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Abstract
Using a gradient expansion of the local microscopic particle current, in the long-time and
large-scale limit, we derive an exact analytical expression for the density and temperature
dependence of the diffusivity in terms of the density dependence of correlation functions on a
rectangular lattice. The latter are calculated by transfer matrix methods, generalized to an
adsorbate with lateral interactions and subjected to an external field. This allows an examination
of the effects of generalized hopping kinetics. Where both initial and final state interactions are
involved, the Reed–Ehrlich factorization, commonly assumed, cannot apply.

Dedicated to Professor Klaus Heinz on the occasion of his 65th birthday.

1. Introduction

Theoretical approaches to the study of diffusion in low-dimensional systems are based on analytic methods, such as the master, Fokker–Planck or Kramers equations, or numerical methods, such as Monte Carlo and molecular dynamics simulations. The former provide physical insight, though usually at the cost of some simplifying assumptions; simulation methods have the advantage of producing realistic, though numerical, results for particular physical systems. Reviews exist, together covering all of these approaches [1–6].

Although the study of collective and tracer diffusion on the basis of the lattice gas model began decades ago [2, 7], the model still provides the best route for examining the effects of multiple binding sites within cells, particle interactions and hops of different lengths on the diffusivity. The standard description of the evolution of the local lattice occupancy is via the master equation with the hopping of particles between lattice sites treated as a Markovian process, i.e. the residence time at sites is long compared to the time of individual hops. In recent formulations a Mori-type equation for the evolution has been constructed so as to treat memory effects in the diffusion process [8–12]. But the associated mathematical intractability has meant that, in practice, the Markovian assumption is employed in these works also. Adsorbate

interactions lead to a strong dependence of the diffusivity on the coverage, θ, of the ad-species via the kinetics assumed for the hopping process. The kinetics are usually simplified to the specification of transition probabilities with a hopping rate, usually of an Arrhenius form, but modified by interactions with neighbouring particles. A common assumption is to consider only the initial neighbouring configuration of the hopping particle. However, the hopping kinetics can be influenced by initial and final state configurations, for instance to mimic saddle-point interactions. This already leads to vastly different diffusion behaviour in 1D [1, 13] and so should be considered in 2D as well.

Another common *a priori* assumption, originally suggested by Reed and Ehrlich [14], is to express the diffusion coefficient as a product of thermodynamic and kinetic (or 'dynamic') factors:

$$D(\theta, T) = \chi^{-1}\langle W \rangle \qquad (1)$$

where χ is the lattice gas susceptibility and $\langle W \rangle$ is the average transition rate (defined in section 2); the standard jump rate is $\langle W \rangle/\theta$. Reed and Ehrlich argued on the basis of non-equilibrium thermodynamics: the diffusion current in the linear regime is given by $\mathbf{j}_{\text{diff}} = L\nabla(\beta\mu) = L[\partial(\beta\mu)/\partial n]\nabla n$. (Here n and μ are the local particle density and chemical potential, $\beta = 1/k_B T$.) Identifying the Onsager coefficient L with the average hopping rate then

gives (1), by construction. But there is no *a priori* reason that this identification extends to the interacting lattice gas, as they assumed; it is also independent of any choice of the microscopic hopping kinetics. Justifications of (1) based on non-equilibrium statistical mechanics followed: Zhdanov [15] made an ad hoc assumption to define a local chemical potential as a ratio of correlators. Others [5, 8–12] have essentially extended Kawasaki's use of linear response theory [16], in which the density fluctuations are expressed in terms of the local chemical potential as the driving force, with the latter variable eliminated subsequently by a Taylor expansion of $\mu = \mu(n)$, i.e. by introducing the susceptibility. In the absence of memory effects this procedure guarantees (1) and, thus, is not a general proof. (Computer simulations have shown memory effects are not crucial to the accuracy of results [17].) Moreover, works employing linear response theory have been limited to initial state kinetics [8, 9, 12, 18, 19]. No analytic formulation has established the Reed–Ehrlich factorization (1) beyond initial state interaction kinetics. We will indeed show that it is invalid for all cases of generalized hopping kinetics where both initial and final state interactions occur, for example, for the physically relevant case of saddle-point interactions.

For diffusion in a 1D system we have recently presented an alternate method of calculating the collective diffusivity, $D(\theta, T)$ [20]. It involves a straightforward gradient expansion of all the correlators appearing in the diffusion current in the continuum limit and is applicable for all choices of hopping kinetics and lateral interactions. Formally, the method is equivalent to obtaining the diffusion equation by a Kramers–Moyal expansion [21] of the lattice gas probability distribution which evolves according to the master equation. However, our approach is more direct and transparent. We proved that the Reed–Ehrlich factorization is exact in 1D for all choices of the hopping kinetics and for all particle interactions, i.e. both pairwise and nonlinear interactions. Importantly, the gradient method bypassed calculational difficulties in linear response theory associated with a general choice of the kinetics.

Here we generalize this gradient method to 2D systems and present the formalism which permits the evaluation of the diffusivity for all kinetics and lateral interactions on a homogeneous substrate [22]. To evaluate the general expression we extend the transfer matrix method, for the calculation of correlators, to adsorbates subject to an external field, namely a density gradient. We give some results for realistic scenarios of the hopping kinetics and for first neighbour interactions for an adsorbate on a rectangular lattice, though the method is not restricted to these interactions or substrate symmetry. The factorization (1) is only correct for initial state *or* final state interaction kinetics; it fails otherwise, in particular for the physically important case of saddle-point interactions.

2. Kinetic lattice gas model

To set up the kinetic lattice gas model, one assumes that the surface of a solid can be divided into N_s cells labelled i, for which one introduces microscopic occupation numbers

$n_i = 1$ or 0, depending on whether cell i is occupied by an adsorbed particle or not. There are 2^{N_s} microstates $\mathbf{n} = (n_1, n_2, \ldots, n_{N_s})$ given by sequences of zeroes and ones. To introduce the dynamics of the system one writes down a model Hamiltonian:

$$H(\mathbf{n}) = E_s \sum_i n_i + V_1 \sum_{i,a} n_i n_{i+a} + \cdots. \tag{2}$$

Arguing that the lattice gas Hamiltonian should give the same Helmholtz free energy as a microscopic Hamiltonian (for noninteracting particles) one can show that the proper identification of E_s is the free energy per particle [23]:

$$E_s = -V_0 - k_B T \ln(q_3 q_{int}) \tag{3}$$

with V_0 the depth of the surface potential. The centre-of-mass vibrations of the adsorbed molecule in this potential well are represented by the partition functions $q_3 = q_z q_{xy}$, with normal (z) and in-plane (x, y) components: $q_{int} = q_{vib} q_{rot}$ is the partition function for the internal degrees of freedom (vibrations, ν_v and hindered rotations, ν_r). These modes are usually described by 1D harmonic oscillators. V_1 is an (isotropic) interaction between nearest-neighbour particles, indexed by sites $i + a$; longer-range and nonlinear interactions can be included.

We introduce a function $P(\mathbf{n}, t)$ which gives the probability that a given microstate $\mathbf{n}$ of the lattice gas is realized at time t and define the transition probability $W(\mathbf{n}, \mathbf{n}')$ per unit time as the probability to go from a state $\mathbf{n}'$ to $\mathbf{n}$. Treating hopping as a Markov process $P(\mathbf{n}, t)$ must satisfy a master equation

$$\frac{dP(\mathbf{n}, t)}{dt} = \sum_{\mathbf{n}'} [W(\mathbf{n}, \mathbf{n}') P(\mathbf{n}', t) - W(\mathbf{n}', \mathbf{n}) P(\mathbf{n}, t)]. \tag{4}$$

To ensure the approach to equilibrium in an isolated system each term in the sum must satisfy detailed balance:

$$W(\mathbf{n}, \mathbf{n}') P_{eq}(\mathbf{n}') = W(\mathbf{n}', \mathbf{n}) P_{eq}(\mathbf{n}) \tag{5}$$

where

$$P_{eq}(\mathbf{n}) = \frac{e^{-(H(\mathbf{n}) - \mu N(\mathbf{n}))/k_B T}}{\Xi} \tag{6}$$

$$\Xi = \sum_{\mathbf{n}} e^{-(H(\mathbf{n}) - \mu N(\mathbf{n}))/k_B T} \tag{7}$$

is the equilibrium probability and Ξ is the grand canonical partition function. In principle, $W(\mathbf{n}', \mathbf{n})$ must be calculated from a Hamiltonian that includes, in addition to (2), coupling terms to the gas phase and the solid phase that mediate mass and energy exchange. In this paper we will rather follow the procedure initiated by Glauber [24] in setting up the kinetic Ising model and guess the appropriate form of $W(\mathbf{n}', \mathbf{n})$.

In the absence of adsorption and desorption the number of adparticles, $N(\mathbf{n})$, is fixed and the form of $W(\mathbf{n}', \mathbf{n})$ simplifies. We restrict our description of diffusion to be that resulting from the hopping of single particles from an occupied site

to a neighbouring unoccupied site. Then we can write this transition probability as [25]

$$W_{\mathrm{diff}}(\mathbf{n}', \mathbf{n}) = \sum_{i,a}[W_i^>(\mathbf{n}) + W_{i+a}^<(\mathbf{n})]$$
$$\times \delta_{n_i'}^{1-n_i} \delta_{n_{i+a}'}^{1-n_{i+a}} \prod_{l \neq i, i+a} \delta_{n_l'}^{n_l}. \quad (8)$$

To allow for anisotropy of particle interaction, we label the sites of the lattice gas by a two-component vector $\mathbf{i} = (i_a, i_b)$ along the primitive axes $\mathbf{a}$ and $\mathbf{b}$ of a rectangular substrate. Here $W_i^>(\mathbf{n})$ is the transition rate from site $\mathbf{i}$ to site $\mathbf{i} + \mathbf{a}$ and is given by

$$W_i^>(\mathbf{n}) = J_0 n_i (1 - n_{i+a})[1 + A_1 n_{i-a} + A_1'(n_{i+b} + n_{i-b}) \\
+ A_2 n_{i-a}(n_{i+b} + n_{i-b}) + A_2' n_{i-b} n_{i+b} + A_3 n_{i-a} n_{i-b} n_{i+b} \\
+ B_1 n_{i+2a} + B_1'(n_{i+a+b} + n_{i+a-b}) \\
+ B_2 n_{i+2a}(n_{i+a+b} + n_{i+a-b}) + B_2' n_{i+a-b} n_{i+a+b} \\
+ B_3 n_{i+2a} n_{i+a-b} n_{i+a+b}] + \cdots. \quad (9)$$

The rate $W_{i+a}^<(\mathbf{n})$ gives the reverse current and follows from (9) with the interchanges $i \rightleftarrows i + a$, $i - a \rightleftarrows i + 2a$. The form of (9) expresses the effect on the rate due to interactions of the hopping particle with m nearest neighbours, either in its initial state, with coefficients A_m, or its final state, with coefficients B_m. In addition, another 29 coefficients are necessary to specify, completely, both initial *and* final state interaction effects for the hopping particle; saddle-point interactions are subsumed in such forms. Detailed balance imposes constraints on less than half of the coefficients. As examples, we have for the coefficients exhibited the relations

$$(1 + A_1)u_a = (1 + B_1)$$
$$(1 + A_1')u_b = (1 + B_1')$$
$$(1 + A_1 + A_1' + A_2)u_a u_b = (1 + B_1 + B_1' + B_2)$$
$$(1 + 2A_1' + A_2')u_b^2 = (1 + 2B_1' + B_2') \quad (10)$$
$$(1 + A_1 + 2A_1' + A_2 + A_2' + A_3)u_a u_b^2$$
$$= (1 + B_1 + 2B_1' + B_2 + B_2' + B_3)$$

with $u_a = \exp(-\beta V_{1a})$, V_{1a} the interaction along axis $\mathbf{a}$. Judicious choices of these coefficients allow us to describe different hopping scenarios that we will discuss below; various choices have been made in the literature [1, 25].

3. Equation of motion and Fick's law

We treat the diffusion as the result of particles hopping along an imposed density gradient, from an occupied site $\mathbf{i}$ to a neighbouring unoccupied site $\mathbf{i} + \mathbf{a}$. Taking the first moment of the master equation, i.e. multiplying (4) by n_i and summing over all microstates $\mathbf{n}$, we obtain the equation of motion for the average occupancy of a site. To write this efficiently we introduce the microscopic particle current through the bond $\mathbf{i} \rightarrow \mathbf{i} + \mathbf{a}$:

$$j_i = a[W_i^>(\mathbf{n}) - W_{i+a}^<(\mathbf{n})] \quad (11)$$

and evaluate its average

$$\langle j_i \rangle = a \sum_{\mathbf{n}}[\langle W_i^>(\mathbf{n}) \rangle - \langle W_{i+a}^<(\mathbf{n}) \rangle]$$

$$= a J_0 \Bigg[\langle \overrightarrow{\bullet_i \circ_{i+1}} \rangle - \langle \overleftarrow{\circ_i \bullet_{i+1}} \rangle + A_1(\langle \bullet_{i-1} \bullet_i \circ_{i+1} \rangle \\
- \langle \circ_i \bullet_{i+1} \bullet_{i+2} \rangle) + 2A_1' \left(\left\langle \begin{matrix} \bullet \\ \bullet_i \circ_{i+1} \end{matrix} \right\rangle - \left\langle \begin{matrix} \bullet \\ \circ_i \bullet_{i+1} \end{matrix} \right\rangle \right) \\
+ 2A_2 \left(\left\langle \begin{matrix} \bullet \\ \bullet \bullet_i \circ \end{matrix} \right\rangle - \left\langle \begin{matrix} \bullet \\ \circ_i \bullet_{i+1} \bullet_{i+2} \end{matrix} \right\rangle \right) \\
+ \cdots + B_1(\langle \bullet_i \circ_{i+1} \bullet_{i+2} \rangle - \langle \bullet_{i-1} \circ_i \bullet_{i+1} \rangle) + \cdots \Bigg]. \quad (12)$$

Here we have represented, diagrammatically, only a few of the terms that result from (8) and (9). The arrows indicate the directions of the hops for the forward and reverse currents. Averages are defined by, as examples:

$$\langle \bullet_i \rangle = \langle n_i \rangle(t) = \sum_{\mathbf{n}} n_i P(\mathbf{n}, t) \quad (13)$$

$$\langle \bullet_i \circ_{i+1} \rangle = \langle n_i(1 - n_{i+1}) \rangle(t) = \sum_{\mathbf{n}} n_i(1 - n_{i+1})P(\mathbf{n}, t). \quad (14)$$

This current then enters the time evolution of the average site occupancy:

$$\frac{\mathrm{d}\langle n_i \rangle}{\mathrm{d}t} = \frac{1}{a}[\langle j_{i-a} \rangle - \langle j_i \rangle]. \quad (15)$$

The diffusion equation emerges from the average current in the long-time and long-wavelength limit for which we can introduce a local density or coverage, $\theta(\mathbf{r}, t) = \langle n_i \rangle(t)$, and a local current, $j(\mathbf{r}, t) = \langle j_i \rangle(t)$, $\mathbf{r} = (x, y) = i_a \mathbf{a} + i_b \mathbf{b}$. The current contains a number of differences of correlation functions with continuous space and time dependence and we get from (9) and (12) the form

$$j(\mathbf{r}, t) = a J_0 \{\theta(\mathbf{r}, t) - \theta(\mathbf{r} + \mathbf{a}, t) \\
+ A_1[F_{2a}(\mathbf{r} - \mathbf{a}, t) - F_{2a}(\mathbf{r} + \mathbf{a}, t) \\
- (F_{3a}(\mathbf{r}, t) - F_{3a}(\mathbf{r} + \mathbf{a}, t))] \\
+ 2A_1'[F_{2b}(\mathbf{r}, t) - F_{2b}(\mathbf{r} + \mathbf{a}, t) \\
- (F_3^>(\mathbf{r}) - F_3^<(\mathbf{r} + \mathbf{a}))] + \cdots \}. \quad (16)$$

Here, again, we introduce just some of the correlators appearing in the complete expression, which will be given below for the diffusion coefficient itself, e.g.

$$F_{2a}(\mathbf{r}, t) = \langle n_i n_{i+a} \rangle(t)$$
$$F_{3a}(\mathbf{r}, t) = \langle n_{i-a} n_i n_{i+a} \rangle(t)$$
$$F_3^>(\mathbf{r}, t) = \langle n_i n_{i+a} n_{i+b} \rangle(t) \quad (17)$$
$$F_3^<(\mathbf{r}, t) = \langle n_{i-a} n_i n_{i+b} \rangle(t)$$

i.e. F_{2a} and F_{3a} are neighbouring pair and linear trio correlators, respectively, along $\mathbf{a}$; $F_3^>(\mathbf{r}, t)$ is a right-directed triangular trio correlator and $F_3^<$ is its left-directed counterpart, obtained by reflection about site $\mathbf{i}$, i.e. $n_{i+a} \rightarrow n_{i-a}$.

For densities varying slowly on the length scale of the lattice constant, i.e. in the continuum limit, we expand the current keeping terms linear in the spatial gradient:

$$j(\mathbf{r}, t) \approx -a^2 J_0 \{\partial_{\mathbf{a}}[\theta(\mathbf{r}, t) + A_1(2F_{2a}(\mathbf{r}, t) - F_{3a}(\mathbf{r}, t)) \\
+ 2A_1'(F_{2b}(\mathbf{r}, t) - F_3^<(\mathbf{r}, t))] + \cdots \\
- a^{-1}[2A_1'(F_3^<(\mathbf{r}, t) - F_3^>(\mathbf{r}, t)) + \cdots]\}. \quad (18)$$

Two classes of terms are represented here: the first involves the gradient of the correlation functions directly, while the second, with four terms in all, involves the difference of left- and right-directed functions at the same position. (Besides $F_3^>(\mathbf{r},t)$, the additional right-directed functions that occur are $F_{3h}^>(\mathbf{r},t) = \langle(1-n_i)n_{i+a}n_{i+b}\rangle$, $F_4^>(\mathbf{r},t) = \langle n_i n_{i+a} n_{i-b} n_{i+b}\rangle$, $F_{4h}^>(\mathbf{r},t) = \langle(1-n_i)n_{i+a}n_{i-b}n_{i+b}\rangle$.) Now for long time and length scales a system is maintained in local equilibrium by much faster relaxation processes. In particular, this implies that the space and time dependence of correlation functions is completely given by that of the local density, i.e. we must have

$$\partial_{\mathbf{a}} F_\alpha(\mathbf{r},t) = \frac{\mathrm{d}}{\mathrm{d}\theta} F_\alpha(\theta(\mathbf{r},t)) \partial_{\mathbf{a}}\theta \qquad (19)$$

and from the first class of terms we obtain directly the form of Fick's first law for the diffusion current:

$$j(\mathbf{r},t) = -D(\theta)\partial_{\mathbf{a}}\theta. \qquad (20)$$

The second class can be written formally in this manner also, because the spatial variation of the density is implicit in such differences; in 1D one can show this straightforwardly [20]. If we define

$$\lim_{a\to 0} a^{-1}(F_\alpha^<(\mathbf{r},t) - F_\alpha^>(\mathbf{r},t)) = D_\alpha(\theta)\partial_{\mathbf{a}}\theta \qquad (21)$$

then we obtain the complete density-dependent diffusion coefficient, exactly, as

$$\begin{aligned}
D(\theta)/D_0 = 1 &+ \frac{\mathrm{d}}{\mathrm{d}\theta}[\langle\tilde{W}_A\rangle - \langle\tilde{W}_B\rangle + A_1\langle\bullet\bullet\rangle] \\
&- 2(A_1' + A_2)D_3 - (A_2' + A_3)D_4 \\
&- 2B_1' D_{3h} - B_2' D_{4h}
\end{aligned} \qquad (22)$$

in terms of the equilibrium correlators at the local density, $\theta(\mathbf{r},t)$. Here $D_0 = a^2 J_0$ is the diffusion coefficient in the absence of lateral interactions. Here we have written, for example, $F_{2a}(\theta) = \langle\bullet\bullet\rangle$ and defined the dimensionless, partial (average) transition rate:

$$\langle\tilde{W}_A\rangle = A_1\langle\bullet\bullet\circ\rangle + 2A_1'\left\langle\begin{array}{cc}\bullet&\\\bullet&\circ\end{array}\right\rangle + 2A_2\left\langle\begin{array}{ccc}&\bullet&\\\bullet&&\circ\end{array}\right\rangle$$
$$+ A_2'\left\langle\begin{array}{cc}\bullet&\\\bullet&\circ\\\bullet&\end{array}\right\rangle + A_3\left\langle\begin{array}{ccc}&\bullet&\\\bullet&&\circ\\&\bullet&\end{array}\right\rangle \qquad (23)$$

with a similar expression for $\langle\tilde{W}_B\rangle$, after exchanging the right-hand particle–hole pair and the coefficients here. Standard relations have been used to simplify, e.g. the term $F_{2a}(\theta) - F_{3a}(\theta)$ becomes $\langle\bullet\bullet\rangle - \langle\bullet\bullet\bullet\rangle = \langle\bullet\bullet\circ\rangle$, etc. In this notation, two of the four directed-difference functions to be evaluated via (21) can be symbolically represented as

$$F_3^<(\mathbf{r},t) - F_3^>(\mathbf{r},t) = \left\langle\begin{array}{cc}&\bullet\\\bullet&\bullet_{\mathbf{r}}\end{array}\right\rangle - \left\langle\begin{array}{cc}\bullet&\\\bullet_{\mathbf{r}}&\bullet\end{array}\right\rangle \qquad (24)$$

$$F_{3h}^<(\mathbf{r},t) - F_{3h}^>(\mathbf{r},t) = \left\langle\begin{array}{cc}&\bullet\\\bullet&\circ\end{array}\right\rangle - \left\langle\begin{array}{cc}\bullet&\\\circ&\bullet\end{array}\right\rangle. \qquad (25)$$

Note that these latter correlators are not equilibrium quantities but reflect the spatial gradient explicitly. Finally, the total average transition rate, corresponding to (9), is

$$\begin{aligned}
\langle W\rangle &= J_o\langle\tilde{W}\rangle \\
&= J_o[\langle\bullet\circ\rangle + \langle\tilde{W}_A\rangle + \langle\tilde{W}_B\rangle].
\end{aligned} \qquad (26)$$

Equations (22) and (26) are the general expressions for the diffusivity and the transition rate (jump rate $\langle W\rangle/\theta$) for single-site hops on a rectangular lattice and clearly reflect the interaction neighbourhoods for the hopping process, as well as any anisotropy, via the specific orientations of the correlators.

4. Correlators in an inhomogeneous adsorbate

The correlators in local equilibrium in an inhomogeneous adsorbate due to conditions of diffusion must involve spatial derivatives as defined in (21). Thus the task remaining is the evaluation of the coverage dependence of the functions in expressions such as (23)–(25). Because derivatives are involved, quasi-analytic rather than simulation methods are necessary.

4.1. Diffusion in a quasi-1D adsorbate

Before presenting the method for the calculation of the diffusivity for the general case we note that an analytic expression is only possible in special cases. For a quasi-1D system with the interaction parallel to the particle gradient treated as negligible, $\beta V_{1a} \approx 0$, the correlators factorize with one-site overlap, e.g. $\langle\bullet\bullet\circ\rangle = \langle\bullet\bullet\rangle\langle\bullet\circ\rangle/\langle\bullet\rangle$. The functions D_α also simplify, e.g. $F_3^< - F_3^> \to (\langle\bullet_{i-1}\rangle - \langle\bullet_{i+1}\rangle)\langle\bullet\bullet\rangle_i^\perp$, where $\langle\rangle^\perp$ denotes a correlator in the direction perpendicular to the gradient (the **b** axis). Then (22) reduces to

$$D(\theta)/D_0 = 1 + \frac{\mathrm{d}}{\mathrm{d}\theta}[\tilde{W}_A'(1-\theta) - \tilde{W}_B'\theta] + 2(\tilde{W}_A' + \tilde{W}_B') \quad (27)$$

with $\tilde{W}_A' = 2A_1'\langle\bullet\bullet\rangle^\perp + A_2'\langle\bullet\bullet\bullet\rangle^\perp$, $\tilde{W}_B' = 2B_1'\langle\circ\bullet\rangle^\perp + B_2'\langle\bullet\circ\bullet\rangle^\perp$. Amongst the various choices of hopping kinetics, three cases have simple forms and a simple physical interpretation, namely (i) initial state interactions ($B_n' = 0$; $A_1' = u_b^{-1} - 1$, $A_n' = (A_1')^n$), (ii) final state interactions ($A_n' = 0$; $B_1' = u_b - 1$, $B_n' = (B_1')^n$) and (iii) symmetric initial and final state interactions ($A_n' = -B_n'$), i.e. where the initial, or final, or both neighbourhoods of the hopping particle are relevant, respectively. Using the standard expressions for $\beta\mu$ and $\langle\bullet\bullet\rangle$ it is easy to show that the Reed–Ehrlich form (1) applies for cases ((i) and (ii)) but not for case (iii). In contrast, for a true-1D system, with particle interactions *along* the population gradient, equation (1) is also correct for case (iii) [20].

The other situation to which the one-site overlap factorization applies is the quasi-chemical approximation (QCA) in which the nearest-neighbour correlator is also given by the 1D expression. The utility of this approximation rests on the simplified expressions for the diffusivity that result. It has been used in many works, beginning with Reed and Ehrlich [14] and continuing up to the near-present [26]. It is known to produce a diffusivity that is qualitatively correct

above the ordering temperature of the system, at least for initial state interactions. For isotropic interactions only, for simplicity, and with the ratios $R_A = \langle\bullet\bullet\rangle/\langle\bullet\rangle$, $R_B = \langle\bullet\circ\rangle/\langle\circ\rangle$, (22) becomes

$$D(\theta)/D_0 = 1 + \frac{\mathrm{d}}{\mathrm{d}\theta}[\langle\tilde{W}_A\rangle - \langle\tilde{W}_B\rangle]$$

$$+ [A_1 + 2(A_1 + A_2)R_A + (A_2 + A_3)R_A^2]\frac{\mathrm{d}\langle\bullet\bullet\rangle}{\mathrm{d}\theta}$$

$$- [2B_1R_B + B_2R_B^2]\frac{\mathrm{d}\langle\circ\circ\rangle}{\mathrm{d}\theta} \qquad (28)$$

where $\langle\tilde{W}_X\rangle = \langle\bullet\circ\rangle[3X_1R_X + 3X_2R_X^2 + X_3R_X^3]$, $X = A, B$. With appropriate expressions for $\exp(\beta\mu)$ one can again show, rigorously, that the form (1) applies for cases ((i) and (ii)) but not for case (iii). For case (i), for example, one has $\langle\tilde{W}\rangle = \langle\bullet\circ\rangle(1 + A_1R_A)^3$, $\chi = \theta(1 - \theta)\alpha$, with $\alpha^2 = 1 - 4\theta(1 - \theta)(1 - u)$; an analogous expression occurs for case (ii).

4.2. Transfer matrix method for an inhomogeneous rectangular lattice

To evaluate (23) (and the corresponding terms in $\langle\tilde{W}_B\rangle$) we use the transfer matrix method, see Kreuzer and Payne [23] and references therein. Its application to the calculation of anisotropic correlators spanning three rows of the rectangular lattice, such as those appearing in (23), is straightforward: the lattice is taken to be an infinite cylinder of axial circumference N sites (along the direction of **b**), i.e. with periodic boundary conditions in the finite dimension. With the basis taken as the states of a strip of length N sites and width 2 rows (rings on the cylinder) one constructs the matrix of Boltzmann factors, in the grand canonical representation with the (rescaled) chemical potential $\tilde{\mu} = (\mu - E_s)$ fixed, with particle interactions within a strip and between neighbouring strips—a 4-row transfer matrix. The left and right eigenvectors of the leading eigenvalue of this matrix determine the coverage $\theta(\mu, T)$; the correlators follow by contraction of appropriate derivatives of the matrix with these vectors. In practice, the inversion to $\mu(\theta, T)$ is performed numerically and the coverage dependence of the correlators follows. Their derivatives can be obtained accurately, e.g. by spline methods on a fine coverage mesh.

To calculate D_α using (21) we introduce a constant external field which maintains a population gradient and then evaluate the factors $\partial\theta/\partial x$ and $F_\alpha^< - F_\alpha^>$ as finite differences, about some position, of averages on a lattice of dimension Ma sites. As M increases the ratio of these factors will tend to D_α. Specifically, for the application of the transfer matrix method, we replace the infinite cylinder by a torus of size $M \times N$ with periodicity in the planar circumference, M, in addition. The single-particle energy, E_s, of the homogeneous system now depends on position through the external potential, ϕ, as $E_s + i\phi$, for site i along the direction of **a**. We choose as the basis for the position-dependent transfer matrix the 2^N states of a single ring and denote the matrix connecting rings i and $i + 1$ by $\mathbf{T}_{i,i+1}$. Then the average site occupation at the central ring, indexed $l = (M - 1)/2$, M odd, is given by

$$\langle n_l \rangle = \frac{1}{N\Xi}\mathrm{Tr}(\mathbf{T}_{1,2}\mathbf{T}_{2,3}\cdots\mathbf{T}_{l,l-1}\mathbf{P}\mathbf{T}_{l,l+1}\cdots\mathbf{T}_{M,1}). \qquad (29)$$

Here **P** is a particle matrix, with elements $P_{\mathrm{rs}} = p_s\delta_{\mathrm{rs}}$, p_s the number of particles in state s and Ξ is the grand partition function of the adsorbate, now on the torus:

$$\Xi(T, \mu, M, N) = \mathrm{Tr}\left(\prod_{i=1}^{M}\mathbf{T}_{i,i+1}\right). \qquad (30)$$

The coverage gradient at site l follows by expanding $\langle n_{l\pm1}\rangle$ about the zero-field values:

$$\theta(x = (l \pm 1)a) = \langle n_{l\pm1}\rangle - \phi Q_{l\pm1}^{(1)} + \mathrm{O}(\phi^2) \qquad (31)$$

and evaluating the limiting three-point difference of the coefficients of the field:

$$\frac{\partial\theta}{\partial x} = -\frac{\phi}{2a}\lim_{M\to\infty}(Q_{l+1}^{(1)} - Q_{l-1}^{(1)}) + \mathrm{O}(\phi^3). \qquad (32)$$

The form (32) is obtained by expanding each matrix in (29) in ϕ and retaining products linear in ϕ overall. For this we set $\mathbf{T}_{i,i+1} = \mathbf{T}_o - \phi\mathbf{U}_i/2$, where $\mathbf{T}_o$ is the 2-row (ring) transfer matrix for the homogeneous system on the torus, with grand partition function Ξ_o, and $\mathbf{U}_i$ is a matrix recording the magnitude of the external potential at the ring labelled i. Its matrix elements between states r and s, at rings $i, i + 1$ respectively, are proportional to those of $\mathbf{T}_o$, which we denote as t_{rs}:

$$(\mathbf{U}_i)_{\mathrm{rs}} = u_{\mathrm{rs}}^{(i)}t_{\mathrm{rs}} \qquad (33)$$
$$u_{\mathrm{rs}}^{(i)} = ip_r + (i + 1)p_s, \qquad i = 1, 2, \ldots, (M - 1)$$
$$= Mp_r + p_s \qquad i = M. \qquad (34)$$

Finally, the difference of field coefficients can be expressed in terms of sums of products of matrices. We find

$$Q_{l+1}^{(1)} - Q_{l-1}^{(1)} = \frac{1}{2N\Xi_o}\mathrm{Tr}(\mathbf{S}_1 + \mathbf{X}_1 + \mathbf{E}_1) \qquad (35)$$

with the definitions

$$\mathbf{S}_1 = \sum_{k=0}^{l-3}\mathbf{T}_o^k(\mathbf{U}_{k+1}\mathbf{D}_{1,l-3-k}\mathbf{T}_o + \mathbf{T}_o\mathbf{D}_{1,l-3-k}\mathbf{U}_{M-k-1})\mathbf{T}_o^{k+1}$$
$$\qquad (36)$$

$$\mathbf{D}_{1,m} = \mathbf{T}_o^m\mathbf{D}_{1,0}\mathbf{T}_o^m \qquad (37)$$

$$\mathbf{D}_{1,0} = \mathbf{T}_o^2\mathbf{P} - \mathbf{P}\mathbf{T}_o^2 \qquad (38)$$

$$\mathbf{X}_1 = \mathbf{T}_o^{l-2}\mathbf{X}_{1,l}\mathbf{T}^{l-2} \qquad (39)$$

$$\mathbf{X}_{1,l} = \mathbf{U}_{l-1}\mathbf{T}_o\mathbf{P} - \mathbf{P}\mathbf{U}_{l-1}\mathbf{T}_o + \mathbf{T}_o\mathbf{U}_l\mathbf{P} - \mathbf{P}\mathbf{T}_o\mathbf{U}_l \qquad (40)$$

$$\mathbf{E}_1 = \mathbf{D}_{1,l-2}\mathbf{U}_M. \qquad (41)$$

The matrices $\mathbf{D}_{1,0}$ and $\mathbf{X}_{1,l}$ are the kernels of the population difference, effectively, across the three rings indexed $l - 1, l, l + 1$; the matrix $\mathbf{X}_1$ encodes crossover terms about $l \pm 1$ which are not in the regular sum $\mathbf{S}_1$; the matrix $\mathbf{E}_1$ contains the end effect of the boundary condition (a difference in site energy of $(N - 1)\phi$ between sites 1 and N) and becomes irrelevant for large enough M. The matrix elements of the kernels are

$$(\mathbf{D}_{1,0})_{ij} = \sum_k(p_j - p_i)t_{ik}t_{kj} \qquad (42)$$

$$(\mathbf{X}_{1l})_{ij} = [l(p_j + p_i) + (p_j - p_i)](\mathbf{D}_{1,0})_{ij}$$
$$+ 2l(p_j - p_i)\sum_k p_k t_{ik}t_{kj}. \qquad (43)$$

The factors $F_\alpha^< - F_\alpha^>$ can be evaluated in a similar manner: differences of pairs of correlators occur, e.g. (24) and (25), which also span the same three rings; each correlator has the form of (29) with, however, a position- and direction-dependent correlator matrix, $\mathbf{C}_{l,l+1}^<$ or $\mathbf{C}_{l,l+1}^>$, in place of $\mathbf{PT}_{l,l+1}$. Again we expand such matrices about their zero-field values and find the difference of their directed averages, i.e. $\mathbf{C}_{l,l+1}^> = \mathbf{C}_o^> - \phi\mathbf{W}_{l,l+1}^>/2$, where $\mathbf{C}_o^>$ is the appropriate matrix for the homogeneous system. For example, for the difference (24) about the central site, we get

$$F_3^< - F_3^> = \langle\mathbf{W}_{l-1,l}^{(3)<}\rangle - \langle\mathbf{W}_{l,l+1}^{(3)>}\rangle$$
$$= -\frac{\phi}{2N_c\Xi_o}\text{Tr}(\mathbf{S}_2 + \mathbf{X}_2 + \mathbf{E}_2) \qquad (44)$$

where the expressions for $\mathbf{S}_2, \mathbf{X}_2, \mathbf{E}_2$ are the same as $\mathbf{S}_1, \mathbf{X}_1, \mathbf{E}_1$ above except for the replacements of the kernels $\mathbf{D}_{1,0}$ and $\mathbf{X}_{1,l}$ by $\mathbf{D}_{2,0}$ and $\mathbf{X}_{2,l}$; N_c is the count of the correlator on the torus. If the matrix elements of $\mathbf{C}_o^>$ are denoted $c_{ij}^> t_{ij}$ then the kernels have elements

$$(\mathbf{D}_{2,0})_{ij} = (\mathbf{T}_o\mathbf{C}_o^> - \mathbf{C}_o^<\mathbf{T}_o)_{ij}$$
$$= \sum_k (c_{jk}^> - c_{ik}^<)t_{ik}t_{kj} \qquad (45)$$
$$(\mathbf{X}_{2,l})_{ij} = (\mathbf{U}_{l-1}\mathbf{C}_o^> - \mathbf{C}_o^<\mathbf{U}_l + \mathbf{T}_o\mathbf{W}_{l,l+1}^> - \mathbf{W}_{l-1,l}^<\mathbf{T}_o)_{ij}$$
$$= [l(p_j + p_i) + (p_j - p_i)](\mathbf{D}_{2,0})_{ij}$$
$$+ 2l\sum_k p_k(c_{jk}^> - c_{ik}^<)t_{ik}t_{kj}. \qquad (46)$$

Here $c_{jk}^> - c_{ik}^<$ is a difference of directed bond counts for states indexed i, j, k in rings $l-1, l, l+1$, respectively.

The end result is that all the differences $F_\alpha^< - F_\alpha^>$ have the same form, proportional to $Q_{l+1}^{(\alpha)} - Q_{l-1}^{(\alpha)}$, ($\alpha = 3, 3h, 4, 4h$) with only the kernels $\mathbf{D}_{n(\alpha),0}$ and $\mathbf{X}_{n(\alpha),l}$ modified according to the bond counts of the homogeneous correlators. Thus there is a well-defined and repetitive procedure for evaluating the functions D_α, proportional to the limiting value of the ratios $(Q_{l+1}^{(\alpha)} - Q_{l-1}^{(\alpha)})/(Q_{l+1}^{(1)} - Q_{l-1}^{(1)})$, in terms of bilinear combinations of elements of the transfer and correlator matrices of the homogeneous system. In practice, for fixed N, a torus of size $M \sim 10^2$ suffices to recover individual correlators to the precision of these calculated on the $\infty \times N$ lattice; finite-size effects (in M) only occur close to special values of coverage with extreme interactions, e.g. at critical coverages. Ultimately, as for the homogeneous system, the accuracy of the results is only limited by the value of N, as the dimension of the matrix $\mathbf{T}_o$ grows with N. Unlike the homogeneous case where, for example, θ and all correlators can be calculated by employing a reduced matrix—the symmetric subblock of $\mathbf{T}_o$—and further reducing the state space by exploiting the dihedral symmetry of the cylinder, one must use $\mathbf{T}_o$ itself in order to reproduce the partition function of the inhomogeneous system (30).

5. Results

It is perhaps not surprising that the diffusivity for the most general case of an interacting adsorbate on a rectangular lattice, obtained by evaluating (22) with the transfer matrix method as just described, follows the same rule as the quasi-1D results.

We find for the scenarios of initial state *or* final state interaction kinetics (cases ((i) and (ii))) that $D(\theta, T)$ is numerically equal to $\chi_N^{-1}\langle W_N\rangle$ for finite values of the axial circumference, N, of the torus, to desired precision (M large enough) and for any values of the interactions V_{1a}, V_{1b}. Here $\langle W_N\rangle$ denotes the set of properly oriented correlators in (26) for some N. This orientation is important even for isotropic interactions because, for N finite, the perpendicular ($\langle\rangle^\perp$) and parallel ($\langle\rangle^\|$) versions of any correlator differ, though this difference diminishes rapidly as N increases. Because the product form is reproduced for any $N = 2, 4, 6, \ldots$ (N must be even for V_{1b} repulsive) it must be true for the infinite lattice as well. An analytic proof of the equality is harder to come by. We suspect that a transformation of the terms in (35) to a representation in which $\mathbf{T}_o$ is diagonal, with appropriate limits taken, is behind our result. For a 1D lattice we have used this transformation to obtain, for example, the analytic form of $\partial\langle\bullet\bullet\rangle/\partial\theta$ from a ratio of finite differences similar to (35). However, the proof is not trivial even in this simplest case. High- and low-temperature series expansions of D, χ and $\langle W\rangle$ in powers of the coverage offer an alternate route to an analytic proof.

We note that, while the Reed–Ehrlich form for case (i) is obtained within linear response theory and has been repeatedly applied to model diffusion in interacting systems, as outlined in section 1, little or no attention has been paid to case (ii). Indeed, it has been assumed to apply [27]. In contrast, for case (iii)—the simplest scenario for initial *and* final state effects— $D(\theta, T)$ is never given by the form (1).

We now present some results for the coverage and temperature dependence of D for these cases. We first consider case (i), the situation most commonly modelled in the literature. To calculate the diffusivity for this case, one calculates $\langle W\rangle$ by evaluating equilibrium correlators, representing clusters of 2–5 neighbouring sites, such as occur in the expression (23), and finds the inverse susceptibility from the chemical potential:

$$\chi^{-1}(\theta, T) = \left.\frac{\partial\beta\mu}{\partial\theta}\right|_T. \qquad (47)$$

The correlators in $\langle W\rangle$ span up to three rows along the **a** axis of the lattice and, in principle, necessitate a 4-row (reduced) transfer matrix construction, while the chemical potential only requires a 2-row (reduced) matrix for its evaluation. One can bypass the 4-row construction by using the relation, valid for initial state interactions only:

$$\langle\tilde{W}\rangle = \exp(\beta\mu)\langle\circ\circ\rangle. \qquad (48)$$

(Here $\langle\circ\circ\rangle = 1 - 2\theta + \langle\bullet\bullet\rangle$ spans only two rows.) Bokun *et al* [11] give a general proof of this result within the canonical ensemble, valid for any lattice with translational and inversion symmetry. However, the relation also follows within the grand canonical formalism by considering the equations of motion for $\theta = \langle\bullet\rangle$ and $\langle\bullet\bullet\rangle$ for adsorption and desorption, in particular, upon eliminating the largest (5-site) correlator between the equations. Figure 1 shows the effect of repulsive isotropic interactions (square lattice) on the coverage dependence of the diffusivity and the average
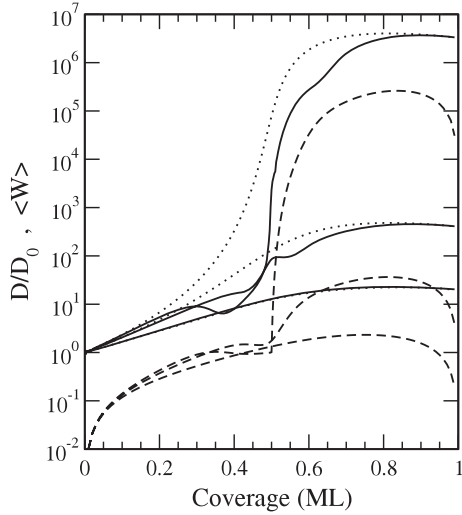
Figure 1. The coverage dependence of the diffusivity (solid lines) and the average transition rate (dashed lines) for repulsive, first neighbour isotropic interactions and the hopping kinetics defined by initial state interactions, with coefficients $A_n = (e^{\beta V_1} - 1)^n$, $B_n = 0$; $\beta V_1 = 5, 2, 1$ (top to bottom at $\theta = 0.75$). Diffusivity normalized by its value for a noninteracting adsorbate, $D_0 = J_0 a^2$, $\langle W \rangle$ normalized by J_0. Dotted lines show D evaluated in the quasi-chemical approximation.
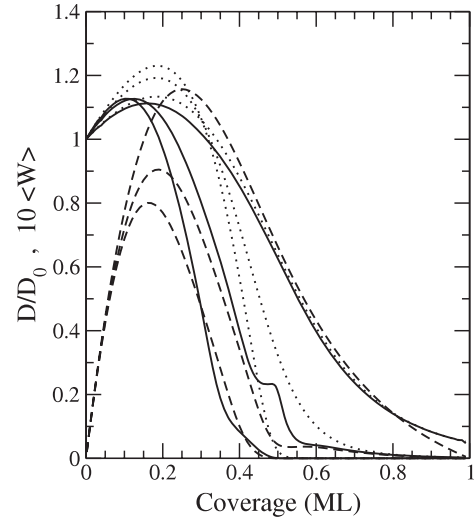

Figure 2. The coverage dependence of the diffusivity (solid lines) and the average transition rate (magnified 10×, dashed lines). The system is as in figure 1, except that the hopping kinetics are controlled by final state interactions, with coefficients $B_n = (e^{-\beta V_1} - 1)^n$, $A_n = 0$; $\beta V_1 = 1, 2, 5$ (top to bottom at $\theta = 0.25$). Dotted lines for D evaluated in the quasi-chemical approximation.

transition rate for initial state kinetics, calculated with a 2-row construction for $N = 18$. For reference we include the diffusivity for QCA (dotted lines); clearly the accuracy of QCA decreases around and below the ordering temperature, $k_B T_c = |V_1|/1.763$. Comparable results for the square lattice, but calculated within the cluster variation method, have been presented by Danani *et al* [8]. However, there are differences for both signs of V_1 and the transfer matrix method is superior. For particle repulsion, $D(\theta)$ develops structure at and below the temperature for the onset of c(2 × 2) order, in particular, local minima or inflections occur for extreme repulsion around 1/2 ML; these deepen with increasing N and arise from the divergence of the susceptibility at the order–disorder boundary and not from minima of $\langle W \rangle$. In fact, $\langle W \rangle$ here is almost exact; it changes little between $N = 12$-site and 18-site calculations. Analyses of the divergence of χ for different lattices (square, hexagonal and honeycomb) can be found elsewhere [9, 28]. Apart from the details associated with the phase transition, the physics behind the variation of D is not dissimilar to that occurring in 1D [20] and has been discussed already for the 2D case here by Danani *et al* [8]; we need not elaborate.

We next consider case (ii), final state interaction kinetics. Here again, we can use the two lowest-order equations of motion for adsorption–desorption to effectively increase the size of the cylindrical lattice on which the transfer matrix is constructed. For final state anisotropic interactions one can write $\langle W \rangle$, equivalently, as

$$\langle \tilde{W} \rangle = \langle \circ \rangle + B_1 \langle \circ \bullet \rangle + 2B_1' \langle \circ \bullet \rangle^\perp + 2B_2 \left\langle \begin{smallmatrix} \bullet \\ \circ \quad \bullet \end{smallmatrix} \right\rangle$$

$$+ B_2' \langle \bullet \circ \bullet \rangle^\perp + B_3 \left\langle \begin{smallmatrix} \bullet \\ \bullet \quad \circ \quad \bullet \end{smallmatrix} \right\rangle^\perp - \exp(-\beta \mu) \langle \circ \bullet \rangle. \tag{49}$$

Here the correlators span up to three sites along the **b** direction and are computed with a 2-row transfer matrix.

In figure 2 we show the coverage dependence of the diffusivity and the average transition rate (49) for particle repulsion on a square lattice for $N = 18$. The increasing presence of neighbours in the final state results in a decreasing diffusivity for most of the coverage range. For βV_1 large enough site blocking dominates and diffusion is negligible above 1/2 ML. The decrease of D towards zero for $\theta \lesssim 1/2$ in this case is opposite to what occurs in 1D; there D diverges as $(1 - \theta)^{-2}$ before plummeting to zero at 1/2 ML [20]. Although $\langle W \rangle$ is also decreasing as $\theta \rightarrow 1/2$ in 1D, χ^{-1} is increasing faster, unlike 2D. Again the onset of c(2 × 2) order, here of the final state, is manifested just below 1/2 ML as a distinct shoulder in $D(\theta)$. In comparison, the QCA result is clearly inadequate for all but weak repulsion and low coverage. The only comparable calculation in the literature is that of Goldstein and Ehrlich [27] for hard-core repulsion, $\beta V_1 \rightarrow \infty$; they evaluated $\langle W \rangle$ by Monte Carlo simulation and used the series expansion of Gaunt and Fisher [29] for χ to obtain D but for $\theta \lesssim 1/3$ only. In passing we remark that, for this special case and low coverage ($\theta \lesssim 1/4$), one can also calculate $\langle W \rangle$ quite accurately by factorizing the 4-site correlator in 2-site overlap [23]. With $B_n^{(\prime)} = (-1)^n$ and $\langle \bullet \circ \rangle = \theta$ for hard-core repulsion, we get for (49)

$$\langle \tilde{W} \rangle = 1 - \theta(4 - R_{3L} - 2R_{3T} + R_{3T}^2 + \exp(-\beta \mu))$$

$$R_{3L} = \langle \bullet \circ \bullet \rangle \theta^{-1}, \qquad R_{3T} = \left\langle \begin{smallmatrix} \bullet \\ \circ \quad \bullet \end{smallmatrix} \right\rangle \theta^{-1}. \tag{50}$$

χ^{-1} can be calculated from the activity by first factorizing the correlators in the expression for the sticking coefficient of an adsorbate with a hard-core repulsion, $S(\theta) = \theta \exp(-\beta \mu)$.

The result for a square lattice reduces to

$$S(\theta) = 1 - 5\theta + \theta(2R_{3L} + 4R_{3T} - 4R_{3T}^2 + R_{3T}^3). \quad (51)$$

Although factorizations of 2D correlators are generally inapplicable over the entire ranges of coverage and temperature, the factorization of the hard-core functions is quite accurate, for example the result (51) reproduces the Gaunt–Fisher expansion [29] for χ^{-1} to $O(\theta^4)$. Returning to the general case, for attractive interactions, $V_1 < 0$, we comment that the behaviour of $D(\theta, T)$ is not very different from that in 1D after allowance is made for the higher lattice coordination [20].

Finally we turn to an example of diffusion with both initial and final state interactions. In figure 3 we show the diffusivity calculated from our gradient formula, equation (22), denoted D_G (solid lines), for $N = 6$, and that of the Reed–Ehrlich form, equation (1), denoted D_{RE} (dotted lines). The interactions are anisotropic, $V_{1a} \neq V_{1b}$, with the former, in the direction of diffusion, attractive and the latter, perpendicular to it, repulsive. The sharp decrease of the diffusivity at low temperature and coverage is similar to that which occurs in a 1D system with nearest neighbour attraction, though in the 2D case the decrease is enhanced by the large repulsion across the rows. This results in a 1×2 ordered structure at coverage $1/2$ so that the average hopping rate is reduced greatly. Above coverage $1/2$ the ordered structure is destroyed and the diffusivity rises dramatically with a dependence on coverage not dissimilar to a 1D system with moderate repulsion for this kinetics [20]. We note that D_G and D_{RE} are in agreement, essentially, below coverage $1/2$ but disagree above this point, the more so the lower the temperature.

A few comments on isotropic interactions [22] is in order for this choice of hopping kinetics, in which a neighbour to the hopping particle in its initial configuration aids the hop and a neighbour in the final configuration hinders it. Weak isotropic repulsion results in D_G being nearly symmetric about $1/2$ ML; it rises then falls. For stronger repulsion the final state configuration limits the diffusivity below $1/2$ ML, so that it resembles case (ii). Above $1/2$ ML D_G decreases smoothly from a sharp maximum, a behaviour not dissimilar to that in 1D for this kinetics choice [20]. In contrast, for isotropic attraction D_G is nearly constant in value if the temperature is low enough. Again D_G and D_{RE} disagree so that the factorization for hopping kinetics not governed by either initial- or final-state effects, alone, is inadequate.

6. Conclusions

The primary purpose of this work has been to present a rigorous and a direct gradient expansion of the particle current, with an imposed density gradient, to obtain an expression for the diffusivity in terms of correlators for the inhomogeneous adsorbate. The latter can be evaluated in terms of the transfer matrix of the homogeneous system; all the advantages of the transfer matrix method come to bear on the evaluation of the diffusivity. We have proven that the Reed–Ehrlich factored form, (1), is only valid for systems where the particle hopping kinetics is governed by either initial or final state interactions; this is exclusive of any memory effects.
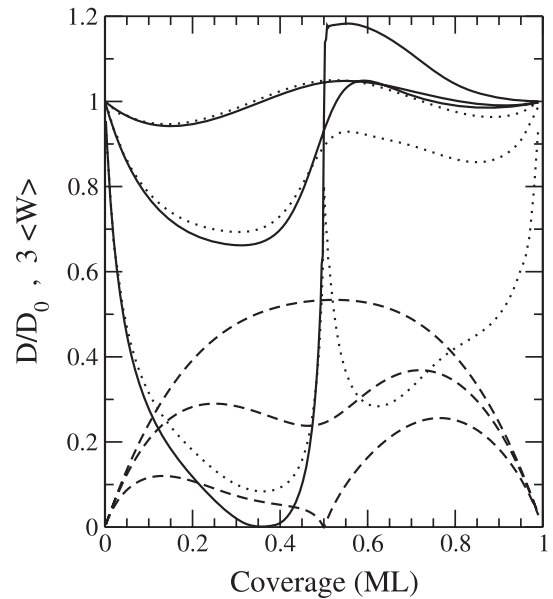

Figure 3. Normalized diffusivity (solid lines) and the average transition rate (magnified $3\times$, dashed lines) on a rectangular lattice with the hopping kinetics of first neighbour anisotropic interactions within both initial and final states, with coefficients given by (10). Interaction in the hopping direction $\beta V_{1a} = -2, -0.8, -0.4$ (bottom to top at coverage $1/4$); perpendicular interaction $V_{1b} = -2.5 V_{1a}$. Also displayed is the factorization (1) (dotted lines).

We comment on other work employing analytic methods and some extensions of our approach. Recently Chvoj [26] has developed a similar method to ours by using the Kramers–Moyal expansion alluded to in section 1. However, his evaluation of the diffusivity for a square lattice is limited to the quasi-chemical approximation. The hopping kinetics includes both initial and final states, through saddle-point interactions; in this case it is only the factorization result of QCA which permits a simplification. The results of works based on linear response theory, applied to homogeneous substrates, have started with (1), effectively, but have employed different methods to calculate χ and $\langle W \rangle$, e.g. transfer matrix (but N small) [18], cluster methods for correlators [8, 19], an expansion of the free energy [11, 12] or real-space renormalization group methods [9, 10] for critical-point behaviour. All these are limited to initial state kinetics. A common purpose has been a comparison with Monte Carlo simulations of D and to estimate the memory effects inherent to the latter method—apparently negligible for the collective diffusivity [17]. However, based on our results for 1D [20], the effects on the variation of $D(\theta, T)$ due to a particular kinetics choice is a much more important issue and a neglected one. In the few examples presented, we have barely touched upon the variability of the diffusivity with the choice of assumed kinetics and interactions. As in 1D, the interplay of these choices can produce similar effects for the coverage and temperature dependence of D, such that a unique interpretation of data, as due to a particular set of interactions, can be impossible. Accordingly we have desisted from exploring the many possible variations of the coverage dependence of diffusion coefficients. This should be done in the context of

specific systems where data are available. An advantage of our formalism is that the effects of any choice of the kinetic parameters, amongst the large number in 2D, is directly and easily examined once the appropriate correlators and their differences have been constructed for some interaction set. The extensions of our formalism to other lattice geometries, longer-range interactions, adsorbates with more than one binding site, etc, are straightforward. Only the number and complexity of the correlators appearing in (22) changes, a feature common to all analytic methods.

Acknowledgments

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