terms should be isolated from the sums in Eq. (28) to be multiplied by  $T - W$  rather than by  $\Gamma - W$ . The contribution due to the jumps occurring at a rate  $R$  in the BWM interaction model can be easily written following the  $(\Phi_{\text{fin}} - \Phi_{\text{in}})^* \Phi_{\text{in}}$  rule. For example, the contribution due to the counterclockwise jumps, represented by a diagram

$$[\bullet \circ_1 \leftarrow \circ_2 \circ_3 \dots \bullet_{m_2} \dots],$$

is  $3 \sum_{m_2=4}^{L-1} (\Phi_{1, m_2} - \Phi_{2, m_2})^* \Phi_{2, m_2}$ , while the diagram for the clockwise jumps is

$$[\bullet \dots \bullet_{m_1} \dots \circ_{L-3} \bullet_{L-2} \rightarrow \circ_{L-1}],$$

giving  $3 \sum_{m_1=1}^{L-4} (\Phi_{m_1, L-1} - \Phi_{m_1, L-2})^* \Phi_{m_1, L-2}$ . The subscripts denote the distance from the reference atom represented by the leftmost  $\bullet$ , while  $\circ$  represents sites which must remain unoccupied, and the linear diagrams should be folded into a circle.

We conclude this section by providing the explicit results for  $\delta \mathcal{M}(k; L, N=3)$  and corresponding to it correction to the diffusive eigenvalue for the WDM model for the lattice gas consisting of  $N=3$  particles. Performing the summations in Eq. (28) we get

$$\begin{aligned} \delta\mathcal{M}(k;L,N=3)/(\Gamma-W) \\ = -6 \left[ 2 + 8(L-4)\cos^2\left(\frac{ka}{2}\right) \right] \sin^2\left(\frac{ka}{2}\right), \end{aligned} \quad (29)$$

which, together with Eqs. (17) and (24), results in

$$\delta\lambda(k) = -4(\Gamma-W) \frac{2 + 8(L-4)\cos^2\left(\frac{ka}{2}\right)}{(L-2)(L-3)} \sin^2\left(\frac{ka}{2}\right). \quad (30)$$

### B. General $N$

For general  $N$  the evaluation of  $\delta\mathcal{M}(k;L,N)$  for the WDM interaction model proceeds along the same lines as illustrated for  $N=3$  in Sec. III A. In fact, the result in Eq. (28) can be immediately generalized. For  $N$  atoms arranged along the ring there are exactly  $N$  ways of pairing two neighboring atoms into a tight pair. Therefore, the factor 3 in Eq. (28) is replaced with  $N$ . The contribution  $A_1-A_0$  is represented by a diagram similar to the  $A_1$  diagram in Fig. 2 with the only difference that the spectator atom  $m_2$  is replaced with  $N-2$  ordered spectator atoms  $[m_2, m_3, \dots, m_{N-1}]$  occupying sites from 3 to  $L-1$ . Similarly,  $B_1-B_0$  is represented by the  $B_1$  diagram with the spectator atom  $m_1$  replaced with  $N-2$  ordered spectator atoms  $[m_1, \dots, m_{N-2}]$  occupying sites from 1 to  $L-3$ . Therefore, the summations in Eq. (28) over  $m_2$  and  $m_1$  satisfying the condition  $3 \leq m_2 \leq L-1$  and  $1 \leq m_1 \leq L-3$ , respectively, are replaced with the ordered summations over all these  $N-2$  indices satisfying, respectively, the conditions  $3 \leq m_2 < m_3 < \dots < m_{N-1} \leq L-1$  and  $1 \leq m_1 < m_2 < \dots < m_{N-2} \leq L-3$ . Generalized in this way  $A_1-A_0$  and  $B_1-B_0$  contributions will be referred to as the contributions of type  $A$  and  $B$ , respectively.

In order to deal with the BHM and the BWM interaction models (cf. Fig. 1) for general  $N$  we have to follow the procedure described for  $N=3$  in the paragraph preceding the one containing Eq. (29). For the transitions occurring at a rate  $T$  one has to extract the terms with in which  $m_2=3$  and  $m_{N-2}=L-3$  from the contributions  $A$  and  $B$ , respectively, and deal with them separately. Dealing with the transitions occurring at the rate  $R$  in the BWM interaction model is also easy—as shown in that paragraph. The result is

$$\begin{aligned} \delta\mathcal{M}(k;L,N) = (\Gamma-W)(\Delta_\Gamma^{(A)} + \Delta_\Gamma^{(B)}) + (T-W)(\Delta_T^{(A)} + \Delta_T^{(B)}) \\ + (R-W)(\Delta_R^{(A)} + \Delta_R^{(B)}), \end{aligned} \quad (31)$$

where the type  $A$  and  $B$  contributions due to the  $\Gamma$  transitions are, respectively,

$$\begin{aligned} \Delta_\Gamma^{(A)} = N \sum_{\substack{m_2, \dots, m_{N-1}=4 \\ \text{ord}}}^{L-1} (\Phi_{2, m_2, \dots, m_{N-1}} \\ - \Phi_{1, m_2, \dots, m_{N-1}})^* \Phi_{1, m_2, \dots, m_{N-1}}, \end{aligned} \quad (32a)$$

$$\begin{aligned} \Delta_\Gamma^{(B)} = N \sum_{\substack{m_1, \dots, m_{N-2}=1 \\ \text{ord}}}^{L-4} (\Phi_{m_1, \dots, m_{N-2}, L-2} \\ - \Phi_{m_1, \dots, m_{N-2}, L-1})^* \Phi_{m_1, \dots, m_{N-2}, L-1}. \end{aligned} \quad (32b)$$

The contributions due to the  $T$  and  $R$  transitions are listed in Appendix D in Eq. (D1). Note that for the  $T$  transitions one spectator atom is fixed at  $m_2=3$  [Eq. (D1a)] and at  $m_{N-2}=L-3$  [Eq. (D1b)] in the  $A$ - and  $B$ -type contributions, respectively.

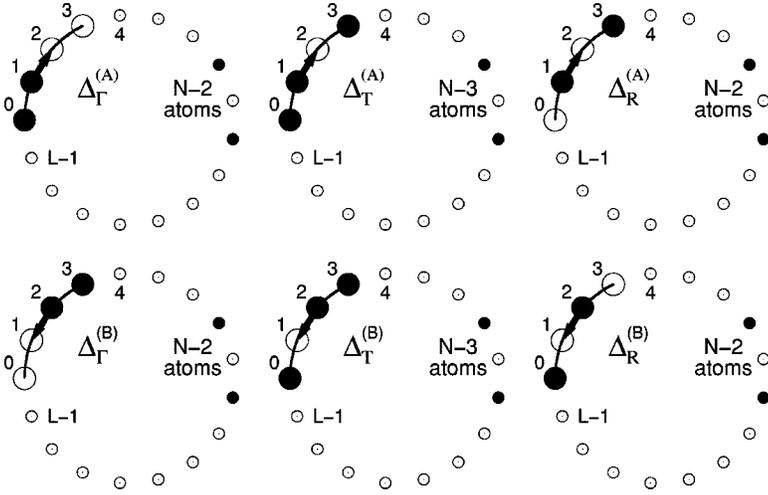
As before, each of the  $B$ -type contributions is a complex conjugate of the corresponding contribution of type  $A$ . The actual evaluation of these expressions is simplified by the fact that in the differences in the round brackets in Eqs. (32) and (D1) all terms depending on the summation indices cancel out. Our goal, however, is to recast these expressions into a form from which generalization to more complicated interaction models and to higher dimensional lattice gases can be easily made.

At this point using the components  $\Phi_{\{m\}}$  becomes inconvenient. Recall that the combined subscript  $\{m\} = [m_1, \dots, m_i, \dots, m_{N-1}]$  denotes a configuration in which the  $i$ th atom is at a distance  $m_i a$  away from the reference atom in the clockwise direction. Equivalently,  $m_i$  can be understood as a lattice position occupied by the  $i$ th atom with  $i=0$  referring to the reference atom at a site  $m_0=0$ . Going back to  $\Phi_{\{m\}}$ , however, we notice that the leading 1 in its definition in Eq. (12) is just an exponential  $\exp(-ikam_0)$  corresponding to the reference atom. The remaining terms account for the phases contributed by the remaining atoms due to their positions with respect to the reference atom. It is, therefore, convenient to introduce a function

$$f_{l,m,n,\dots} = e^{-ikal} + e^{-ikam} + e^{-ikan} + \dots, \quad (33)$$

in which the number of subscripts is equal to the number of phase factors added [a special case,  $f_m$ , was already introduced above Eq. (C5)]. In this notation we have  $\Phi_{m_1, m_2, \dots, m_{N-1}} = f_{0, m_1, m_2, \dots, m_{N-1}}$ . One can now replace all  $\Phi_{\{m\}}$ 's in Eq. (32) with the appropriate  $f$ 's. This results in Eq. (34a), below, for  $\Delta_\Gamma^{(A)}$ . In  $\Delta_\Gamma^{(B)}$  we use the identity  $f_{l+s, m+s, n+s, \dots} = \exp(-ikas) f_{l, m, n, \dots}$  for  $s=3$  to shift all subscripts by +3. After renaming the summation indices  $m_i+3 \rightarrow m_{i+1}$  they run over exactly the same values as in the  $A$ -type contribution. The last subscripts,  $L+1$  and  $L+2$  can be replaced with 1, and 2, respectively, using the periodic boundary condition (9), and then shifted to the first position. One gets Eq. (34b) for  $\Delta_\Gamma^{(B)}$ . The summation limits in both contributions are now exactly the same

$$\begin{aligned} \Delta_\Gamma^{(A)} = N \sum_{\substack{m_2, \dots, m_{N-1}=4 \\ \text{ord}}}^{L-1} (f_{0, 2, m_2, \dots, m_{N-1}} \\ - f_{0, 1, m_2, \dots, m_{N-1}})^* f_{0, 1, m_2, \dots, m_{N-1}}, \end{aligned} \quad (34a)$$



$$\Delta_{\Gamma}^{(B)} = N \sum_{\substack{m_2, \dots, m_{N-1}=4 \\ \text{ord}}}^{L-1} (f_{1,3,m_2, \dots, m_{N-1}} - f_{2,3,m_2, \dots, m_{N-1}})^* f_{2,3,m_2, \dots, m_{N-1}}. \quad (34b)$$

Both contributions in Eq. (34) can be represented by diagrams shown in two panels at the left hand side of Fig. 3. The entire lattice is divided into two parts: an “active” cell consisting of  $l_a=4$  sites, labeled 0, 1, 2, and 3, with  $n_a=2$  atoms in it and the “environment” consisting of the remaining  $L-l_a=L-4$  sites containing all remaining  $N-n_a=N-2$  atoms. In the active cell an atom (referred to as a “participant atom” from now on) jumps across the line bisecting the cell. The initial occupation pattern and the jump direction in the active cell corresponding to  $\Delta_{\Gamma}^{(B)}$ , [ $\circ\circ \leftarrow \bullet\bullet$ ], are obtained from those for the cell corresponding to  $\Delta_{\Gamma}^{(A)}$ , [ $\bullet\bullet \rightarrow \circ\circ$ ], by a mirror reflection in this line. Now, almost all exponents in the round brackets in Eqs. (34) cancel out leaving  $(f_2-f_1)^*$  in the type *A* contribution and  $-(f_2-f_1)^*$  in the type *B*. They can be pulled outside the summation and upon adding both contributions we encounter again the difference in which all terms depending on the summation indices cancel out leaving just  $(f_{0,1}-f_{2,3})$  which also can be pulled outside the sum. Consequently, no phase factors are left under the sum so the summation merely counts the number of possible configurations of ordered  $N-2$  atoms in the environment consisting of  $L-4$  sites. It is multiplied by  $N$  because any atom in the gas may be a participant around which the active cell is constructed. Exactly the same procedure can be applied to the contributions given in Eqs. (D1) due to transitions occurring at the rates  $T$  (for which the active cell has  $n_a=3$  atoms) and  $R$ . Collecting all final results we have

$$\Delta_{\Gamma}^{(A)} + \Delta_{\Gamma}^{(B)} = (f_2 - f_1)^* (f_{0,1} - f_{2,3}) \mathcal{D}(4, 2; L, N), \quad (35a)$$

$$\Delta_T^{(A)} + \Delta_T^{(B)} = (f_2 - f_1)^* (f_{0,1,3} - f_{0,2,3}) \mathcal{D}(4, 3; L, N), \quad (35b)$$

FIG. 3. Graphical representation of contributions to Eq. (31). The diagrams in three columns provide a transparent interpretation to expressions given in Eqs. (34) and (D1). They allow, however, one to write the final expressions given in Eqs. (35) by following a set of simple rules. All  $N-2$  or  $N-3$  atoms within the environment cell are represented by two small black dots. The sites (labeled 0, 1, 2, and 3) and the spectator and the relevant participant atoms within the active cell are shown using somewhat larger symbols. See text for details.

$$\Delta_R^{(A)} + \Delta_R^{(B)} = (f_2 - f_1)^* (f_{1,3} - f_{0,2}) \mathcal{D}(4, 2; L, N), \quad (35c)$$

where

$$D(l_a, n_a; L, N) = N \sum_{\substack{m_1, \dots, m_{N-n_a}=1 \\ \text{ord}}}^{L-l_a} 1. \quad (36)$$

The summation indices were renamed and the summation limits shifted with respect to those in Eqs. (34) and (D1). The arguments  $l_a$  and  $n_a$  denote, respectively, the number of sites and the number of atoms in the active cell. The precise meaning of the factor  $\mathcal{D}$  will be given shortly [see text below Eq. (37) later].

Note that the factor  $(f_{0,1,3} - f_{0,2,3})$  is, in fact, equal to  $(f_1 - f_2)$  but the form used in Eq. (35b) is preferable for the purpose of formulating the rules of dealing with an arbitrary interaction model. These rules are summarized in the next section.

### C. Summary of the general rules

We generalize now the description already given and formulate the general rules allowing to evaluate the numerator  $\delta\mathcal{M}(k; L, N)$  in Eq. (17).

Each of the expressions in Eq. (35) is represented by a diagram in Fig. 3 which are constructed as follows.

(1) The entire lattice is divided into two sublattices: an active cell and the environment. The active cell contains  $n_a$  atoms: one atom executing a jump (called a participant atom) between two sites across the line bisecting the cell and  $n_a - 1$  “spectator” atoms, whose presence cause the jump rate of the participant atom to differ from that of an isolated atom. The size of the active cell (i.e., the number of its sites,  $l_a$ ) must be the smallest possible but large enough for the jump rate of the participant atom to be independent of positions of all  $N-n_a$  atoms placed within the environment.

(2) The initial occupations in the active cells corresponding to the type *A* and *B* contributions must be exact mirror images of each other with respect to the line bisecting the jump path of the participant atom. The sites within the active cell are labeled by consecutive integers which can be arbitrary.

trary but must be the same for both diagrams representing the type  $A$  and  $B$  contributions.

(3) The number of the spectator atoms,  $n_a - 1$ , within the active cell should be varied from one up to the maximum number which can be fitted within it without inhibiting the jump of the participant atom. Each topologically inequivalent arrangement of  $n_a - 1$  spectators in the active cell must be considered separately even if they might correspond to the same jump rate.

(4) With all that the factor multiplying the difference between the unperturbed  $W$  and the actual transition rates ( $\Gamma$ ,  $T$ ,  $R$ , etc.) is

$$\Delta^{(A)} + \Delta^{(B)} = \mathcal{D}(l_a, n_a; L, N) [f_{\text{part.fin}}^{(A)} - f_{\text{part.fin}}^{(B)}]^* [f_{\text{occ.in}}^{(A)} - f_{\text{occ.in}}^{(B)}]. \quad (37)$$

The first factor,  $\mathcal{D}$ —given in Eq. (36), is a product of  $N$  which accounts for the possibility that any of the  $N$  atoms in the system can be selected as a participant atom around which an active cell is constructed and the ordered sum yielding a number of all possible configurations in which  $N - n_a$  atoms may be distributed among  $L - l_a$  sites of the environment provided that no permutations of the atoms are allowed [i.e., the atoms are tagged and placed in the environment in a particular order—we stress that the sum in Eq. (36) is ordered].  $\mathcal{D}$  will be referred to as the “environment factor.”

The remaining two factors in Eq. (37), referred to as the “active cell factor,” are the only ones which contain the information about the structure of the active cell and the particular process occurring within it. Here, “part.fin” stands for the label of the site occupied within the active cell by the participant atom *after* the jump while “occ.in” denotes a collection of labels of all occupied sites within the cell *before* the jump. Eq. (33) should be used once the indices corresponding to “part.fin” and “occ.in” are identified.

(5) Each contribution given in Eq. (37) corresponding to a particular actual transition rate must be multiplied by the corresponding difference of the unperturbed jump rate and the actual rate, the results must be added [cf. Eq. (31)] and divided by the normalization factor  $\mathcal{N}(L, N)$  to yield the correction  $\delta\lambda(k)$  to the diffusive eigenvalue of the rate matrix  $\mathbb{M}(k)$  [cf. Eq. (17)].

The active cell with four sites is sufficient to assure for all interaction models considered here that no atom in the environment affects the jump rate of the participant atom within the active cell. The participant atom needs two sites so  $n_a$  can be equal 2 or 3 (the minimum is 2 because the active cell must contain at least one spectator atom).<sup>23</sup> For  $n_a = 2$  there are two topologically inequivalent arrangements of spectators with respect to the initial position of the participant atom so, according to the Rule 3, both  $A$ -type diagrams with  $n_a = 2$ , [ $\bullet \bullet \rightarrow \circ \circ$ ] and [ $\circ \bullet \rightarrow \circ \bullet$ ], together with their  $B$ -type counterparts must be considered even when  $R = \Gamma$  (the latter drops out, of course, when  $R = W$ ).

The rules formulated above apply also to interaction models for which the interactions have longer range than in the models considered here. In such a case the active cell would be comprised of more than just four sites. The rules can also

be used to evaluate  $\Phi^\dagger(k) \cdot \delta\mathbb{M}(k) \cdot [\mathbf{P}^{\text{var}} \Phi(k)]$  {or even  $\Phi^\dagger(k) \cdot \mathbb{M}(k) \cdot [\mathbf{P}^{\text{var}} \Phi(k)]$ , see Ref. 23} with  $\mathbf{P}^{\text{var}}$  better adjusted to the actual equilibrium occupations than assumed so far. One such example will be considered in Sec. IV.

## D. Results

The environment factor  $\mathcal{D}(l_a, n_a; L, N)$  [defined in Eq. (36)] must be divided by the normalization factor  $\mathcal{N}(L, N)$  [cf. Eqs. (17), (31), and (35)]. Evaluating them one has to assure that all atoms in the system are tagged and distributed among the lattice site in some specific order—evaluating the number of possible configurations of the system one is not allowed to consider configurations obtained by switching positions of two atoms. In other words, among  $N$  different configurations corresponding to  $N$  atoms occupying specific sites on the lattice only one is legitimate—the one in which the order of atoms is consistent with condition (5).

It is worth to note here that the restriction imposed by labeling and ordering the atoms in the lattice gas may be entirely removed from the considerations. When the ordering is ignored the number of configurations increase and the numerator  $\mathcal{D}(l_a, n_a; L, N)$  and the denominator  $\mathcal{N}(L, N)$  get multiplied by  $(N - 1)!$  leaving the ratio unchanged (cf. Appendixes C and E for more details). This is a minor point in this work but it becomes important when the method will be applied to a two dimensional lattice gas for which ordering of atoms would be, at least, inconvenient [cf. Sec. V].

Using Eqs. (C13) and (E1) we get

$$\Omega(l_a, n_a; L, N) = \frac{\mathcal{D}(l_a, n_a; L, N)}{\mathcal{N}(L, N)} = \frac{\mathfrak{D}(l_a, n_a; L, N)}{\mathfrak{N}(L, N)} = \frac{\binom{L - l_a}{N - n_a}}{\binom{L - 2}{N - 1}}. \quad (38)$$

Entire  $\Omega(l_a, n_a; L, N)$  will also sometimes be referred to as an environment factor. On the right hand side we use the quantities  $\mathfrak{N}$  and  $\mathfrak{D}$ , defined in Eqs. (C2) and in the paragraph containing Eq. (E2), respectively. They differ from  $\mathcal{N}$  and  $\mathcal{D}$  in this respect that the restriction imposed by the ordering of atoms [cf. Eq. (5)] is removed.

In the most general interaction model considered here, BWB, the correction  $\delta\lambda(k)$  to the diffusive eigenvalue of the rate matrix consists of three contributions,  $\delta\lambda_\Gamma(k)$ ,  $\delta\lambda_T(k)$ , and  $\delta\lambda_R(k)$  corresponding, respectively, to the special rates  $\Gamma$ ,  $T$ , and  $R$ . Using Eqs. (17), (31), (33), (35), and (38), we get

$$\frac{\delta\lambda_\Gamma(k)}{\Gamma - W} = -16 \sin^2\left(\frac{ka}{2}\right) \cos^2\left(\frac{ka}{2}\right) \frac{(N - 1)(L - N - 1)}{(L - 2)(L - 3)}, \quad (39a)$$

$$\frac{\delta\lambda_R(k)}{R - W} = +8 \sin^2\left(\frac{ka}{2}\right) \cos(ka) \frac{(N - 1)(L - N - 1)}{(L - 2)(L - 3)}, \quad (39b)$$



ther at a fast rate  $T$  the initial slow step is a bottleneck allowing to ignore the configurations with two neighboring holes. These configurations are  $R/\Gamma \ll 1$  less likely than the configurations in which every hole is separated from another one by at least one atom. Configurations with clusters of more than two holes or with more than one pair of holes are even less likely. Therefore, diffusion is due to the random walk of a kink, jumping at a fast rate  $T$  at a distance  $2a$ , so the diffusion coefficient is  $T(2a)^2 = 4Ta^2$ . The only configurations involved, referred to as the “ $0_h$ -pair” ones in what follows, are those in which there are no pairs of holes (thus the subscript  $h$ ). Configurations in which only one pair of holes is present in the entire system are denoted by  $1_h$ -pair, etc. Recall that the  $\{m\}$ th component of  $\mathbf{P}^{\text{eq}}$  is, up to a common multiplicative factor, equal to the probability of the configuration  $\{m\}$  in equilibrium. Therefore, the components of  $\mathbf{P}^{\text{eq}}$  corresponding to the  $0_h$ -pair configurations dominate over all the remaining ones which are at least  $R/\Gamma \ll 1$  times less probable.  $\mathbf{P}^{\text{eq}}$  is also [cf. discussion later Eq. (A2)] an eigenvector of  $\mathbb{M}(k=0)$  and if terms proportional to the slow rates  $W$  and  $R$  were to be ignored in this matrix then all components in  $\mathbf{P}^{\text{eq}}$  except the  $0_h$ -pair ones would vanish identically. All  $0_h$ -pair components could be set equal to 1 because these configurations are equally likely in equilibrium.

The earlier considerations suggest how to select  $\mathbf{P}^{\text{var}}$  and  $\Phi_{\text{var}}(k)$  in the variational expression (10) for the diffusive eigenvalue  $\lambda(k)$ . The former should be as close to  $\mathbf{P}^{\text{eq}}$  as possible so we choose  $\mathbf{P}^{\text{var}}$  to have all  $0_h$ -pair components equal to 1 and all the rest equal to 0 [the overall normalization is irrelevant because it is taken care of by the denominator in Eq. (10)]. We denote it  $\mathbf{P}_0^{\text{eq}}$ . In ignoring all but  $0_h$ -pair components the important role is played by the fact that transitions between  $0_h$ -pair configurations occur at a fast rate  $T$ . We can set to 0 all matrix elements of  $\mathbb{M}(k)$  which are proportional to the slow rate  $W$  and the fast rate  $\Gamma$  because they correspond to transitions in which  $0_h$ -pair configurations are neither the initial nor the final ones. We can set to zero also those matrix elements which involve the slow rate  $R$  because these transitions take the system from a  $0_h$ -pair configuration to a  $1_h$ -pair one which we ignore anyway. The resulting matrix, denoted  $\mathbb{M}_T(k)$ , contains only rates  $T$ .

Next, we choose  $\Phi_{\text{var}}(k)$  to be the same as before, i.e., it is  $\Phi(k)$  with its components given in Eq. (12). We see that the product  $\mathbf{P}_0^{\text{eq}}\Phi(k)$  has all  $0_h$ -pair components the same as those of  $\Phi(k)$  but all the remaining ones are 0. The product  $\mathbb{M}_T(k) \cdot [\mathbf{P}_0^{\text{eq}}\Phi(k)]$ , is now a one column array (proportional to  $T$ ) having only the  $0_h$ -pair components (the rest are 0) because all transitions between the  $0_h$ -pair configurations occur solely at a rate  $T$ . Consequently, only the  $0_h$ -pair components are relevant in  $\Phi_{\text{var}}^\dagger(k)$  in both the numerator and the denominator in Eq. (10), i.e.,  $\Phi_{\text{var}}^\dagger(k)$  can be replaced there with  $[\mathbf{P}_0^{\text{eq}}\Phi(k)]^\dagger$ :

$$-\lambda(k) \approx \frac{[\mathbf{P}_0^{\text{eq}}\Phi(k)]^\dagger \cdot \mathbb{M}_T(k) \cdot [\mathbf{P}_0^{\text{eq}}\Phi(k)]}{[\mathbf{P}_0^{\text{eq}}\Phi(k)]^\dagger \cdot [\mathbf{P}_0^{\text{eq}}\Phi(k)]} = \frac{\mathcal{M}_T(k; L, N)}{\mathcal{N}(k; L, N)}. \quad (42)$$

The numerator  $\mathcal{M}_T(k; L, N)$  can be evaluated using the rules formulated in Sec. III C to evaluate  $\Phi^\dagger(k) \cdot \delta\mathbb{M}(k) \cdot \Phi(k)$ . The

denominator  $\mathcal{N}(k; L, N)$ , which will depend on  $k$  this time, must be evaluated separately.

Evaluation of the numerator in Eq. (42) is easy. We use Eq. (37) and the result will be multiplied by  $T$ . The active cells  $A$  and  $B$  are those given in the central panels in Fig. 3, i.e.,  $[\bullet\bullet \rightarrow \circ\bullet]$  and  $[\bullet\circ \leftarrow \bullet\bullet]$ , respectively. The remaining two pairs of active cells in Fig. 3 are disallowed because they admit hole pairs either before or after the jump. The environment factor  $\mathcal{D}(l_a, n_a; L, N)$  ( $l_a=4, n_a=3$ ) is formally defined in Eq. (36) with the difference that the summation is only over the  $0_h$ -pair configurations. The sum is still ordered and the result is equal to the number of the  $0_h$ -pair configurations of the environment in which  $N-3$  atoms are distributed among  $L-4$  sites. This means that in arranging  $N-3$  atoms along a line at most one hole can be placed between two neighboring atoms. There can also be at most one hole at the edges of the environment because both active cells have atoms at each edge. Consequently, there are  $(N-3)+1$  bins (spaces between atoms), each one capable of accepting no more than one hole from the total number  $(L-N)-1$  of them (because one hole is already in the active cell). The number of possibilities is  $\binom{N-2}{L-N-1}$  and the numerator in Eq. (42) is

$$\mathcal{M}_T(k; L, N) = -4T \sin^2\left(\frac{ka}{2}\right) N \binom{N-2}{L-N-1}. \quad (43)$$

The denominator

$$\begin{aligned} \mathcal{N}(k; L, N) &\equiv [\mathbf{P}_0^{\text{eq}}\Phi(k)]^\dagger \cdot [\mathbf{P}_0^{\text{eq}}\Phi(k)] \\ &= \sum_{\substack{\{m\} \\ \text{ord}}}^{0_h} |(1 + e^{-ikam_1} + \dots + e^{-ikam_{N-1}})|^2 \end{aligned} \quad (44)$$

cannot be evaluated exactly this time. The sum  $\sum_{\substack{\{m\} \\ \text{ord}}}^{0_h}$  denotes here the sum over all  $0_h$ -pair configurations. It implies that apart from the ordering condition [Eq. (5)], extra conditions

$$m_1 \leq 2,$$

$$m_{i+1} - m_i \leq 2, \quad \text{for } i = 1, \dots, N-2,$$

$$m_{N-1} \geq L-2, \quad (45)$$

must be met to assure that the distance between two consecutive atoms is not greater than  $2a$ , i.e., that each hole has necessarily occupied sites as its neighbors [the first and the last condition in Eq. (45) assure that also the reference atom has no more than one hole at each of its sides]. The number of terms in such a sum is equal to  $\binom{N}{L-N}$ —the number of ways in which  $L-N$  holes can be distributed among  $N$  bins (i.e.,  $N$  intervals between consecutive atoms arranged along a circle) each one accommodating at most one hole. Using condition (9) and indexing the atoms to the left of the reference atom by negative integers  $j=-1, -2, \dots$  for which  $m_j = m_{-j} < 0$ , one can show (cf. Appendix F) that

$$\mathcal{N}(k; L, N) = N \left[ \binom{N}{L-N} + \sum_{\substack{j=-(N-1)/2 \\ j \neq 0}}^{+(N-1)/2} \left( \sum_{\substack{0_h \\ \{m\} \\ \text{ord}}} e^{ikam_j} \right) \right], \quad (46)$$

for odd  $N$ . For even  $N$  the sum runs from  $j=-N/2$  to  $j=+N/2-1$ , excluding  $j=0$ . The first term in the square bracket is, in fact, due to the  $j=0$  term extracted from the sum in the next term.

Unfortunately, the expression in Eq. (46) cannot be evaluated exactly and approximations are needed. Note the order of summations in Eq. (46): the summation over the configurations must be done first [cf. discussion below Eq. (F2)]. One focuses attention first on a fixed atom ( $j$ th, say), adds all phase contributions due to its positions in all configurations scanned by the inner summation. Doing that for each atom one adds the results, as required by the outside summation. For each atom (each  $j$ ) the result of the summation over the configurations is, in general, different. We approximate this result by introducing an average  $\langle \exp(ikam_j) \rangle_{\{m\}}$  of  $\exp(ikam_j)$  over all configurations to replace the summation over the configurations with a multiplication of the average by the number of the configurations

$$\sum_{\substack{0_h \\ \{m\} \\ \text{ord}}} e^{ikam_j} \approx \binom{N}{L-N} \langle e^{ikam_j} \rangle_{\{m\}}. \quad (47)$$

The average is different for each consecutive atom (i.e., for each  $j$ ). Consider the first atom,  $j=1$ . If there is a hole between it and the reference atom,  $\bullet\circ\bullet\dots$ , then  $m_1=2$ , otherwise, for  $\bullet\bullet\dots$ , we have  $m_1=1$  (the leftmost  $\bullet$  denotes the reference atom). The corresponding phase factors are  $\exp(2ika)$  and  $\exp(ika)$ , respectively. Therefore

$$\langle e^{ikam_1} \rangle_{\{m\}} = p e^{2ika} + (1-p) e^{ika}, \quad (48)$$

where

$$p = \frac{L-N}{N} = \frac{1}{\theta} - 1, \quad (49)$$

is the probability that there is a hole between any two consecutive atoms [because there are  $L-N$  holes and  $N$  bins (intervals between consecutive atoms)] capable of accepting at most one hole. For the second atom,  $j=2$  there are four possibilities:  $\bullet\circ\circ\bullet\dots$  with  $m_2=4$ , contributing  $p^2 \exp(4ika)$ ;  $\bullet\circ\bullet\dots$  and  $\bullet\bullet\circ\dots$  with  $m_2=3$  contributing together  $2p(1-p) \exp(3ika)$ ; and  $\bullet\bullet\dots$  with  $m_2=2$  contributing  $(1-p)^2 \exp(2ika)$ . The sum of these three terms is just a square of the right hand side in Eq. (48). These considerations can be extended and the result is

$$\langle e^{ikam_j} \rangle_{\{m\}} = (p e^{\pm 2ika} + (1-p) e^{\pm ika})^{|j|}, \quad (50)$$

where the minus sign in the exponent corresponds to negative  $j$ 's. The error in this approximation is due to the fact that the actual probability of having a hole between any two consecutive atoms depends on that how many holes were already used to fill spaces between earlier atoms whereas in Eq. (50) this effect is ignored. In particular, for  $j > L-N$  (which is possible because the number of atoms  $N$  is greater

than the number of holes  $L-N$ ) some terms at the right hand side of Eq. (50) correspond to the configurations with more holes than their actual total number  $L-N$ .

Inserting Eq. (50) into Eq. (47) and substituting the result into Eq. (46) one ends up with a sum of a geometric progression of terms at the right hand side of Eq. (50) summed up to  $j=(N-1)/2$  plus its complex conjugate due to negative  $j$ 's. The upper limit is spurious due to the approximation error mentioned below Eq. (50) and should be extended to  $\infty$  for  $N \gg 1$ . The result is

$$\mathcal{N}(k; L, N) \approx N \binom{N}{L-N} \frac{p(1-p) \sin^2\left(\frac{ka}{2}\right)}{(1-p)^2 \sin^2\left(\frac{ka}{2}\right) + p \sin^2(ka)}. \quad (51)$$

Note that  $\mathcal{N}$  depends now on  $k$ , in contrast to the result in Eq. (C13).

Inserting Eqs. (43) and (51) into Eq. (42), using  $\theta=N/L$  and Eq. (49), we get  $\lambda=(ka/\theta)^2$  for  $ka \ll 1$  and  $N \gg 1$ , i.e.:

$$D(\theta)/a^2 = \frac{T}{\theta^2}, \quad \text{for } \theta > 0.5. \quad (52)$$

This is a surprisingly simple result. For  $\theta=0.5$  we get the expected  $D=4Ta^2$  and for  $\theta=1$  we have  $D=Ta^2$  which is also expected because at full coverage isolated holes jump at a rate  $T$  at a distance  $a$ . It is worthwhile to compare the above result with the result in Eq. (41) which was obtained assuming that every configuration satisfying condition (5) is equally likely. For  $T=\Gamma$  and  $W=R$  the latter gives

$$D(\theta)/a^2 = W + (T-W)\theta(4-3\theta), \quad (53)$$

in which one can ignore  $W$  for  $W \ll T$  (we keep  $W$  in because the above expression is valid also for  $\theta \ll 1$ ). For  $\theta=0.5$  we get, not surprisingly, a very different result than from Eq. (52) because in Eq. (53) the equilibrium correlations present around half coverage are entirely ignored. For  $\theta \approx 1$ , however, both results predict  $D=Ta^2$  and the same slope  $-2T$  of  $D(\theta)$ .

### B. Case $\theta < 0.5$

Superficially, one might argue that the approach presented in the preceding section applies also for  $\theta < 0.5$  and the only modification needed is to interchange the role which the holes and atoms play in the considerations. This would replace  $\theta$  with  $1-\theta$  and  $T$  with  $W$  in the final result giving  $D(\theta) = Wa^2/(1-\theta)^2$ . Unfortunately, such an approximation misses contributions to  $D$  which are of the same order of magnitude as those which are preserved.

To see this clearly it is best to start with considerations, analogous to those at the beginning of the  $\theta > 0.5$  subsection, but for coverages now slightly less than 0.5. The kink is now formed by a pair of holes and the  $0_a$ -pair,  $1_a$ -pair,  $2_a$ -pair configurations are those containing none, one, or two pairs of atoms. As before we start with the  $0_a$ -pair configuration:



considered in the central panel of Fig. 3 so the active cell factor is the same as in Eq. (39c). The contribution must be multiplied by the rate  $T$  and by the probability factor  $R/\Gamma$  corresponding to the initial  $1_a$ -pair configuration. The number of holes in the environment is  $L-N-1$  but the number of bins among which  $N-3$  atoms are distributed is only  $L-N-2$  because both sites in the environment adjacent to the active cell cannot be occupied by an atom. The result is

$$\mathcal{M}_T(k;L,N) = -4T \left(\frac{R}{\Gamma}\right) \sin^2\left(\frac{ka}{2}\right) (L-N) \binom{L-N-2}{N-3}. \quad (58)$$

Note that each contribution listed in Eqs. (55)–(58) is, effectively, of the order  $W$ .

To evaluate the normalizing denominator in Eq. (10) we note first that the right hand side factor of the dot product, i.e.,  $\mathbf{P}^{\text{var}}\Phi_{\text{var}}(k)$ , has  $1_a$ -pair components which are  $R/\Gamma$  times smaller than its  $0_a$ -pair components, while the weights of all components in the left hand side factor, i.e.,  $\Phi_{\text{var}}^\dagger(k)$ , are the same. Consequently, the contribution due to the  $1_a$ -pair components is  $R/\Gamma$  times smaller than that due to the  $0_a$ -pair components and can be neglected. In this approximation we get for  $N < L/2$  the expression for  $\mathcal{N}(k;L,N)$  which is the same as in the second line of Eq. (44). The only difference is that the summation is over the configurations with no pairs of atoms ( $0_a$ -pair configurations) while in Eq. (44)—valid for  $N > L/2$ —it was over the configurations with no pairs of holes ( $0_h$ -pair configurations). The sum of  $N$  exponential terms  $\exp(-ikam_i)$ , including 1 which is  $\exp(-ikam_0)$  can be replaced with the sum of  $L-N$  exponential terms in which  $m_0, \dots, m_{L-N-1}$  are positions of *holes* rather than atoms. This is because the sum of the exponential terms corresponding to holes and atoms add up to zero according to Eq. (C5) [a direct consequence of Eq. (9) resulting from the periodic boundary conditions]. In other words, we get formally the same expression as Eq. (44) with the roles of holes and atoms interchanged. Therefore, the approximate result is given in Eq. (51) in which  $N$  and  $L-N$  are interchanged and  $p$  is replaced with  $1/p$  [with  $p$  still being defined in Eq. (49) but no longer being smaller than 1]:

$$\begin{aligned} \mathcal{N}(k;L,N) \approx & (L-N) \binom{L-N}{N} \\ & \times \frac{(p-1) \sin^2\left(\frac{ka}{2}\right)}{(p-1)^2 \sin^2\left(\frac{ka}{2}\right) + p \sin^2(ka)}. \end{aligned} \quad (59)$$

Adding contributions (55)–(58), setting  $W=R$  and  $T=\Gamma$ , dividing by  $\mathcal{N}$  given in Eq. (59), taking the limit  $ka \ll 1$  and  $L, N \gg 1$ , setting  $\theta=N/L$  and using Eq. (49), we get

$$D(\theta)/a^2 = \frac{W}{(1-2\theta)^2}, \quad \text{for } \theta < 0.5, \quad (60)$$

which has a proper limit for  $\theta=0$  but is not expected to be very accurate for  $\theta \approx 0.5$ . In fact, the result diverges for  $\theta=0.5$ . The reason is simple—keeping  $W$  finite we effectively

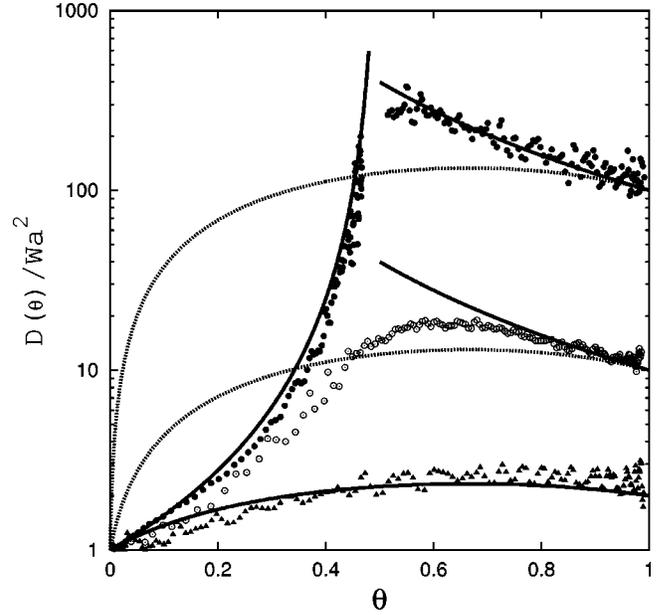


FIG. 4. Comparison of  $D(\theta)/Wa^2$ , Eq. (52) for  $\theta > 0.5$  and Eq. (60) for  $\theta < 0.5$  (continuous lines terminating at  $\theta=0.5$ ) with the results of the Monte Carlo simulations (points). The simulations are done for  $R=W$ ,  $T=\Gamma$  with  $T/W=100$  (solid points),  $T/W=10$  (open points), and  $T/W=2$  (triangles). For the latter case the theoretical continuous line curve is from Eq. (53). For comparison,  $D(\theta)/Wa^2$  from Eq. (53) is plotted also for  $T/W=100$  and 10 (dotted lines).

set  $T \rightarrow \infty$  so with the diffusion coefficient controlled by  $T$  at  $\theta=0.5$  it is not surprising that the result is infinite. Therefore, a better approximation scheme would require dealing with finite  $T$  near  $\theta=0.5$ . We note also that result (53) has very different behavior than that in Eq. (60)—only the value of the diffusion coefficient at  $\theta=0$  is the same in both but the slopes of  $D(\theta)$  in these two approximations are very different.

We compare the analytic results for the strong repulsion case, Eqs. (52) and (60), with the results of the recent Monte Carlo simulations<sup>27,28</sup> in a one dimensional lattice gas with vastly different rates  $W$  and  $T$ . The simulations were performed for  $W/T=0.01, 0.1$ , and  $0.5$  (the latter cannot qualify as a strong repulsion case).  $D(\theta)/Wa^2$  is shown Fig. 4 as a function of coverage over the entire range from 0 to 1. As expected, the simulation results for  $W$  and  $T$  differing by two orders of magnitude agree better with the analytic results in Eqs. (52) and (60) than those for the rates differing only by one order of magnitude. The agreement between the analytic and the simulation results extends, however, for more than two orders magnitude (for  $\theta < 0.5$ ). For comparable  $R$  and  $T$  ( $T=2R$ ) the agreement with the strong repulsion version of the theory is poor but in such case the theoretical result in Eq. (53) reproduces the simulation data quite well. The latter fails, however, for the strong repulsion cases except, perhaps, close to  $\theta \approx 1$  where  $D$  is close to its  $\theta=1$  value. This is understandable in view of the fact that the result in Eq. (53) is effectively the perturbation theory result. Near  $\theta=0$  the diffusion coefficient varies too rapidly with  $\theta$  for any perturbation theory result to be reliable.

The analytic result for the strong repulsion case has a discontinuity at half coverage while the simulations merely

predict a sudden change in the behavior of  $D(\theta)$  there. As discussed earlier, the discontinuity [and, in fact, the divergence in  $D(\theta)$ ], are related to the fact that in the analytic result for  $\theta < 0.5$  we effectively have  $T \rightarrow \infty$  while  $W \approx 0$  is assumed for  $\theta > 0.5$ .

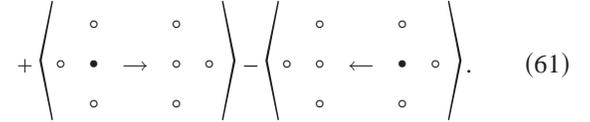
## V. TWO DIMENSIONS

The variational approach used to evaluate the coverage dependence of the collective diffusion coefficient in an interacting lattice gas can be easily generalized to the two dimensional case. In two dimensions the lattice gas may undergo a structural phase transition at certain coverages. In principle, the information about the structural phase at a given coverage—determined by the same interactions between the atoms which determine the actual jump rates, is contained in  $\mathbf{P}^{\text{eq}}$ , the eigenvector of  $\mathbb{M}(k=0)$ . Consequently, by a proper choice of  $\mathbf{P}^{\text{var}}$ —the variational candidate for  $\mathbf{P}^{\text{eq}}$ —one can build into the calculation the information about the structural phase and account for the coverage dependence of the diffusion coefficient within this phase. In this work we will, for the purpose of a demonstration only, limit our attention to a two dimensional analog of the case considered in Sec. III, i.e., the case in which the jump rates are only moderately modified by the atom-atom interactions. Phase transformation is not expected in this case. The work on cases in which the transformations do occur is in progress.

The variational expression for the diffusive eigenvalue of the rate matrix is a ratio of the “expectation value” and a normalizing denominator [cf. Eq. (10)]. In both of them a summation over the configurations  $\{m\}$  is involved. In one dimension the atoms in the system are tagged,  $i = 1, 2, \dots, N-1$ , and their positions with respect to the reference atom,  $m_i$ 's, are ordered according to Eq. (5). This ordering restricts a set of configurations  $\{m\}$  admitted in the summations. We have seen, however, that this ordering—although convenient in deriving the rules listed in Sec. III C—is unnecessary when they are applied. Namely, to evaluate the denominator  $\mathcal{N}(L, N)$  in Appendix C we have removed any restriction due to the ordering right at the start. The result is an increase of the denominator by a factor  $(N-1)!$ . We have also shown in Appendix E that when the numerator  $\mathcal{D}(l_a, n_a; L, N)$  is evaluated, removing the restriction due to ordering leads to its increase by the same factor  $(N-1)!$  so the ratio remains unchanged. Consequently, one might ignore the ordering of the atomic positions within a configuration right from the beginning without changing the final result [cf. Eq. (38)]. This can be taken advantage of in two dimensions where tagging of atoms is still possible but there is no easy way of ordering their positions with respect to the reference atom. One can, however, ignore any ordering scheme (and the restrictions imposed by it on the summations over the configurations) in the two dimensional case as long as it is done in both the numerator and the denominator of the variational expression.

We consider a lattice gas on a square lattice of adsorption sites with a lattice constant  $a$ . As before, we denote by  $W$  the jump rate of an isolated atom and consider a model in which the jump rates differ from  $W$  only when at least one bond

between nearest atoms is either broken or formed (i.e., the jumping atom has at least one nearest neighbor either before or after the jump). It is easy to see that it is sufficient to limit the active cell  $l_a=8$  sites. For example, a pair of active cells,  $A$  and  $B$ , which must be considered for jumps along the  $x$  axis are



Not shown are the sites in the four corners because they do not belong to cell. Signs + and – remind that the contributions evaluated due to the cell  $B$  must be subtracted from those due to the cell  $A$ . Only the participant atom is shown as • and among the remaining  $l_a-1=7$  sites ◦ in the cell at least one but no more than  $l_a-2=6$  should be filled with the spectator atoms:  $n_a$  varies between<sup>23</sup> 2 and 7. All possible occupation patterns should be considered and all cases can be classified as  $(n_a, n_B, n_F)$ , i.e., by specifying the total number of the atoms in the active cell ( $n_a$ ), the number of bonds broken ( $n_B$ ) and formed ( $n_F$ ) as a result of the atomic jump indicated by the arrow. Both  $n_B$  and an additional label (say  $a, b, c, \dots$ ) may be needed to distinguish among several diagrams with the same  $n_a, n_B$ , and  $n_F$ . The jumps along the  $y$  axis are easily accounted for by adding to the expressions evaluated from the diagrams the expressions obtained by interchanging  $k_x$  with  $k_y$  [in the two dimensional case  $k$  is replaced by a vector  $\mathbf{k}=(k_x, k_y)$ ]. The sites in the active cell are labeled by specifying their position with respect to a fixed reference site which can be chosen arbitrarily. A convenient choice is, for example, such for which the sites occupied by the participant atom before the jump are at  $a(1, 1)$  and  $a(2, 1)$  in the left (type  $A$ ) and the right (type  $B$ ) cell, respectively, in Eq. (61): i.e, the  $(0, 0)$  site itself which would be in the lower left corner does not belong to the cell and is not shown.

The environment factor associated with a diagram  $(n_a, n_B, n_F)$  is  $\Omega(l_a=8, n_a; L^2, N)$  given in Eq. (38). Among the two remaining factors in Eq. (37), the first one is the same for all diagrams and for the earlier described choice of the reference site it is

$$[f_{\text{part.fin}}^{(A)} - f_{\text{part.fin}}^{(B)}]^* = (X^2Y - XY)^* = \frac{1-X}{X^2Y}, \quad (62)$$

where  $X = \exp(-iak_x)$  and  $Y = \exp(-iak_y)$ . The second factor,  $f_{\text{occ.in}}^{(A)} - f_{\text{occ.in}}^{(B)}$ , must be evaluated for each group of diagrams separately. We note here that each of the factors depends on the choice of the reference site but their product does not.

There are, in total, 39 groups of diagrams. One third of them contain one  $A$ -type and one  $B$ -type diagram (the occupation pattern is the same above as it is below the line connecting the initial and the final site of the jumping atom). The remaining 26 groups contain two  $A$ -type and two  $B$ -type diagrams. For example, one of five possible  $(n_a=5, n_B=2, n_F=2)$  configurations is

TABLE I. Coverage dependent corrections to the unperturbed diffusion coefficient  $Wa^2$  due to atomic jumps breaking  $n_B$  and forming  $n_F$  bonds of the jumping atom with its nearest neighbors. Each entry in the table has to be multiplied by  $(\Gamma_{n_B, n_F})a^2$ . The entries in the last line and the last column are sums of all entries above it or to the left of it, respectively.

	$n_B=0$	$n_B=1$	$n_B=2$	$n_B=3$	
$n_F=0$	–	$8\theta(1-\theta)^5$	$13\theta^2(1-\theta)^4$	$6\theta^3(1-\theta)^3$	$\theta(1-\theta)^3(\theta^2-3\theta+8)$
$n_F=1$	$-2\theta(1-\theta)^5$	$9\theta^2(1-\theta)^4$	$24\theta^3(1-\theta)^3$	$13\theta^4(1-\theta)^2$	$\theta(1-\theta)^2(15\theta-2)$
$n_F=2$	$-7\theta^2(1-\theta)^4$	$-6\theta^3(1-\theta)^3$	$9\theta^4(1-\theta)^3$	$8\theta^5(1-\theta)$	$\theta^2(1-\theta)(15\theta-7)$
$n_F=3$	$-4\theta^3(1-\theta)^3$	$-7\theta^4(1-\theta)^2$	$-2\theta^5(1-\theta)$	$\theta^6$	$\theta^3(5\theta-4)$
	$\theta(1-\theta)^3(\theta^2-3\theta-2)$	$-\theta(1-\theta)^2(15\theta-8)$	$-\theta^2(1-\theta)(15\theta-13)$	$-\theta^3(5\theta-6)$	

$$\begin{aligned}
 & + \left\langle \begin{array}{ccc} \bullet & \bullet & \\ \bullet & \bullet & \rightarrow \circ & \circ \\ \circ & & \bullet & \end{array} \right\rangle - \left\langle \begin{array}{ccc} \bullet & \circ & \\ \circ & \circ & \leftarrow \bullet & \bullet \\ \bullet & & \bullet & \end{array} \right\rangle \\
 & + \left\langle \begin{array}{ccc} \circ & \bullet & \\ \bullet & \bullet & \rightarrow \circ & \circ \\ \bullet & & \bullet & \end{array} \right\rangle - \left\langle \begin{array}{ccc} \bullet & \bullet & \\ \circ & \circ & \leftarrow \bullet & \bullet \\ \bullet & & \bullet & \circ \end{array} \right\rangle. \quad (63)
 \end{aligned}$$

and results in the  $(k_x, k_y)$ -dependent factor

$$\begin{aligned}
 & -8 \left\{ 3 \left( \sin^2 \frac{k_x}{2} + \sin^2 \frac{k_y}{2} \right) - 4 \left( \sin^4 \frac{k_x}{2} + \sin^4 \frac{k_y}{2} \right) \right. \\
 & \left. + 4 \sin^2 \frac{k_x}{2} \sin^2 \frac{k_y}{2} \right\} \approx -6(ka)^2, \quad (64)
 \end{aligned}$$

which must still be multiplied by  $\Omega(8, 5; L^2, N)$ . The final approximate result is obtained for  $ka \ll 1$ . In fact, only 15 out of the total of 39 groups of diagrams must be evaluated because for many of them the  $(k_x, k_y)$ -dependent factor is the same. For example, it is easy to see that the expression given in Eq. (64) corresponds not only to the group given in Eq. (63) but also a similar group in which the pair of atoms in the top or in the bottom row are removed (but not the lone atom in these rows). The resulting group is one of five possible (3,1,1) configurations and must be multiplied by  $\Omega(8, 3; L^2, N)$ .

The limit  $L^2 \rightarrow \infty$ ,  $N \rightarrow \infty$  with the condition that  $N/L^2 = \theta$  is a finite coverage (between 0 and 1) affects only the environment factor. It is easy to show that in this limit

$$\Omega(8, n_a; L^2, N) \rightarrow \theta^{n_a-1} (1-\theta)^{7-n_a}, \quad (65)$$

which for  $n_a$  varying from 2 to 7 gives the coverage dependence of the type  $\theta^n(1-\theta)^{6-n}$  with  $n=1, 2, \dots, 6$ . We present the results in Table I. In order to get the correction to the diffusion coefficient due to all transitions breaking  $n_B$  bonds and simultaneously forming  $n_F$  bonds one has to multiply the expression given at the intersection of the  $n_B$ th column and  $n_F$ th row by  $(\Gamma_{n_B, n_F} - W)a^2$ , where  $\Gamma_{n_B, n_F}$  is the jump rate for such particular jumps. The element  $n_B = n_F = 0$  is not specified because jumps which neither break nor form new bonds result in the coverage independent diffusion coefficient  $D_0 = Wa^2$ . If the jump rates depend only on the number of bonds broken (formed) irrespectively how many bonds are formed (broken) then the correction can be obtained from the last

row (column). It is interesting to see that terms proportional to  $\theta^5$  and  $\theta^6$  cancel out in such cases except for  $n_B=0$  or  $n_F=0$ . Alternative specific models of the jump rates can be used, for example such in which the rate does not depend on the number of bonds formed but only on the number of bonds broken and the number of nearest neighbors at the barrier site which the atom passes through.

As a particular example we consider the case in which the only jump rates which are not equal to  $W$  are those in which one, two, or three bonds are broken and assume that the rates,  $\Gamma_1$ ,  $\Gamma_2$ , and  $\Gamma_3$ , respectively, do not depend on the number of bonds formed in the process. This case is a two dimensional counterpart of the WDM interaction model in one dimension (cf. Fig. 1). If we further write  $\Gamma_1 = \gamma W$  and assume that  $\Gamma_2 = \gamma^2 W$  and  $\Gamma_3 = \gamma^3 W$ , which is a reasonable assumption based on a thermal activation of the atomic jumps, then the diffusion coefficient is obtained by adding to  $Wa^2$  the  $n_B=1, 2$ , and 3 terms in the last row in Table I multiplied by  $W(\gamma-1)a^2$ ,  $W(\gamma^2-1)a^2$ , and  $W(\gamma^3-1)a^2$ , respectively. We get

$$D(\theta)/a^2 = W[1 + \theta(5\theta-6)(1-\gamma)][1 - \theta(1-\gamma)]^2. \quad (66)$$

Presently, two dimensional models with strong repulsive interactions and structural transformations are being investigated and the results will be reported elsewhere.

## VI. SUMMARY AND DISCUSSION

We have applied a kinetic lattice gas model to investigate diffusion in systems of interacting particles executing a random walk among sites arranged in a regular lattice. Particle-particle interactions modify the inter site hopping rates and affect a long range mass transport within the gas. We have designed a variational method allowing to derive an analytic expression for the gas density (coverage) dependent diffusion coefficient  $D(\theta)$  for a wide class of the interaction models. The diffusion coefficient is extracted directly from the master rate equations for the nonequilibrium probabilities of microscopic states of the system. Employing the microscopic equations as the starting point for the calculations is a feature which distinguishes our approach from all existing ones in the literature which usually start from a hierarchy of equations for the averaged quantities like the local particle density and site-site correlation functions. Consequently, we are free of uncertainties associated with various truncation schemes used in these approaches.

The main goal of this paper is to provide a detailed derivation of simple, intuitively attractive rules allowing to obtain the coverage dependent diffusion coefficient in an analytic form. The derivation is presented for a one dimensional lattice gas but the resulting rules are provided in a form allowing for an immediate generalization to a lattice gas in two dimensions. The equilibrium correlations present in the interacting lattice gas are accounted for by a proper choice of the variational candidates for the system microstates equilibrium probabilities. This allows, in principle, to account for the structural phase transformations present in two dimensional systems.

In one dimension the method is applied to two cases: the one in which the interparticle interactions modify the hopping rates only moderately and the one with strong repulsive interactions capable of changing some rates by orders of magnitude. In both cases simple algebraic expressions for  $D(\theta)$  excellently agree with the results of the Monte Carlo simulations. Only the simplest two dimensional system—the one with moderate modification of the rates—is considered in this paper, mainly for the purpose of illustrating the application of the method in two dimensions. Diffusion in other two dimensional systems, in which structural phase transformations are expected at certain coverages, is now being investigated and will be presented in a future publication.

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#### APPENDIX A

Essential properties of the  $k$ -space rate matrix  $\mathbb{M}(k)$  are summarized here. The transition rates in the master Eq. (3) do not depend on the position of the reference atoms,  $X$  and  $X'$ , of the microstates involved, i.e.,  $W(\{c\}, \{c'\}) = W_{\{m\}, \{m'\}}$  [cf. Eq. (4)]. The transition rates  $W_{\{m\}, \{m'\}}$  are equal to  $W$ ,  $\Gamma$ ,  $R$ ,  $T$ , or any other rate which a particular interaction model requires.

In the first sum at the right hand side of Eq. (3)—the in terms in the Master equation—one encounters several types of transitions  $\{c'\} \rightarrow \{c\}$ . (i) First, we have transitions leaving the reference atom in its original site so both microstates  $\{c\}$  and  $\{c'\}$  have the same  $X$ . The index corresponding in the set  $\{m\}$  to the jumping atom differs by  $\pm 1$  from the corresponding index in  $\{m'\}$ . All other indices in  $\{m\}$  are equal to the corresponding ones in  $\{m'\}$ . The transition rate  $W_{\{m\}, \{m'\}}$  multiplies in this case the probability  $P(\{c'\}, t) = P_{\{m'\}}(X, t)$  and, after the lattice Fourier transform (7) is taken, the resulting term becomes  $W_{\{m\}, \{m'\}} P_{\{m'\}}(k, t)$ . (ii) Next, we have transitions in which the reference atom jumps in the counterclockwise (clockwise) direction from  $X' = X \pm a$  to  $X$ . The corresponding terms are  $W_{\{m\}, \{m'\}} P_{\{m'\}}(X \pm a, t)$  where all integers

in the set  $\{m'\}$  are equal to the corresponding ones in  $\{m\}$  minus (plus) 1 (moving the reference atom changes positions of all the remaining ones with respect to it). The lattice Fourier transform results in  $\exp(\mp ika) W_{\{m\}, \{m'\}} P_{\{m'\}}(k, t)$ .

The  $k$ -dependent factor  $\exp(\mp ika)$  can be incorporated into the definition of the “ $k$ -space jump rates”  $W_{\{m\}, \{m'\}}(k)$  which are just equal to  $W_{\{m\}, \{m'\}}$  in case (i) and  $\exp(\mp ika) W_{\{m\}, \{m'\}}$  in (ii). In general

$$W_{\{m\}, \{m'\}}(k) = F_{\{m\}, \{m'\}}(k) W_{\{m\}, \{m'\}}, \quad (\text{A1})$$

with  $F_{\{m\}, \{m'\}}(0) = 1$  and  $|F_{\{m\}, \{m'\}}(k)| = |\exp(\mp ika)| = 1$ . For  $N=2$  for which  $\{m\} = m$  the condition  $|F_{m, m'}(k)| = 1$  is not satisfied but all essential conclusions listed later concerning the rate matrix still hold. The matrix elements of the  $k$ -space rate matrix  $\mathbb{M}(k)$  are then

$$M_{\{m\}, \{m'\}}(k) = W_{\{m\}, \{m'\}}(k) - \delta_{\{m\}, \{m'\}} \sum_{\{m''\}} W_{\{m''\}, \{m\}}, \quad (\text{A2})$$

where  $\delta_{\{m\}, \{m'\}}$  is a Kronecker delta equal to 1 only when all indices in  $\{m\}$  are equal to the corresponding ones in  $\{m'\}$ . The term containing  $\delta_{\{m\}, \{m'\}}$  is generated by the second (out) term at the right hand side of Eq. (3).

In equilibrium, the probability of the microstate  $\{c\} = [X; \{m\}]$  does not depend on  $X$ . The equilibrium probability of the corresponding configuration  $\{m\}$  is  $P_{\{m\}}^{\text{eq}}$ . The detailed balance condition for  $W_{\{m\}, \{m'\}}$  implies a similar condition for  $W_{\{m\}, \{m'\}}(k)$ . We have

$$W_{\{m\}, \{m'\}} P_{\{m'\}}^{\text{eq}} = W_{\{m'\}, \{m\}} P_{\{m\}}^{\text{eq}}, \quad (\text{A3a})$$

$$W_{\{m\}, \{m'\}}(k) P_{\{m'\}}^{\text{eq}} = W_{\{m'\}, \{m\}}^*(k) P_{\{m\}}^{\text{eq}}. \quad (\text{A3b})$$

Denoting  $\mathbb{W}(k)$ ,  $\mathbb{W}$ , and  $\mathbb{F}(k)$  the square matrices formed by the matrix elements  $W_{\{m\}, \{m'\}}(k)$ ,  $W_{\{m\}, \{m'\}}$ , and  $F_{\{m\}, \{m'\}}(k)$ , respectively, we see that  $\mathbb{W}$  and  $\mathbb{M}(0)$  are real but not symmetric,  $\mathbb{W}(k)$  and  $\mathbb{M}(k)$  are not hermitian, while  $\mathbb{F}(k)$  is hermitian. The same real diagonal matrix transformation  $\mathbb{U}$  with elements

$$U_{\{m\}, \{m'\}} = \frac{\delta_{\{m\}, \{m'\}}}{\sqrt{P_{\{m\}}^{\text{eq}}}}, \quad (\text{A4})$$

which transforms  $\mathbb{W}$  and  $\mathbb{M}(0)$  into symmetric matrices, also transforms  $\mathbb{W}(k)$  and  $\mathbb{M}(k)$  into hermitian ones. Consequently, the eigenvalues of  $\mathbb{M}(k)$ , denoted  $-\lambda^{(\mu)}(k)$ , are real and one can show that  $\lambda^{(\mu)}(k)$ 's are nonnegative for any  $\mu$ . Otherwise, deviations from equilibrium would grow without bounds. The formal proof is provided in Ref. 25 for  $k=0$  only but it can be easily generalized.

Let  $\tilde{\mathbf{e}}^{(\mu)}(k)$  and  $\mathbf{e}^{(\mu)}(k)$  be, respectively, the left and the right eigenvectors of  $\mathbb{M}(k)$  corresponding to the eigenvalue  $-\lambda^{(\mu)}(k)$ . In order to use the usual matrix multiplication rules  $\tilde{\mathbf{e}}^{(\mu)}(k)$  must be understood as a single row array of  $\tilde{e}_{\{m\}}^{(\mu)}(k)$ 's while the components of  $\mathbf{e}^{(\mu)}(k)$  are arranged into a single column. The rate matrix  $\mathbb{M}(k)$  is not hermitian so its left and right eigenvectors are not hermitian conjugates of each other.

Instead, using the detailed balance condition one can show<sup>25</sup> that

$$\mathbf{e}^{(\mu)}(k) = \mathbb{U}^{-2} \cdot \tilde{\mathbf{e}}^{(\mu)\dagger}(k) = [\mathbf{P}^{\text{eq}} \tilde{\mathbf{e}}^{(\mu)\dagger}(k)]. \quad (\text{A5})$$

At the right hand side, the hermitian conjugate of  $\tilde{\mathbf{e}}^{(\mu)}(k)$  converts it into a one-column array and complex conjugates each its component which is then multiplied by the corresponding component of  $\mathbf{P}^{\text{eq}}$ , resulting in a one-column array  $[\mathbf{P}^{\text{eq}} \tilde{\mathbf{e}}^{(\mu)\dagger}(k)]$ .

From Eq. (A2) one gets

$$\sum_{\{m\}} M_{\{m\},\{m'\}}(0) = 0, \quad (\text{A6})$$

which is a mathematical consequence of the particle conservation. Consequently, there exists an eigenvalue, say  $\lambda^{(0)}(k)$  which tends to zero as  $k \rightarrow 0$ . This ‘‘diffusive eigenvalue’’ accounts for chemical diffusion. The left hand side of Eq. (A6) can be written as  $\tilde{\mathbf{e}}^{(0)}(0) \cdot \mathbb{M}(0)$  implying that the left eigenvector  $\tilde{\mathbf{e}}^{(0)}(0)$  of  $\mathbb{M}(0)$  corresponding to  $-\lambda^{(0)}(0)=0$  has all components equal to each other. The corresponding right eigenvector contains as its components, according to Eq. (A5), the equilibrium probabilities of all configurations:  $\mathbf{e}^{(0)}(0) = \mathbf{P}^{\text{eq}}$ .

The left eigenvectors are orthogonal to the right ones if they belong to different eigenvalues<sup>25</sup> and each eigenvalue can be then evaluated as

$$-\lambda^{(\mu)}(k) = \frac{\tilde{\mathbf{e}}^{(\mu)}(k) \cdot \mathbb{M}(k) \cdot [\mathbf{P}^{\text{eq}} \tilde{\mathbf{e}}^{(\mu)\dagger}(k)]}{\tilde{\mathbf{e}}^{(\mu)}(k) \cdot [\mathbf{P}^{\text{eq}} \tilde{\mathbf{e}}^{(\mu)\dagger}(k)]}, \quad (\text{A7})$$

provided the left eigenvectors of  $\mathbb{M}(k)$  and the equilibrium probabilities  $P_{\{m\}}^{\text{eq}}$  corresponding to  $\mathbb{M}(0)$  are known. In this paper we approximate the diffusive eigenvalue  $-\lambda^{(0)}(k)$  by evaluating Eq. (A7) using plausible ‘‘variational’’ candidates for  $\tilde{\mathbf{e}}^{(0)}(k)$  and  $\mathbf{P}^{\text{eq}}$ . In the main body of the paper we denote the diffusive eigenvalue of  $\mathbb{M}(k)$  by  $\lambda(k)$  skipping the superscript  $\mu=0$ .

## APPENDIX B

We provide a proof that  $\Phi(k)$  is a right eigenvector of  $\mathring{\mathbb{M}}(k)$  corresponding to  $-\lambda_0(k)$  for the noninteracting system with the site blocking, cf Eqs. (13), (12), and (14). Note that  $\mathring{\mathbb{M}}(k)$  is hermitian so the relation between its left and right eigenvectors is a hermitian conjugation. Consequently [cf. discussion below Eq. (A6)] all components of  $\mathbf{P}^{\text{eq}}$  are equal to each other.  $\mathring{\mathbb{M}}(k)$  is given in Eqs. (A1) and (A2) with all nonvanishing  $W_{\{m\},\{m'\}}$ 's equal to  $W$  so, the left hand side of Eq. (14) can be written as  $\mathring{\mathbb{M}} \cdot \Phi(k) \equiv W \mathbf{A}(k)$  with the rate  $W$  factored out for convenience:  $A_{\{m\}}$  contains only the phase factors  $F_{\{m\},\{m'\}}$ . Recall that the composite matrix index  $\{m\}$  is a set of  $N-1$  integers  $m_i$ ,  $i=1, \dots, N-1$  ordered according to the condition given in Eq. (5). Each matrix element  $A_{m_1, \dots, m_{N-1}}$  can be now identified by a careful consideration of all transitions contributing to the annihilation or destruction of the microstate  $[X; m_1, \dots, m_{N-1}]$  similarly like we

have done it in Appendix A above Eq. (A1). We split  $A_{\{m\}} \times(k)$  into five contributions

$$A_{m_1, \dots, m_{N-1}}(k) = \sum_{\ell=0}^4 A_{m_1, \dots, m_{N-1}}^{(\ell)}(k). \quad (\text{B1})$$

The  $\ell=0$  term is generated by the second (diagonal) term at the right hand side of Eq. (A2), so it is proportional to  $-\Phi_{m_1, \dots, m_{N-1}}$  (the proportionality coefficient is equal to the number of nonvanishing terms in the sum over  $\{m''\}$ ). The remaining four contributions in Eq. (B1) are due to the first term in Eq. (A2), i.e.,  $A_{\{m\}} = \sum_{\{m'\}} F_{\{m\},\{m'\}} \Phi_{\{m'\}}$ . The  $\ell=1$  term accounts for jumps of the reference atom in the clockwise direction (to the right), i.e., creating microstates  $[X; \{m\}] = [X; m_1, \dots, m_{N-1}]$  from  $[X-a; \{m'\}] = [X-a; m_1+1, \dots, m_{N-1}+1]$ 's, so  $F_{\{m\},\{m'\}} = \exp(ika)$  [cf. considerations above Eq. (A1)]. Similarly, the  $\ell=2$  term accounts for the jumps of the reference atom in the counterclockwise direction:  $F_{\{m\},\{m'\}} = \exp(-ika)$ . The term  $\ell=3$  accounts for all possible transitions from the microstates  $[X; \{m'\}] = [X; m_1, \dots, m_i+1, \dots, m_{N-1}]$  to  $[X; \{m\}] = [X, m_1, \dots, m_i, \dots, m_{N-1}]$ 's in which the  $i$ th atom jumps in the counterclockwise direction. Similar clockwise jumps correspond to  $\ell=4$ . In both cases  $F_{\{m\},\{m'\}} = 1$  and one has to sum contributions from all possible initial configurations  $\{m'\}$  from which the configuration  $\{m\}$  can be reached.

A generic case is for the configuration  $\{m\} = [m_1, \dots, m_{N-1}]$  with  $m_1 \neq 1$  and  $m_{N-1} \neq L-1$  (the reference atom has a free site at each its side) and  $m_i \neq m_{i-1}+1$  ( $i=2, \dots, N-1$ ) (no two atoms occupy neighboring sites). Consequently, none of the  $2N$  jumps creating the configuration  $\{m\}$  nor  $2N$  jumps destroying it are prevented by the site blocking. We get (the explicit reference to the  $k$  dependence is suppressed)

$$A_{m_1, \dots, m_{N-1}}^{(0)} = -2N \Phi_{m_1, \dots, m_{N-1}}, \quad (\text{B2a})$$

$$A_{m_1, \dots, m_{N-1}}^{(1)} = e^{ika} \Phi_{m_1+1, m_2+1, \dots, m_{N-1}+1} = e^{ika} - 1 + \Phi_{m_1, \dots, m_{N-1}}, \quad (\text{B2b})$$

$$A_{m_1, \dots, m_{N-1}}^{(2)} = e^{-ika} \Phi_{m_1-1, m_2-1, \dots, m_{N-1}-1} = e^{-ika} - 1 + \Phi_{m_1, \dots, m_{N-1}}, \quad (\text{B2c})$$

$$\begin{aligned} A_{m_1, \dots, m_{N-1}}^{(3)} &= \sum_{i=1}^{N-1} \Phi_{m_1, \dots, m_i+1, \dots, m_{N-1}} \\ &= 1 - e^{-ika} + (N-2 + e^{-ika}) \Phi_{m_1, \dots, m_{N-1}}, \end{aligned} \quad (\text{B2d})$$

$$\begin{aligned} A_{m_1, \dots, m_{N-1}}^{(4)} &= \sum_{i=1}^{N-1} \Phi_{m_1, \dots, m_i-1, \dots, m_{N-1}} \\ &= 1 - e^{ika} + (N-2 + e^{ika}) \Phi_{m_1, \dots, m_{N-1}}. \end{aligned} \quad (\text{B2e})$$

Except for  $A_{\{m\}}^{(0)}$  in Eq. (B2a) the collective subscript of  $\Phi$  in the first form given denotes the initial configuration  $\{m'\}$  from which the configuration  $\{m\}$  can be reached [in Eqs. (B2d) and (B2e) we have a sum over all such initial configurations]. The final expressions were obtained using the definition of  $\Phi_{m_1, \dots, m_{N-1}}$  given in Eq. (12). Adding all expressions at the right side of Eqs. (B2) we see that all terms not containing  $\Phi$  and the terms proportional to  $N$  cancel out and we get

$$A_{m_1, \dots, m_{N-1}} = -4 \sin^2\left(\frac{ka}{2}\right) \Phi_{m_1, \dots, m_{N-1}}(k), \quad (\text{B3})$$

as expected if Eq. (14) is valid.

What remains is to check if the same result is obtained for  $A_{\{m\}}$  corresponding to configurations  $\{m\}$  which do not satisfy the condition given above Eq. (B2). We consider now a configuration  $\{m\} = [m_1, \dots, m_{N-1}]$  in which  $m_1 \neq 1$  and  $m_{N-1} \neq L-1$  (i.e., the reference atom still has a free site on its both sides) but we allow for a tight cluster of  $n+1$  atoms to occupy  $n+1$  consecutive neighboring sites. The cluster starts with the  $l$ th atom (counting from the atom next to the reference atom) being at a distance  $m_l a$  away from the reference atom. The atoms  $m_1$  and/or  $m_{N-1}$  may or may not belong to the cluster ( $l=1$  or  $l+n=L-1$ , respectively, when one of them does). Consequently, the sequence of  $N-1$  integers  $[m_1, \dots, m_{N-1}]$  contains a subsequence of  $n+1$  consecutive integers  $[m_l, m_{l+1}, \dots, m_{l+n}]$ , i.e.,

$$m_{l+j} = m_l + j, \quad \text{for } j = 1, 2, \dots, n. \quad (\text{B4})$$

The cluster is specified by its beginning  $l$  and length  $n$ .

Starting now with  $A_{\{m\}}^{(0)} = A_{m_1, \dots, m_{N-1}}^{(0)}$  we note that the configuration  $\{m\}$  can be destroyed in less than  $2N$  ways because  $n-1$  atoms inside the tight cluster cannot be moved and each of the two atoms at the cluster ends can move only in one direction instead of two. Consequently the number of possible ways of destroying the configuration is  $2N - 2(n-1) - 1 - 1 = 2(N-n)$  and we get

$$A_{m_1, \dots, m_{N-1}}^{(0)} = -2(N-n) \Phi_{m_1, \dots, m_{N-1}}, \quad (\text{B5})$$

which replaces Eq. (B2a) in this case.

The contributions  $A_{m_1, \dots, m_{N-1}}^{(1)}$  and  $A_{m_1, \dots, m_{N-1}}^{(2)}$  are due to the creation of the configuration  $[m_1, \dots, m_{N-1}]$  due to the jumps of the reference atom. For  $m_1 \neq 1$  and  $m_{N-1} \neq L-1$  the reference atom is not restricted so both contributions still are given by expressions in Eqs. (B2b) and (B2c), respectively.

Turning to  $A_{m_1, \dots, m_{N-1}}^{(3)}$  we note that it is still defined as a sum Eq. (B2d) with the restriction, however, that the terms have to be excluded which would result in two identical  $m_i$ 's in the subscript of  $\Phi$ . This excludes from the sum the initial configurations with  $m_{i+1} = m_i + 1$  in which the  $(i+1)$ th atom would occupy the site next to the right of the site occupied by the  $i$ th atom. In other words, the sum in Eq. (B2d) must exclude  $n$  terms with  $i = l, l+1, \dots, l+n-1$  corresponding to all atoms in the cluster except the last (the rightmost) one which could have arrived from the site further to the right. Using the definition of  $\Phi$ 's in Eq. (12) we get

$$\Phi_{m_1, \dots, m_i, m_{i+1}, \dots, m_{N-1}} = \Phi_{m_1, \dots, m_{N-1}} + (e^{-ika} - 1) e^{-ikam_i}. \quad (\text{B6})$$

After summing this over all  $i$ 's with  $i \neq l, l+1, \dots, l+n-1$  the first term gets multiplied by the number of terms  $N-n-1$  in the sum while the second term contains the sum exponentials excluding the atoms within the cluster (except the last one) which, using Eqs. (12) and (B4), can be converted into

$$\sum_{\substack{i=1 \\ i \neq l, l+1, \dots, l+n-1}}^{N-1} e^{-ikam_i} = \Phi_{m_1, \dots, m_{N-1}} - 1 - \sum_{j=0}^{n-1} e^{-ikam_{l+j}}. \quad (\text{B7})$$

Combining Eqs. (B6) and (B7) we get

$$\begin{aligned} A_{m_1, \dots, m_{N-1}}^{(3)} &= \sum_{\substack{i=1 \\ i \neq l, l+1, \dots, l+n-1}}^{N-1} \Phi_{m_1, \dots, m_i, m_{i+1}, \dots, m_{N-1}} \\ &= (1 - e^{-ika}) \left( 1 + \sum_{j=0}^{n-1} e^{-ikam_{l+j}} \right) \\ &\quad + (N-2-n + e^{-ika}) \Phi_{m_1, \dots, m_{N-1}}, \end{aligned} \quad (\text{B8})$$

which replaces Eq. (B2d) in this case and reduces to it for  $n=0$ . Exactly in the same way  $A_{m_1, \dots, m_{N-1}}^{(4)}$  is obtained. Here the summation in Eq. (B2e) must exclude all atoms in the cluster except the first (the leftmost) one. The result replacing Eq. (B2e) is

$$\begin{aligned} A_{m_1, \dots, m_{N-1}}^{(4)} &= \sum_{\substack{i=1 \\ i \neq l+1, l+2, \dots, l+n}}^{N-1} \Phi_{m_1, \dots, m_{i-1}, \dots, m_{N-1}} \\ &= (1 - e^{ika}) \left( 1 + \sum_{j=1}^n e^{-ikam_{l+j}} \right) \\ &\quad + (N-2-n + e^{ika}) \Phi_{m_1, \dots, m_{N-1}}. \end{aligned} \quad (\text{B9})$$

The results given in Eqs. (B2b), (B2c), (B5), (B8), and (B9) have to be added and the Eq. (B4) used for atomic positions within the cluster. The terms not containing  $\Phi_{m_1, \dots, m_{N-1}}$  cancel out and the result is again the same as in Eq. (B3). This proof holds, of course, when the configuration  $[m_1, \dots, m_{N-1}]$  contains several clusters separated by at least one unoccupied site. The special case in which  $m_1 = 1$  can be analyzed in a similar way. Here the reference atom cannot jump to the right nor could have arrived from the right so  $A_{m_1, \dots, m_{N-1}}^{(2)} = 0$  and the contributions  $A_{m_1, \dots, m_{N-1}}^{(0)}$  and  $A_{m_1, \dots, m_{N-1}}^{(4)}$  also get modified. The result is again Eq. (B3). For  $m_{N-1} = L-1$  similar situation occurs but, in addition, the periodic boundary condition (9) must be utilized. This comment completes the proof of Eq. (14).

APPENDIX C

We derive here the expression for the normalization factor

$$\mathcal{N}(L,N) \equiv \Phi^\dagger(k) \cdot \Phi(k) = \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ \text{ord}}}^{L-1} |\Phi_{m_1, \dots, m_{N-1}}|^2 \tag{C1}$$

for general  $N$ . The summation is over all possible values of  $N-1$  ordered indices  $[m_1, \dots, m_{N-1}]$  allowed by the condition in Eq. (5). If  $N-1$  integers in the sequence  $[m_1, \dots, m_{N-1}]$  were not ordered but still were different from each other then, as seen from Eq. (12),  $\Phi_{m_1, \dots, m_{N-1}}(k)$  would be fully symmetric with respect to arbitrary permutation of indices in the subscript. This allows to replace the ordered sum in Eq. (C1) with the non ordered one having  $(N-1)!$  times more terms and divide the result by  $(N-1)!$  to compensate for the overcounting. Thus,  $\mathcal{N}(L,N) = \mathfrak{N}(L,N)/(N-1)!$  with

$$\mathfrak{N}(L,N) = \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ (\neq)}}^{L-1} |(1 + e^{-ikam_1} + \dots + e^{-ikam_{N-1}})|^2. \tag{C2}$$

The  $(\neq)$  symbol below the sum reminds that for each term in the non ordered  $(N-1)$ -fold sum over  $[m_1, \dots, m_{N-1}]$  each index may assume *any* value from 1 to  $L-1$  except values already assumed by the remaining  $N-2$  indices Expanding  $|\dots|^2$  we get

$$\mathfrak{N}(L,N) = \{NC(L,N) + (N-1)[A(L,N) + A^*(L,N)] + (N-1)(N-2)B(L,N)\}, \tag{C3}$$

where

$$C(L,N) = \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ (\neq)}}^{L-1} 1, \tag{C4a}$$

$$A(L,N) = \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ (\neq)}}^{L-1} e^{-ikam_i} \equiv \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ (\neq)}}^{L-1} e^{-ikam_{N-1}}, \tag{C4b}$$

$$B(L,N) = \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ (\neq)}}^{L-1} e^{-ika(m_i-m_j)} \equiv \sum_{\substack{m_1, \dots, m_{N-1}=1 \\ (\neq)}}^{L-1} e^{-ika(m_{N-2}-m_{N-1})}. \tag{C4c}$$

The final forms in Eqs. (C4b) and (C4c) are obtained by renaming the summation indices in the original form. In principle, each of the earlier quantities,  $A$ ,  $B$ , and  $C$ , is a

function of  $k$  but, as we shall see, this dependence disappears due to the periodic boundary condition (9).

The quantities  $A$ ,  $B$ , and  $C$  can be evaluated by deriving first the recurrence relations for each of them. We provide some details for  $A(L,N)$ . To make the expressions a bit shorter we denote  $f_m = \exp(-ikam)$ . From the periodic boundary condition (9) we get

$$A(L,2) = \sum_{m=1}^{L-1} e^{-ikam} \equiv \sum_{m=1}^{L-1} f_m = -1, \tag{C5}$$

for all values of  $k$  allowed by Eq. (9), except for  $k=0$ . Using Eq. (C4b) we get for  $A(L,N)$  the following sequence of equalities

$$A(L,N) = \sum_{\substack{m_1, \dots, m_{N-2}=1 \\ (\neq)}}^{L-1} \left[ \left( \sum_{m_{N-1}=1}^{L-1} f_{m_{N-1}} \right) - f_{m_1} - \dots - f_{m_{N-2}} \right] = -C(L,N-1) - (N-2)A(L,N-1). \tag{C6}$$

The expression following the first equality is obtained by extracting the innermost sum over  $m_{N-1}$  from the sum in Eq. (C4b), letting its summation index to assume all values from 1 up to  $L-1$  and subtracting  $N-2$  terms  $f_{m_i}$ ,  $i=1, \dots, N-1$  to compensate for the resulting overcounting. The expression after the second equality follows after using Eq. (C5) to replace the expression inside the round bracket with  $-1$  and using then Eqs. (C4a) and (C4b). In effect, Eq. (C6) is a recurrence relation for  $A(L,N)$  valid down to  $N=2$ . A recurrence relation,  $C(L,N) = (L-N+1)C(L,N-1)$ —valid also down to  $N=2$ , is obtained in the same way for  $C(L,N)$  from Eq. (C4a). Together with  $C(L,2) = \sum_{M=1}^{L-1} 1 = L-1$  it gives

$$C(L,N) = \frac{(L-1)!}{(L-N)!} = (N-1)! \binom{L-1}{N-1}. \tag{C7}$$

where  $\binom{m}{n} = m!/[n!(m-n)!]$  is a binomial coefficient. The recurrence relation (C6) can be solved by its repeated application to its right hand side. The result, using Eq. (C5) and then Eq. (C7) gives

$$A(L,N) = (-1)^N (N-2)! \left[ 1 + \sum_{\ell=1}^{N-2} \frac{(-1)^\ell}{\ell!} C(L, \ell+1) \right] = -\frac{(L-2)!}{(L-N)!} = -\frac{C(L,N)}{L-1}. \tag{C8}$$

To get the last result in Eq. (C8) one of the sum rules for the binomial coefficients was used.<sup>26</sup> We see that  $A(L,N)$  is real, as expected from Eqs. (C4b) and (9).

A similar procedure can be applied to  $B(L, N)$ . The recurrence relation can be derived which after introducing auxiliary functions

$$D(L, N) = [C(L, N) + A(L, N)](N - 1), \quad (\text{C9a})$$

$$F(L, N) = B(L, N)(N - 2), \quad (\text{C9b})$$

has the same form as that in Eq. (C6):

$$F(L, N) = -D(L, N) - (N - 2)F(L, N - 1), \quad (\text{C10})$$

but it is valid only down to  $N=3$  because  $B(L, N)$  is not defined for  $N < 3$ , cf. Eq. (C4c). With  $F(L, 3) = B(L, 3) = -(L-2)$  the solution is

$$\begin{aligned} F(L, N) &= (-1)^N (N-2)! \left[ L - 2 + \sum_{\ell=1}^{N-3} \frac{(-1)^\ell}{(\ell+1)!} \right. \\ &\quad \left. \times D(L, \ell+2) \right] \\ &= -(N-2) \frac{(L-2)!}{(L-N)!} = (N-2)A(L, N), \quad (\text{C11}) \end{aligned}$$

from which we get

$$B(L, N) = A(L, N) = -\frac{C(L, N)}{L-1}. \quad (\text{C12})$$

To get the final result in Eq. (C11), results from Eqs. (C7) and (C8) were used in Eq. (C9a) to get  $D(L, \ell+2)$  and comparing the result with the intermediate result in Eq. (C8).

Using Eqs. (C7), (C8), and (C12) in Eq. (C3) we get

$$\mathfrak{N}(L, N) = N \frac{(L-2)!}{(L-N-1)!} = N! \binom{L-2}{N-1} = \mathcal{N}(L, N)(N-1)!. \quad (\text{C13})$$

This result, although formally derived for  $N \geq 3$  is, in fact, valid for  $N=1$  and 2 also. For  $N=3$ , the earlier result agrees with the results obtained by direct evaluation in Eq. (24).

It is quite amazing that the earlier calculation proceeds without major modifications for the lattice gas on a two dimensional square lattice. In this case the atoms are labeled again  $(0, 1, 2, \dots, i, \dots, N-1)$  with 0 denoting the reference atom placed at the site  $(0, 0)$ . Positions of all remaining atoms with respect to the reference atom are specified using two dimensional vectors  $\mathbf{m}_i = (m_i^x, m_i^y)$  with  $m_i^x, m_i^y = 0, 1, \dots, L-1$  with the restriction that both  $m_i^x$  and  $m_i^y$  cannot simultaneously be zero. The unnormalized eigenvector of the rate matrix without interactions (but with the site blocking) is, in this case, given by the expression formally similar to that in Eq. (12) in which  $kam_i$  is replaced with  $a\mathbf{k} \cdot \mathbf{m}_i$ . Its components  $\Phi_{\{\mathbf{m}\}}$  are equal to the coefficients in the expansion of  $\mathcal{P}(\mathbf{k}, t)$  analogous to Eq. (11). In one dimension the atoms were tagged,  $i=1, 2, \dots, N-1$ , and an ordering [Eq. (5)] of the atomic positions with respect to the reference atom was introduced. Although tagging the atoms is possible also in two dimensions, ordering  $\mathbf{m}_i$ 's within a configuration  $\{\mathbf{m}\}$  is not. Evaluating, however, the ‘‘ordered’’ normalization de-

nominator  $\mathcal{N}(L, N)$  in one dimension the restriction due to the ordering was removed right at the start by introducing its  $(N-1)!$  times larger ‘‘nonordered’’ counterpart  $\mathfrak{N}(L, N)$ . The only restriction remaining was that no two atoms may simultaneously reside at the same site:  $m_i \neq m_j$  for any term in the sum in Eq. (C2). In two dimensions all calculations are done without ordering to start with, so the appropriate normalization denominator is  $\mathfrak{N}(L^2, N)$  defined in Eq. (C14) later in which the symbol  $\sum_{\mathbf{m}_1, \dots, \mathbf{m}_{N-1}=1}^{L-1}$  must be understood as the

sum over all configurations with the only restriction that in each term  $\mathbf{m}_i \neq \mathbf{m}_j$  and that for any  $i$  in the sum  $m_i^x$  and  $m_i^y$  are not equal to zero simultaneously [such site,  $(0, 0)$ , is reserved for the reference atom]. With these comments, the evaluation of the norm of the eigenvector proceeds along the same lines as shown earlier in this Appendix and the result is

$$\begin{aligned} \mathfrak{N}(L^2, N) &= \sum_{\substack{\mathbf{m}_1, \dots, \mathbf{m}_{N-1}=1 \\ (\neq)}}^{L-1} |(1 + e^{-ia\mathbf{k} \cdot \mathbf{m}_1} + \dots + e^{-ia\mathbf{k} \cdot \mathbf{m}_{N-1}})|^2 \\ &= N \binom{L^2 - 2}{N-1} (N-1)!. \quad (\text{C14}) \end{aligned}$$

This is, of course, the same  $\mathbf{k}$ -independent result as in Eq. (C13) except that now the number of sites is  $L^2$  rather than  $L$ . We will show in Appendix E that ignoring ordering in one dimension increases the numerator  $\mathcal{D}$  also  $(N-1)!$  times [cf. Eq. (E2)] leaving the ratio unchanged.

## APPENDIX D

The type A and B contributions in Eq. (31) due to the transitions occurring at the rates  $T$  and  $R$  are

$$\begin{aligned} \Delta_T^{(A)} &= N \sum_{\substack{m_3, \dots, m_{N-1}=4 \\ \text{ord}}}^{L-1} (\Phi_{2,3,m_3, \dots, m_{N-1}} \\ &\quad - \Phi_{1,3,m_3, \dots, m_{N-1}})^* \Phi_{1,3,m_3, \dots, m_{N-1}}, \quad (\text{D1a}) \end{aligned}$$

$$\begin{aligned} \Delta_T^{(B)} &= N \sum_{\substack{m_1, \dots, m_{N-3}=1 \\ \text{ord}}}^{L-4} (\Phi_{m_1, \dots, m_{N-3}, L-3, L-2} \\ &\quad - \Phi_{m_1, \dots, m_{N-3}, L-3, L-1})^* \Phi_{m_1, \dots, m_{N-3}, L-3, L-1}, \quad (\text{D1b}) \end{aligned}$$

$$\begin{aligned} \Delta_R^{(B)} &= N \sum_{\substack{m_2, \dots, m_{N-1}=4 \\ \text{ord}}}^{L-1} (\Phi_{1, m_2, \dots, m_{N-1}} \\ &\quad - \Phi_{2, m_2, \dots, m_{N-1}})^* \Phi_{2, m_2, \dots, m_{N-1}}, \quad (\text{D1c}) \end{aligned}$$

$$\begin{aligned} \Delta_R^{(A)} &= N \sum_{\substack{m_1, \dots, m_{N-2}=1 \\ \text{ord}}}^{L-4} (\Phi_{m_1, \dots, m_{N-2}, L-1} \\ &\quad - \Phi_{m_1, \dots, m_{N-2}, L-2})^* \Phi_{m_1, \dots, m_{N-2}, L-2}. \quad (\text{D1d}) \end{aligned}$$

**APPENDIX E**

To evaluate the environment factor  $\mathcal{D}(l_a, n_a; L, N)$  defined in Eq. (36) we consider a lattice gas consisting of  $N$  atoms placed in  $L$  sites distributed uniformly around a circle. The system is divided into an active cell with  $l_a$  sites containing  $n_a$  atoms and the environment with  $L-l_a$  sites and  $N-n_a$  atoms. The ordered sum  $\sum_{\substack{m_1, \dots, m_{N-n_a} \\ \text{ord}}}^{L-l_a}$  in Eq. (36) may be replaced with the sum  $\sum_{\substack{m_1, \dots, m_{N-n_a} \\ (\neq)}}^{L-l_a}$  [cf. below Eqs. (6) and (C2) for the explanation of the notation] divided by  $(N-n_a)!$  because  $N-n_a$  summation indices are permuted in all possible ways as the result of such a replacement. Using then Eqs. (C4a) and (C7) we get

$$\begin{aligned} \mathcal{D}(l_a, n_a; L, N) &= \frac{N}{(N-n_a)!} C(L-l_a+1, N-n_a+1) \\ &= N \binom{L-l_a}{N-n_a}, \end{aligned} \quad (\text{E1})$$

which completes the derivation.

We want, however, to offer a method of dealing with systems in which no reference is made to any ordering of atoms right from the start. We start with a somewhat different look at the lattice gas in which atoms are tagged and ordered. The lattice consists of  $L$  sites arranged around the circle. A cell consisting of  $l_a$  specific consecutive sites is selected as an active cell, while the remaining  $L-l_a$  sites constitute an environment.  $N$  atoms are then randomly distributed among all sites ( $N \leq L$ ) and then labeled  $i=1, 2, \dots, N$  starting with a randomly chosen atom as  $i=1$  and proceeding in a clockwise direction. In this process a certain number  $n_a$  of consecutively labeled atoms ends up in the active cell determining certain geometrical occupation pattern of this cell.  $\mathcal{D}(l_a, n_a; L, N)$ —given in Eq. (36)—is a number of all possible ways in which  $N$  labeled atoms can be distributed among  $L$  sites with exactly the same occupation pattern of the active cell but with arbitrary occupation pattern in the environment as long as atoms remain ordered clockwise along the circle. The sum in Eq. (36) counts all possibilities of distributing  $N=n_a$  atoms among the  $L-l_a$  sites while preserving the order of the atomic labels while the factor  $N$  in front of the sum accounts for the possibility that any of the  $N$  atoms can be the leftmost atom in the active cell.

To remove the restriction due to the ordering of the atomic labels we fix the geometrical occupation pattern within the active cell but allow the atomic labels, both within the active cells and the environment, form an arbitrary sequence of integers. We denote by  $\mathfrak{D}(l_a, n_a; L, N)$  the total number of configurations consistent with this requirements. Each one of the  $\mathcal{D}$  ordered configurations considered in the preceding paragraph gives rise to an arbitrary ordered configuration by permuting the atoms in the former among the occupied sites. There are  $N!$  permutations but  $N$  among them are cyclic ones which convert an ordered configuration into an ordered one due to the cyclic boundary condition imposed on the system. Consequently, to each ordered configuration there correspond  $N!/N=(N-1)!$  configurations in which the

label ordering is arbitrary but which have the same overall occupation pattern. Therefore

$$\mathfrak{D}(l_a, n_a; L, N) = (N-1)! \mathcal{D}(l_a, n_a; L, N). \quad (\text{E2})$$

We see that this is the same relation as the one between the normalization factors  $\mathcal{N}(L, N)$  and  $\mathfrak{N}(L, N)$  appropriate, respectively, for the lattice with and without the ordering condition. This proves the first two equalities in Eq. (38).

It remains to evaluate  $\mathfrak{D}(l_a, n_a; L, N)$  independently, without any reference to labeling and ordering. Specific  $n_a$  sites within the active cell are occupied in each of  $\mathfrak{D}$  configurations. The first among these sites can be occupied by any of all  $N$  atoms. For each such choice the next site can be taken up by one of the remaining  $N-1$  atoms. Proceeding in this way we arrive to the  $n_a$ th site which can be occupied by one of the remaining  $N-(n_a-1)$  atoms. Consequently, the number of possibilities of getting  $n_a$  atoms to occupy specific  $n_a$  sites within the active cell is  $N(N-1) \cdot \dots \cdot (N-n_a+1) = N! / (N-n_a)!$ . The remaining  $N-n_a$  atoms must be distributed among all  $L-l_a$  sites of the environment. The reasoning is similar to the one just made with the role of atoms and sites reversed. The first atom can get onto any of the  $L-l_a$  available sites. The next atom has only  $L-l_a-1$  sites available and proceeding in this way we see that the last,  $(N-n_a)$ th atom has only  $L-l_a-(N-n_a-1)$  available sites. Consequently, the total number of possibilities of distributing  $N-n_a$  atoms among  $L-l_a$  sites of the environment is  $(L-l_a)(L-l_a-1) \cdot \dots \cdot (L-l_a-N+n_a+1) = (L-l_a)! / (L-l_a-N+n_a)!$ . The product of the two derived numbers is exactly  $\mathfrak{D}(l_a, n_a; L, N)$ :

$$\mathfrak{D}(l_a, n_a; L, N) = \frac{N!}{(N-n_a)!} \frac{(L-l_a)!}{(L-l_a-N+n_a)!} = N! \binom{L-l_a}{N-n_a}, \quad (\text{E3})$$

which is consistent with Eqs. (E1) and (E2).

The derivation leading to the result in Eq. (E3) does not require any labeling and ordering of the atoms. It does not rely on the one dimensional character of the lattice gas either and for the lattice gas in two dimensions one simply has to replace  $L$  with  $L^2$ .

**APPENDIX F**

We want to prove Eq. (46) starting from the definition (44). Note that  $N > L/2$  and that the summation in Eq. (44) runs only over such configurations of labeled and ordered atoms in which distances between two consecutive atoms are not larger than  $2a$  ( $0_h$ -pair configurations).

For the purpose of this calculation we label the reference atom as  $j=0$  with  $m_0 \equiv 0$ . We then write  $|\dots|^2$  in Eq. (44) as a product of  $[\exp(ikam_0) + \exp(ikam_1) + \dots + \exp(ikam_{N-1})]$  times its complex conjugate and expand the sum. The result is  $\mathcal{N}(k; L, N)$  being a sum of  $N$  terms labeled  $j=0, 1, \dots, N-1$ . The  $j$ th one is

$$\sum_{\substack{0_h \\ \{m\} \\ \text{ord}}} [e^{ika(m_0-m_j)} + e^{ika(m_1-m_j)} \dots + e^{ika(m_{N-1}-m_j)}]. \quad (\text{F1})$$

Consider a particular configuration  $\{m\}$ . In the exponents we have the distances between the  $j$ th atom and all remaining ones in a given configuration  $\{m\}$  with the distances in the counterclockwise direction taken as negative,  $m_s - m_j < 0$  for  $s=0, 1, \dots, j-1$ . Using the cyclic boundary condition [Eq. (9)], the negative  $a(m_s - m_j)$  can be replaced with  $a(m_s + L - m_j)$  which is positive and equal to the distance from the  $j$ th to the  $s$ th atom counted now in the clockwise direction. Consequently, the exponents effectively list distances from the  $j$ th atom to all remaining atoms in the clockwise direction in this particular configuration. Summation over  $\{m\}$  explores all possible distances between the  $j$ th atom and all the others, consistent with  $0_h$ -pair configurations. The  $j$ th atom is not privileged in any way so the entire contribution in Eq. (F1) is the same for each  $j$ . Choosing  $j=0$  with  $m_{j=0}=0$  to represent each of them we get

$$\begin{aligned} \mathcal{N}(k; L, N) &= N \sum_{\substack{\{m\} \\ \text{ord}}}^{0_h} \left( 1 + \sum_{j=1}^{N-1} e^{ikam_j} \right) \\ &= N \sum_{\substack{\{m\} \\ \text{ord}}}^{0_h} \left( 1 + \sum_{\substack{j=-(N-1)/2 \\ j \neq 0}}^{+(N-1)/2} e^{ikam_j} \right). \end{aligned} \quad (\text{F2})$$

To get the last result in Eq. (F2) we have assumed that  $N$  is odd and note that instead of counting the atoms in the clockwise direction as  $1, 2, 3, \dots, N-1$ , we can count them in the counterclockwise direction using negative integers  $-1, -2, \dots, -(N-1)$  and consider the distances from the reference atom in the counterclockwise direction as negative ( $m_{-j} < 0$  for  $j > 0$ ). The  $j$ th atom in the clockwise direction counts as  $(N-j)$ th in the counterclockwise direction and the sum of distances to the same atom in both directions equals  $aL$ , i.e.,  $m_j - m_{j-N} = L$ . Replacing thus  $m_j$  with  $m_{j-N} + L$  in all terms with  $j=(N-1)/2, \dots, N-1$ , using the periodic boundary condition [Eq. (9)], and renaming  $j-N$  to  $j$  (being now negative) we get the final result in Eq. (F2). The first term in the bracket in Eq. (F2) (i.e., 1) gives the first term in the square bracket of Eq. (46). In the second term in Eq. (F2) one can reverse the order of both summations because each term  $\exp(ikam_j)$  for some configuration  $\{m\}$  reappears for some other configuration as  $\exp(ikam_{j'})$ . This completes the derivation of Eq. (46).

Note that the restriction of the summation over  $\{m\}$  to  $0_h$ -pair configurations is irrelevant for the considerations made in this appendix. Consequently, Eq. (46) (without  $0_h$  restriction above the sum) is valid also for  $\mathcal{N}(L, N)$  defined in Eq. (C1).

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- <sup>22</sup>This is the simplest choice for  $\Phi_{\text{var}}(k)$  which assures that Eq. (10) results in  $\lambda(k) \propto (ka)^2$  in the long wavelength limit—the only restriction placed on  $\Phi_{\text{var}}(k)$ . Other choices may be desirable in special cases to be considered in future.
- <sup>23</sup>The minimum  $n_a=2$  is due to the fact that we have already extracted in Eq. (17) the “noninteracting” part,  $\lambda_0(k)$ , of the diffusive eigenvalue. This is not necessary and when the rules are applied to the entire  $\mathbb{M}(k)$  rather than to  $\delta\mathbb{M}(k)$  then the entire diffusive eigenvalue  $\delta(k)$  is obtained, provided the active cell with  $n_a=1$  (i.e., a participant atom only) are also considered. Such an approach is used in Sec. IV.
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