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## Dynamics of adsorbed atoms under non-equilibrium conditions

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**Abstract.** This paper deals with the determination of the tracer ( $D_T$ ) and chemical ( $D_{ch}$ ) surface diffusion coefficients in the presence of a gradient of the coverage  $\Theta$ . The lattice gas model and quasi-chemical approximation are taken as accepted in the theory. The results are discussed with respect to the interaction energy of particles, which influences the equilibrium energy of atoms as well as the saddle-point energy. Such interactions break the symmetry of jumps in the systems with gradient  $\text{grad } \Theta$ . This model predicts a decrease of  $D_T$  with the square of the gradient of the coverage  $\Theta$ .  $D_{ch}$  depends on the coefficient of proportionality of the difference between the mean jump rate in the direction of  $\text{grad } \Theta$  and that in the opposite direction. It has been found that, in the case of repulsive interaction, the coverage dependencies of  $D_T$  and  $D_{ch}$  have local maxima, whose positions depend on the rates of change of the saddle-point energy and of the equilibrium energy of the atoms due to the interaction. For attractive interaction,  $D_T$  either decreases with  $\Theta$  or increases depending on the saddle-point energy changes. At low temperatures our results differ substantially from those of the calculations made within dynamical mean-field theory.

### 1. Introduction

In recent years, surface diffusion has been intensively studied from many viewpoints. The dynamics of adsorbates on solid surfaces plays a fundamental role in many physical and chemical processes such as adsorption, melting, crystal and film growth, catalysis, and corrosion (see e.g. [1–3]). From the theoretical point of view the dynamics of adsorbed atoms in non-equilibrium conditions has been intensively studied, especially for systems in which ordered phases are formed [4–7]. In such systems, experimentally determined diffusion coefficients usually show local extrema (maxima or minima), which are explained by the presence of an ordered phase [8, 9]. The diffusion processes were simulated by Monte Carlo calculations [4, 5] or by methods based on the master equation [6, 7]. The Green–Kubo formula is usually used in the interpretation of such results. It fits within the framework of linear response theory and determines  $D_{ch}$  as a time correlation of density fluctuations in the system in equilibrium multiplied by the thermodynamic factor. The standard approximation for further calculations of the chemical diffusion coefficient is the dynamical mean-field (DMF) theory, which neglects memory effects. Within the framework of this approximation, we encounter problems in the determination of the chemical diffusion coefficient in the vicinity of the phase boundaries. In [10] the roles of memory effects on tracer and chemical diffusion coefficients

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were studied by means of Monte Carlo simulations for complex systems. It was shown that in strongly interacting cases with order present, the memory effects play an important role and influence the effective energy barrier for diffusion considerably. In this case, Monte Carlo simulation results differ substantially from DMF theory results.

The phase transformations are consequences of the interaction of the atoms on the surface, and thus the distribution of atoms plays a decisive role in the formation and relaxation of the system into the equilibrium state. In conditions in which the system is far from equilibrium and for strongly interacting particles, the gradient of the coverage ( $\text{grad } \Theta$ ) breaks the symmetry of the jumps of adsorbed atoms, and atoms move preferentially in the direction of this gradient or in the opposite direction, depending on the interaction. This dynamics cannot be respected in standard DMF theory. To achieve better insight into the mechanism of diffusion, we used another method for analytical determination of the diffusion coefficient in non-equilibrium conditions. Within the framework of the lattice gas model for diffusion, we determine the tracer ( $D_T$ ) and chemical ( $D_{ch}$ ) surface diffusion coefficients. In our model, the interaction influences the equilibrium energy of adsorbed atoms as well as the saddle-point energy, to an extent depending on the occupation of positions adjacent to the initial or final positions of the jumping atom. This model of interaction enables us to incorporate the breaking of jump symmetry in our calculations for systems with a gradient of coverage. A similar model was used in previous papers describing surface diffusion within the framework of Monte Carlo simulations or the Green–Kubo formula; see e.g. [7]. The equilibrium properties of the system will be described within the quasi-chemical approach, which has the advantage of giving simple analytical results in closed form and which is correct far from phase transformations.

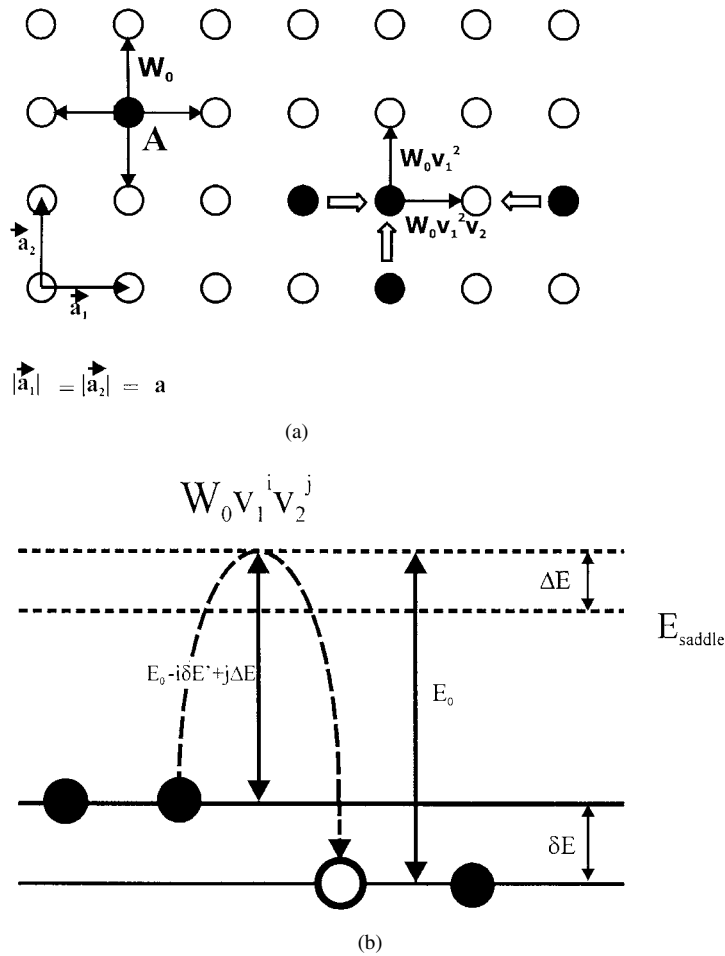
Towards the end of this paper, our results are compared with the Green–Kubo formula within the DMF approximation (with the same microscopic model and approximations). The differences between the DMF theory and our model are more substantial at lower temperatures. We shall discuss possible sources of this difference and the role of the coverage gradient in the dynamics of adatoms.

## 2. Model of the dynamics of adsorbed particles

Since we are investigating the basic features of the dynamics of adsorbed atoms in non-equilibrium conditions, we select a simple model which enables us to give a clear interpretation of our results. The model of the surface symmetry and possible jumps of adsorbed atoms that we use is displayed in figure 1. The surface is represented by a square lattice with the lattice constant  $a$ . We suppose jumps to occur only into the nearest-neighbour positions. The interaction of atoms is restricted to the nearest-neighbour sites. The dynamics of atoms on surfaces will be described in terms of the dependence of the probabilities per unit time of jumps of individual atoms on the environment. The probability of a single-atom jump, where the nearest positions are empty, is supposed to be of Arrhenius form:

$$W_0 = \nu \exp\left(-\frac{E_0}{k_B T}\right) \quad (1)$$

where  $\nu$  is a frequency factor,  $E_0$  the basic value of the activation energy of diffusion,  $k_B$  the Boltzmann factor, and  $T$  the temperature. Furthermore, we introduce the changes of the energy barrier to diffusion that arise as a result of the interaction of adatoms. The total change of the energy barrier is constituted of two contributions. The first part results from the change of the equilibrium energy of the particle due to the interaction with atoms in adjacent positions. The energy barrier is changed by  $\delta E$  if an adjacent site is occupied and this change is additive; this means that if two adjacent sites are occupied, the energy barrier is changed by  $2\delta E$ . So for



**Figure 1.** (a) The definition of the adsorption positions on the surface of square symmetry, together with the definition of the basic parameters of the lattice. The jump rates are indicated; these depend on the occupation of adjacent sites. (b) The energy diagram of the adatoms and the energy barrier to diffusion.

the particular configuration, the energy barrier to diffusion,  $E$ , is

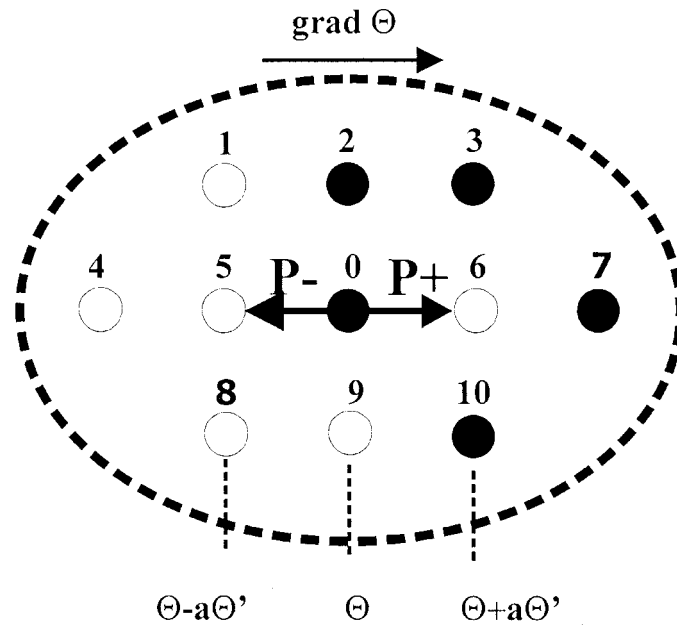
$$E(i) = E_0 - i \delta E \tag{2}$$

if  $i$  adjacent sites of site  $A$  are occupied.  $\delta E > 0$  for the repulsive interaction.

We introduce the parameter  $v_0$  describing the interaction:

$$v_0 = \exp\left(\frac{\delta E}{k_B T}\right). \tag{3}$$

Beside these changes of the energy barrier, for diffusion the effect of the lateral interaction at the saddle-point position is taken into account. This additional influence of atomic interaction considerably intensifies the breaking of the symmetry of the jumps in inhomogeneous systems. Such models were studied also in [5, 7] where the importance of this type of interaction for the dynamics of adatoms was demonstrated. It can accelerate or retard the diffusion. In our microscopic model the additive change of the saddle-point energy is an increase by  $k \Delta E$ ,



**Figure 2.** The microscopic model of the probability of jumps in a particular configuration, showing all adjacent sites which influence the dynamics of the adatom.

where  $k$  represents the number of atoms which influence the energy barrier at a saddle point. We assume that particles at positions 2, 3, 9, 10 (figure 2) as well as those at positions 5, 7 make the same contribution to the energy of the saddle point (between 0 and 6). In [7] it was assumed that only the atoms at 2, 3, 9, and 10 make contributions. In our model we include also the contributions of atoms at positions 5 and 7, even though their distance from the above-mentioned saddle point is larger and thus their influence is weaker. We neglect this difference, since we would like to emphasize the significance of the gradient of the coverage and thus the difference in occupation probability between positions 5 and 7. Within this approximation, the total energy barrier  $E$  has the form

$$E = E_0 - i \delta E + (i + j) \Delta E = E_0 - i(\delta E - \Delta E) + j \Delta E. \quad (4)$$

$i$  is the number of atoms at positions adjacent to the initial position and  $j$  is the number of atoms at positions adjacent to the final position of the jumping atom. The resulting change of the energy barrier can be interpreted as the change due to the occupation of sites adjacent to the initial position (the change of energy is characterized by  $\delta E' = \delta E - \Delta E$ ) and due to the occupation of the sites adjacent to the final position (with the change of energy  $\Delta E$ ). To describe this feature of adatom dynamics, we introduce two parameters:

$$v_1 = \exp\left(-\frac{\delta E'}{k_B T}\right) \quad (5)$$

$$v_2 = \exp\left(-\frac{\Delta E}{k_B T}\right). \quad (6)$$

$\Delta E > 0$  for the repulsive interaction;  $v_0 = v_1/v_2$ . We shall study the dynamics of the system above the temperature of the phase transition. In a square lattice with a repulsive interaction, the highest temperature of the order–disorder phase transition occurs at  $\Theta = 0.5$  and corresponds

to  $\delta E = 1.76 k_B T$ ; this means that  $v_0 = 5.81$  (see e.g. [7]). For example, for  $\delta E = 0.1$  eV, the phase transition temperature is  $T = 660$  K. In our model, we accept values of  $v_0 \ll 5.81$ . The probability per unit time of a jump of the adatom from position  $i$  to position  $j$ ,  $P_{i \rightarrow j}$ , is given in this model by the relation

$$P_{i \rightarrow j} = W_0 v_1^k v_2^l (1 - p_j) \quad (7)$$

where  $p_j$  is the occupation number for the  $j$ th position and it is  $p_j = 1$  if the  $j$ th position is occupied and  $p_j = 0$  if it is empty. The mean value of  $p_j$  is equal to the mean coverage  $\Theta(j)$  at position  $j$ , which is the relative occupancy of adsorption sites. Relation (7) reflects the dependence of the jump probability on the environment of the jumping atom:

$$k = \sum_n^{\text{NN}_i} p_n \quad (8)$$

$$l = \sum_{m \neq i}^{\text{NN}_j} p_m. \quad (9)$$

' $\text{NN}_i$ ' indicates that the summation is over the positions that are nearest neighbours of  $i$ . The probability of a jump can be rewritten in the more useful form

$$P_{i \rightarrow j} = W_0 (1 - p_j) \prod_{k \neq j}^{\text{NN}_i} (1 + p_k (v_1 - 1)) \prod_{l \neq i}^{\text{NN}_j} (1 + p_l (v_2 - 1)). \quad (10)$$

The diffusion process is a stochastic process. We determine the ensemble mean value of the probability of jumps. This value— $\langle P_{ij} \rangle$ —is given by

$$\langle P_{ij} \rangle = \frac{1}{\Theta} \langle p_i P_{i \rightarrow j} \rangle = \frac{W_0}{\Theta} \left\langle p_i (1 - p_j) \prod_{k \neq j}^{\text{NN}_i} (1 + p_k (v_1 - 1)) \prod_{l \neq i}^{\text{NN}_j} (1 + p_l (v_2 - 1)) \right\rangle. \quad (11)$$

Relation (11) gives the correlation function for the simultaneous occupation of clusters of one to eight sites. We express the correlation function for occupation of positions in larger clusters in terms of the two-point correlation function and the average occupation of individual positions by employing the cumulant expansion method [11]. Assuming a Gaussian distribution of the different configurations of adatoms on the surface is the main approximation of this method. In this case the cumulants of third and higher orders are equal to zero and we can express each three-point correlation function as a combination of a two-point correlation function and  $\Theta$ . Similarly, each four-point correlation function can be expressed as a combination of a three-point and a two-point correlation function and  $\Theta$ , and so on.

We start our analysis from the equilibrium state of the system. As regards the extension of our model to non-equilibrium systems, we use for equilibrium a simple approximation—the quasi-chemical approximation. This determines the distribution only for clusters with two adjacent sites, but in an analytical form. More exact methods which are suitable especially for use near the phase transformations are published in for example [7] (e.g. the cluster variation method). We denote the equilibrium ensemble mean values of the jump rates, taken over all possible configurations of atoms, as  $\langle P_{ij} \rangle^0$ . Since the probability of a jump depends on the occupation of the nearest-neighbour sites, we introduce  $n_0$  as the equilibrium mean value of the density of occupied pairs of adjacent sites.

### 3. Equilibrium conditions

We describe the equilibrium configuration of the atoms, characterized by  $\text{grad } \Theta = 0$ , within the framework of the quasi-chemical approximation [12]. We consider the three possible

different configurations of adjacent sites as independent clusters and denote them by the symbol  $(i, j)$ , where both  $i$  and  $j$  can be either 0 (empty) or 1 (occupied). We will thus represent the clusters by  $(0, 0)$ ,  $(1, 0)$ ,  $(1, 1)$ . The relative concentrations of these pairs in equilibrium will be denoted by  $c_{ij}$ . This means that  $n_0 = c_{11}$ . The  $c_{i,j}$  have to obey the balance equations and the quasi-chemical equilibrium condition:

$$c_{10}^2 = c_{00}n_0v_0^2. \quad (12)$$

The solution of (12) under the condition of constant number of atoms has for  $n_0$  the form

$$n_0 = \frac{2\Theta(v_0^2 - 1) - v_0^2 + \sqrt{S_n}}{2(v_0^2 - 1)} \quad (13)$$

$$S_n = [v_0^2 + 2\Theta(1 - v_0^2)]^2 + 4\Theta^2(v_0^2 - 1). \quad (14)$$

For completely disordered systems,  $n_0 = \Theta^2$ .

If we input these relations in (11), we obtain the equilibrium mean value of the probability of jumps. The particular configuration of atoms and the cluster which includes all of the atoms influencing one jump (e.g. from position 0 to 6) is shown in figure 2. The numbering of the positions is retained in the next equation and, indeed, throughout the whole paper:

$$\begin{aligned} \langle P_{06} \rangle^0 &= \frac{W_0}{\Theta} \{ p_0(1 - p_6)[(1 + p_2(v_1 - 1))(1 + p_5(v_1 - 1))(1 + p_9(v_1 - 1))] \\ &\quad \times [(1 + p_3(v_2 - 1))(1 + p_7(v_2 - 1))(1 + p_{10}(v_2 - 1))] \} \\ &= W_0 \left( 1 - \frac{n_0}{\Theta} \right) (1 + (v_2 - 1)\Theta)^3 \left( 1 + (v_1 - 1)\frac{n_0}{\Theta} \right)^3. \end{aligned} \quad (15)$$

The higher-order correlation functions in (15) were expressed in terms of  $n_0$  and  $\Theta$  by employing the cumulant expansion method [11]. At this point we suppose a Gaussian distribution of the configuration of atoms on the surface. In the case of no interaction ( $v_0 = v_1 = v_2 = 1$ ), the result is  $\langle P_{06} \rangle^0 = (1 - \Theta)$ . In equilibrium conditions, we obtain the same formula for jumps from 6 to 0; this means that in this case the detailed-balance condition is fulfilled.

#### 4. Non-equilibrium systems characterized by grad $\Theta$

The non-equilibrium state of the system of adatoms will be characterized by grad  $\Theta$ . We shall suppose grad  $\Theta$  to be constant over time. Furthermore, we restrict our calculations to terms which are linear in grad  $\Theta$  and we neglect higher derivatives of  $\Theta(x)$ . This means that we suppose deviations from the equilibrium distribution of adatoms to be small. We focus on the study of one-dimensional diffusion in the direction of grad  $\Theta$ , which we suppose to be in direction (06)—see figure 2. In order to proceed with the determination of the mean value of the jump probability, we introduce some simplifications. Firstly, we assume local equilibrium in the lines of atoms perpendicular to the gradient of the coverage. For these lines we introduce a mean value of the coverage, which is a function of lattice site  $i$ —namely  $\Theta(i)$ —but changes only in the direction of grad  $\Theta$ . So the coverage is a function of the space coordinate:

$$\text{grad } \Theta = \Theta' = \frac{\Theta(6) - \Theta(0)}{a} \quad (16)$$

$$\Theta(2) = \Theta(9) = \Theta(0) \quad (17)$$

$$\Theta(8) = \Theta(5) = \Theta(1) = \Theta(0) - a\Theta' \quad (18)$$

etc. To evaluate the mean value of the probability of a jump from position 0 to position 6 we determine the mean value for fully occupied pairs of adjacent sites in non-equilibrium

conditions. As an extension of the pair correlation function in equilibrium conditions  $n_0(\Theta)$ , we define a function  $n(\Theta_1, \Theta_2)$  denoting the correlation function for the simultaneous occupation of a randomly chosen pair in a system with a gradient  $\text{grad } \Theta$ . This means that the pair is formed by atoms in adjacent positions which can belong to different lines with different values of the coverage  $\Theta$ . The correlation function thus depends on both values of the coverage. This function was determined in [13]. In fact, we do not know the form of  $n$  as a function of the two independent variables, but it is considered at  $\Theta_1 = \Theta_2 = \Theta$  (where adjacent atoms are in positions which have the same coverage) to be equal to  $n_0(\Theta)$  ( $n(\Theta, \Theta) = n_0(\Theta)$ ). Since  $\Theta_1 = \Theta_2 \pm a \text{ grad } \Theta$ , we have

$$\frac{d\Theta_1}{d\Theta} = \frac{d\Theta_2}{d\Theta} = 1.$$

We can deduce

$$\frac{dn(\Theta_1, \Theta_2)}{d\Theta} = \frac{\partial n(\Theta_1, \Theta_2)}{\partial \Theta_1} \frac{d\Theta_1}{d\Theta} + \frac{\partial n(\Theta_1, \Theta_2)}{\partial \Theta_2} \frac{d\Theta_2}{d\Theta} = \frac{\partial n(\Theta_1, \Theta_2)}{\partial \Theta_1} + \frac{\partial n(\Theta_1, \Theta_2)}{\partial \Theta_2}. \quad (19)$$

At the point  $\Theta_2 = \Theta_1$ , we have

$$\frac{dn(\Theta_1, \Theta_1)}{d\Theta} = 2 \frac{\partial n(\Theta_1, \Theta_1)}{\partial \Theta_1} = \frac{dn_0(\Theta)}{d\Theta}. \quad (20)$$

If we now evaluate the mean value of the probabilities of jumps per unit time, we obtain

$$\langle P_{06} \rangle = \langle P_{06} \rangle^0 [1 + a\Theta' B] \quad (21)$$

$$B = \frac{4(v_2 - 1)}{1 + (v_2 - 1)\Theta} - \frac{v_1(1 + (v_0^2 - 1)n_0/\Theta)}{\sqrt{S_n}(1 - n_0/\Theta)(1 + (v_1 - 1)n_0/\Theta)}. \quad (22)$$

For the repulsive interaction, we have  $v_0 > 1$ ,  $v_2 < 1$ , and thus  $B < 0$ . The preferred jumps are in the opposite direction to  $\text{grad } \Theta$ . For attractive interaction,  $B$  can be positive, and in this case atoms move mostly in the direction of the coverage gradient. It is also possible that  $B = 0$  for  $v_1 < 1$ ; this means that the attractive interaction of atoms is compensated for by the tendency of increase of the entropy of the system, and the dynamics of the atoms is similar to that in the equilibrium state. In the case where  $v_0 = v_2 = 1$ , we have  $n_0 = \Theta^2$ , and we obtain

$$B = -\frac{1}{1 - \Theta} \quad (23)$$

and  $\langle P_{06} \rangle = (1 - \Theta) - a\Theta'$ . In this case the change of the jump probability with the gradient of the coverage does not depend on  $\Theta$ . For the jumps in the opposite direction (see figure 2) we obtain

$$\langle P_{05} \rangle = \langle P_{06} \rangle^0 [1 - a\Theta' B]. \quad (24)$$

To simplify the notation, we introduce for the jumps in the direction of  $\text{grad } \Theta$  the probability  $\bar{P}_+$ , for those in the opposite direction  $\bar{P}_-$ , and for the equilibrium mean value  $\bar{P}_0 = \langle P_{06} \rangle^0$ . I should like to emphasize that the gradient of the coverage breaks the symmetry of the jumps and that the difference between  $\bar{P}_+$  and  $\bar{P}_-$  is proportional to the value of this gradient. The coefficient  $B$  is a measure of this proportionality.

## 5. Tracer diffusion coefficient $D_T$

To determine the tracer diffusion coefficient, we accept the definition based on the mean square displacement of the individual atoms [14, 15]. Since we shall study one-dimensional diffusion, the diffusion coefficient,  $D_T$ , is scalar. In our model,  $D_T$  depends on the number of atoms on



the surface  $N$  (and thus on coverage  $\Theta$ ) as well as on the interaction of the adatoms and the temperature, i.e. on coefficients  $v_1, v_2$ :

$$D_T(\Theta, v_1, v_2) = \lim_{t \rightarrow \infty} \frac{1}{4Nt} \sum_{i=1}^N \langle (\Delta R_i)^2 \rangle \quad (25)$$

where  $t$  is time and  $\Delta R_i$  is displacement of the  $i$ th atom from a defined position during time interval  $t$ . We suppose the motion of the atom on the surface to be a random walk with the probabilities  $\bar{P}_+$  of jumps in the direction of grad  $\Theta$  and  $\bar{P}_-$  of jumps in the opposite direction. The mean number of jumps per long time interval  $t$  is  $M(t) = t\bar{P}_0$ . The probability  $P_n(m)$  that at time  $t$  the observed atom is at the position  $R(t) = R(0) + a(m - (n - m))$  is given by the binomial distribution:

$$P_n(m) = \binom{n}{m} (W_+)^m (1 - W_+)^{n-m} \quad (26)$$

where

$$W_+ = \frac{\bar{P}_+}{2\bar{P}_0} \quad (27)$$

$$W_- = \frac{\bar{P}_-}{2\bar{P}_0} \quad (28)$$

giving

$$W_+ + W_- = 1. \quad (29)$$

$m$  is the number of jumps in the direction of grad  $\Theta$ ;  $n = M(t)$  is the mean total number of jumps during time  $t$ . The following relations are valid for the binomial distribution:

$$\langle m \rangle = nW_+ \quad (30)$$

$$\langle (m - \langle m \rangle)^2 \rangle = nW_+W_- \quad (31)$$

$$\langle (R(t) - R(0))^2 \rangle = a^2[\langle 4m^2 \rangle - 4n\langle m \rangle + n^2] = a^2n[4W_+W_- + n(2W_+ - 1)^2]. \quad (32)$$

If we determine the mean square displacement from the mean position of the atom at the actual time  $t$ :

$$\langle (R(t) - \langle R(t) \rangle)^2 \rangle = a^2M(t)[1 - (aB\Theta')^2] \quad (33)$$

we obtain for the tracer diffusion coefficient

$$D_T = \frac{a^2}{4} \bar{P}_0 (1 - (aB \text{grad } \Theta)^2). \quad (34)$$

This value does not depend on time. It is evident that the tracer diffusion coefficient is proportional to the square of grad  $\Theta$  in non-equilibrium systems. The coefficient of this proportionality is  $-(a^2\bar{P}_0/4)(aB)^2$ . Such a dependence is to be expected, since this kinetic coefficient cannot depend on the direction of the gradient of the coverage. The interesting feature of the result is that the tracer diffusion coefficient always decreases with increase of the coverage gradient. The particular dependencies of  $D_T$  on the model parameters will be discussed later.

## 6. Chemical diffusion coefficient $D_{ch}$

We start our analysis of the chemical diffusion coefficient  $D_{ch}$  from the general equation describing the time evolution of the probability distribution of the atoms on the surface,

namely  $P(\dots, p_i, \dots, t)$ :

$$\begin{aligned} \partial_t P(\dots, p_i, \dots, t) = & \sum_i \sum_j^{\text{NN}} [P_{j \rightarrow i}(p_j + 1)P(\dots, p_i - 1, p_j + 1, \dots, t) \\ & - p_i P_{i \rightarrow j}P(\dots, p_i, p_j, \dots, t)]. \end{aligned} \quad (35)$$

$p_i$  is the occupation number of the  $i$ th position at time  $t$ ; the symbol NN means that the sum is over the positions that are nearest neighbours of the  $i$ -position.  $P_{i \rightarrow j}$  represents the discrete jump given by equation (10). To rewrite equation (35) as a continuous diffusion equation, we use the method described in [11]. First, we introduce continuous variables. We will move a window with a small area  $V$  over the whole surface. Each position of the window is characterized by the position vector  $\vec{r}$  of its centre of mass and by the number of atoms  $x$  that lie within its area at time  $t$ . We introduce the continuous function  $\Theta(\vec{r}, t)$ :

$$x(t) = V\Theta(\vec{r}, t). \quad (36)$$

If  $\vec{r}$  coincides with the lattice site  $i$  ( $\vec{r} = \vec{r}_i$ ), then  $\Theta(\vec{r}_i, t) = \Theta(i)(t)$  and  $x = x_i = V\Theta(i)(t)$ . The product  $x_i P_{i \rightarrow j}$  represents the flux of atoms from the area surrounding the position  $i$  to the area surrounding position  $j$ . The flux depends on the volume of this area and on the probability of jumps per unit time  $P_{i \rightarrow j}$ . Since we can arbitrarily extend the volume in the direction perpendicular to  $\text{grad } \Theta$  (in this direction, we suppose equilibrium conditions), the number of atoms  $x_i$  could be large even for a small dimension in the direction of  $\text{grad } \Theta$ . The following procedure proceeds within the framework of the Kramers–Moyal expansion. In the limit  $x_i P_{i \rightarrow j} \rightarrow \infty$ , we restrict consideration to terms up to second order in the expansion in  $1/(x_i P_{i \rightarrow j})$  of equation (35). This procedure results in the approximate equation

$$\partial_t P(x, t) = \sum_l \partial_l (A_l(x)P(x, t)) + \frac{1}{2} \sum_{l,k} \partial_l \partial_k (B_{lk}(x)P(x, t)) \quad (37)$$

where

$$A_l(x) = - \sum_j D_{jl} x_j \quad (38)$$

$$B_{lk} = d_{lk} \sum_j (D_{jl} x_l + D_{jl} x_j) - D_{lk} x_l - D_{kl} x_k \quad (39)$$

$$D_{jl} = P_{j \rightarrow l} - d_{jl} \sum_k P_{l \rightarrow k}. \quad (40)$$

$d_{jl}$  is standing for the Kronecker delta. This approximation means that in the case of a very high number of jumps per unit of time, the solution of equation (37) is identical to the solution of (35) in the limit  $x_i P_{i \rightarrow j} \rightarrow \infty$ .

The matrix with elements  $D_{i,j}$ , determined by discrete jumps, is in our model a function of the position vector  $\vec{r}$  and the jump distance  $\vec{\delta}$ :

$$D_{ij} \rightarrow D(\vec{r}_i, \vec{r}_j - \vec{r}_i) = D(\vec{r}, \vec{\delta}). \quad (41)$$

For various restrictions which we impose on the system, the function  $D(\vec{r}, \vec{\delta})$  fulfils the following conditions:

(1) The system is in equilibrium,  $\Theta$  is constant:

$$\sum_j D_{ji} = 0 \rightarrow \int (d\vec{\delta}) D(\vec{r} + \vec{\delta}, -\vec{\delta}) = 0. \quad (42)$$

(2) The number of particles on the surface is constant:

$$\frac{d}{dt} \sum_i p_i = 0 \rightarrow \int (d\vec{\delta}) D(\vec{r}, \vec{\delta}) = 0. \quad (43)$$

(3) The detailed balance in equilibrium conditions (this condition is not used in the non-equilibrium model):

$$D_{ij} = D_{ji} \rightarrow D(\vec{r} + \vec{\delta}, -\vec{\delta}) = D(\vec{r}, \vec{\delta}). \quad (44)$$

The function  $D(\vec{r}, \vec{\delta})$  represents the distribution function of the length of jumps  $\vec{\delta}$ . The following treatment needs the introduction of the momenta of this distribution function:

$$\vec{M}(\vec{r}) = \int (d\vec{\delta}) \vec{\delta} D(\vec{r}, \vec{\delta}) \quad (45)$$

$$\hat{D}(\vec{r}) = \frac{1}{2} \int (d\vec{\delta}) \vec{\delta} \vec{\delta} D(\vec{r}, \vec{\delta}). \quad (46)$$

At this step we introduce a second approximation: we neglect the higher moments of  $D(\vec{r}, \vec{\delta})$ . This approximation corresponds to the neglecting the terms proportional to the third and higher powers of the lattice constant  $a$ . Within this model we evaluate the coefficients  $A$  and  $B$  in equations (38)–(40) (see [11]):

$$A(\vec{r}, \Theta(\vec{r})) = - \int (d\vec{\delta}) D(\vec{r} + \vec{\delta}, -\vec{\delta}) \Theta(\vec{r} + \vec{\delta}) = \vec{\nabla}(\vec{M}(\vec{r}) \Theta(\vec{r})) - \vec{\nabla} \vec{\nabla}(\hat{D}(\vec{r}) \Theta(\vec{r})) \quad (47)$$

$$B(\vec{r}, \vec{r}') = 2 \vec{\nabla}' \vec{\nabla} : [\hat{D}(\vec{r}) \Theta(\vec{r}) \delta(\vec{r} - \vec{r}')]. \quad (48)$$

We derive the deterministic equation for the time evolution of the mean value of the coverage, which is determined from

$$\bar{\Theta}(\vec{r}, t) = \int d\Theta \Theta(\vec{r}, t) P(\Theta(\vec{r}, t)) \quad (49)$$

where  $P(\Theta(\vec{r}, t))$  is the solution of equation (37) in which we have substituted  $\Theta(\vec{r}, t)$  for  $x$  using definition (36). Finally, we obtain a diffusion equation in the form

$$\partial_t \bar{\Theta}(\vec{r}, t) = \vec{\nabla}(\hat{D} \vec{\nabla} \bar{\Theta}) - \vec{\nabla}[(\vec{M} - \vec{\nabla} \hat{D}) \bar{\Theta}]. \quad (50)$$

Within the framework of our microscopic model we can easily evaluate the moments  $\vec{M}$  and  $\hat{D}$ :

$$\vec{M}(\vec{r}) = a[\bar{P}_+ - \bar{P}_-] = 2a\bar{P}_0 a B \Theta' \quad (51)$$

$$\hat{D}(\vec{r}) = a^2 \bar{P}_0 \quad (52)$$

$$\vec{\nabla} \hat{D} = a^2 \frac{\partial \bar{P}_0}{\partial \Theta} \Theta' \quad (53)$$

where

$$\begin{aligned} \frac{\partial \bar{P}_0}{\partial \Theta} = & W_0 \left(1 + (v_1 - 1) \frac{n_0}{\Theta}\right)^2 (1 + (v_2 - 1) \Theta)^2 \left\{ 3 \left(1 - \frac{n_0}{\Theta}\right) \right. \\ & \times \left[ (1 + (v_2 - 1) \Theta) \frac{v_1 - 1}{\Theta} \left(\frac{\partial n_0}{\partial \Theta} - \frac{n_0}{\Theta}\right) + \left(1 + (v_1 - 1) \frac{n_0}{\Theta}\right) (v_2 - 1) \right] \\ & \left. - \frac{1}{\Theta} \left(1 + (v_1 - 1) \frac{n_0}{\Theta}\right) (1 + (v_2 - 1) \Theta) \left(\frac{\partial n_0}{\partial \Theta} - \frac{n_0}{\Theta}\right) \right\} \end{aligned} \quad (54)$$

$$\frac{\partial n_0}{\partial \Theta} = \frac{2\Theta}{\sqrt{S_n}} \left(1 + (v_0^2 - 1) \frac{n_0}{\Theta}\right). \quad (55)$$

The final expression of equation (52) has the form of the second Fick law:

$$\partial \bar{\Theta}_t = \bar{\nabla}[(D - D_1) \bar{\nabla} \bar{\Theta}] \quad (56)$$

where

$$D = a^2 \bar{P}_0 \quad (57)$$

$$D_1 = a^2 \left( 2B \bar{P}_0 - \frac{\partial \bar{P}_0}{\partial \Theta} \right) \Theta. \quad (58)$$

The difference  $D - D_1$  plays the role of a chemical diffusion coefficient:

$$D_{ch} = D - D_1 = a^2 W_0 * D_a \quad (59)$$

where

$$D_a = \frac{\bar{P}_0}{W_0} [1 - \alpha \Theta] \quad (60)$$

$$\alpha = 2B - \frac{\partial \ln \bar{P}_0}{\partial \Theta}. \quad (61)$$

The role of the interaction in the non-equilibrium system is characterized by the function  $\alpha(\Theta, v_1, v_2)$ . For repulsive interaction and weak attraction, the interaction is  $\alpha < 0$  and thus  $D_{ch} > 0$ .

In the case of non-interacting atoms, this means that if  $v_0 = v_2 = 1$ , then

$$\alpha = -\frac{1}{1 - \Theta} = B$$

and  $D_a = 1$ , and we obtain a simple expression for the diffusion equation with the constant diffusion coefficient in the usual form:

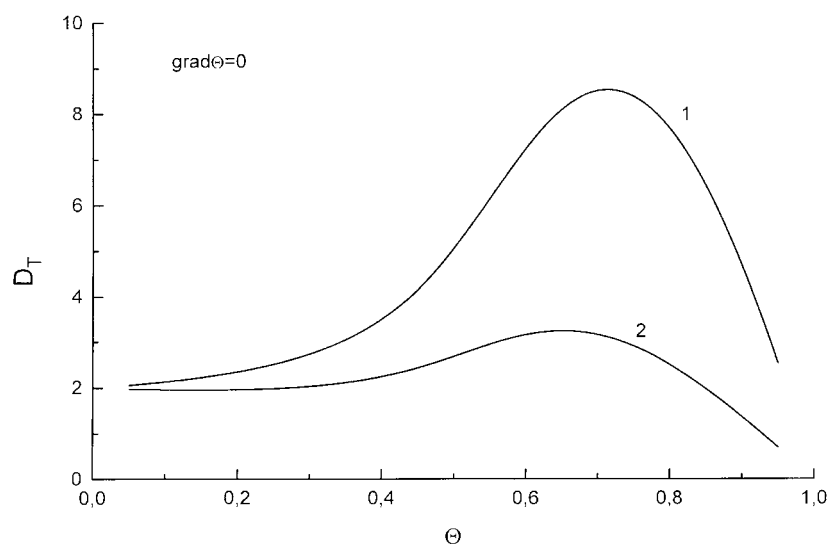
$$\partial_t \bar{\Theta} = a^2 W_0 \Delta \bar{\Theta}. \quad (62)$$

The derivation of  $D_{ch}$  has been carried out for the presence of a gradient  $\text{grad } \Theta \neq 0$ . In the next section we compare our results with the Green–Kubo formula in the DMF approximation, which gives the chemical diffusion coefficient within the framework of linear response theory, i.e. for the system near to equilibrium.

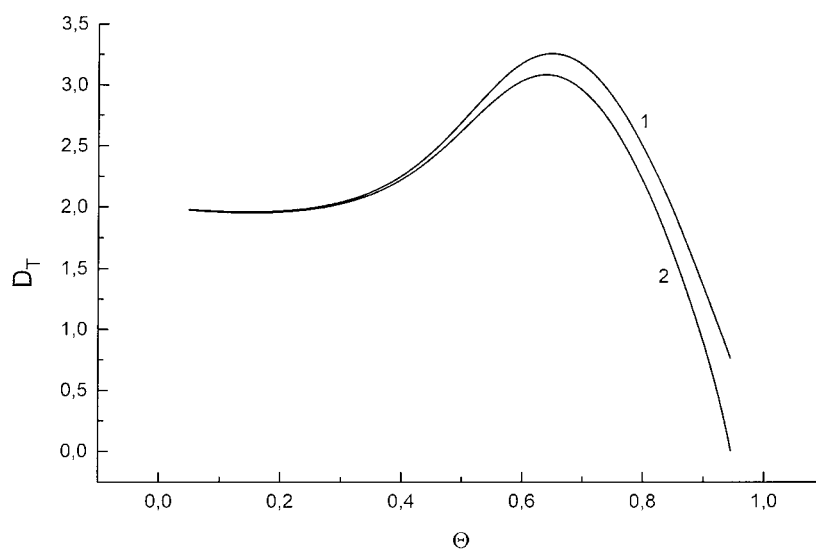
## 7. Coverage dependencies of the tracer ( $D_T$ ) and chemical ( $D_{ch}$ ) diffusion coefficients

In this paper we have answered the question of how the presence of a gradient of the coverage in a system of interacting adatoms influences the kinetic coefficients—namely, the tracer and the chemical surface diffusion coefficients. In such systems the symmetry of the probability of jumps of atoms is broken and, depending on the kind of interaction, atoms preferentially move in the direction of  $\text{grad } \Theta$  or in the opposite direction. We respect this feature of non-equilibrium systems in our microscopic model. To emphasize this feature of the dynamics, we suppose that not only the equilibrium energies of adatoms, but also the saddle-point energies are influenced by the interaction. Such dependencies of jump probabilities on the environment are described by the factors  $v_1$  and  $v_2$ , and we studied the influence of these parameters on the coverage dependence of both  $D_T$  and  $D_{ch}$ . Representative results are presented in figures 3–5.

All calculations were carried out for small values of  $\Theta'$  and high temperatures, above the critical temperature  $T_c$  of the phase transition:  $T > T_c$ . Thus we excluded the possibility of ordered phase formation. In such a temperature region the quasi-chemical approximation is acceptable. The case of  $T < T_c$ , which is more interesting, will be discussed in future papers.

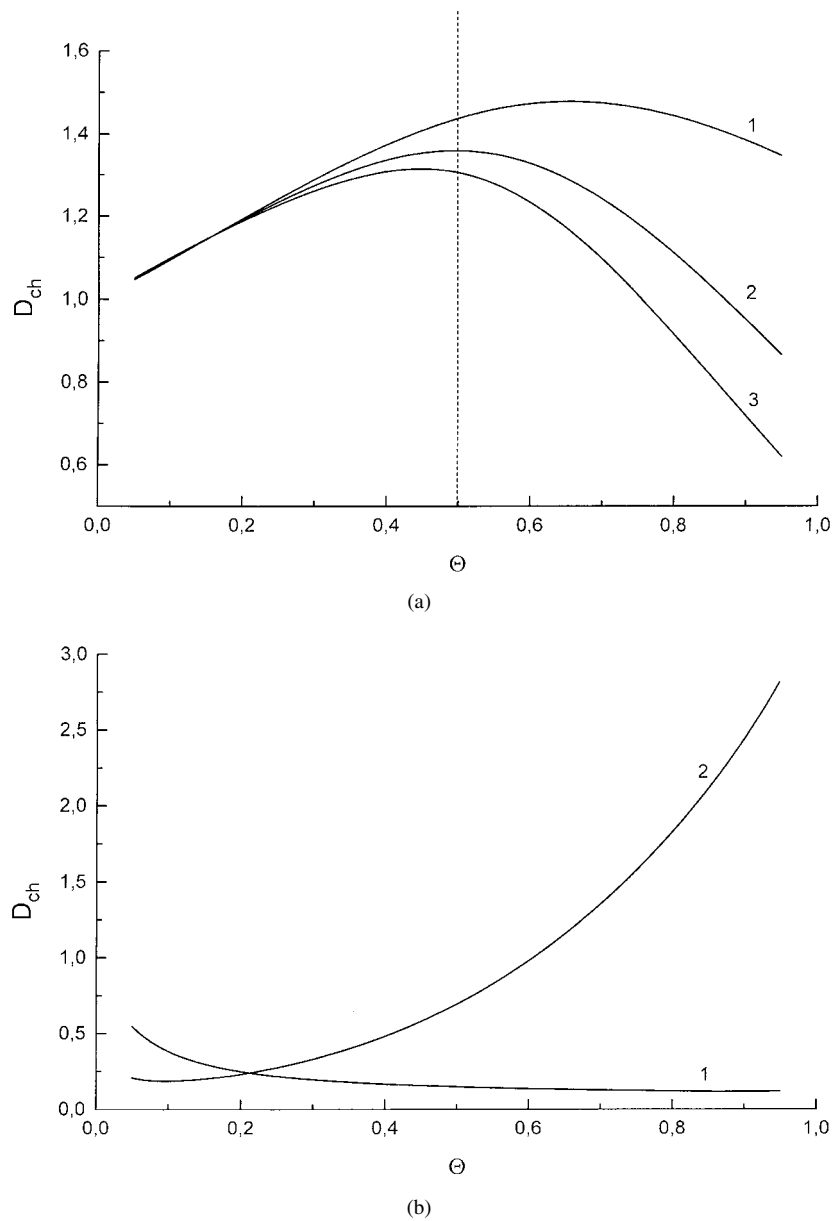


**Figure 3.** The dependence of the tracer diffusion coefficient  $D_T$  on the coverage  $\Theta$  for different values of the repulsive interaction energies changing the saddle-point energy:  $v_0 = 3$ ;  $v_2 = 1$  (curve 1);  $v_2 = 0.8$  (curve 2).  $\text{grad } \Theta = 0$ : the system is in equilibrium.



**Figure 4.** The dependence of the tracer diffusion coefficient  $D_T$  on the coverage  $\Theta$  and its gradient in the case of repulsive interaction.  $v_0 = 3$ ,  $v_2 = 0.8$ ;  $\text{grad } \Theta = 0$  (curve 1);  $\text{grad } \Theta = 0.05$  (curve 2).

The influence of the parameter  $v_1$  ( $v_2 = 1$ ) on the coverage dependence of both  $D_T$  and  $D_{ch}$  corresponds to the results published in [4–7]. For the tracer diffusion coefficient for repulsive interaction, the coefficient  $v_2$  substantially decreases the value of  $D_T$ , without changing the qualitative dependence of  $D_T$  on  $\Theta$ . For this kind of interaction,  $D_T(\Theta)$  shows a maximum above  $\Theta = 0.5$ . On the other hand, in the case of attractive interaction,  $D_T$  increases with  $v_2$ .



**Figure 5.** (a) The dependence of the chemical diffusion coefficient  $D_{ch}$  on the coverage  $\Theta$  for different values of the repulsive interaction changing the saddle-point energy:  $v_1 = 1.15$ ;  $v_2 = 0.7$  (curve 1);  $v_2 = 0.8$  (curve 2);  $v_2 = 0.95$  (curve 3). (b) The dependence of the chemical diffusion coefficient  $D_{ch}$  on the coverage  $\Theta$  for different values of the attractive interaction changing the saddle-point energy:  $v_1 = 0.5$ ;  $v_2 = 1$  (curve 1);  $v_2 = 3$  (curve 2).

This is to be expected, since in the first case the presence of atoms on sites adjacent to the final position of the jumping atom send the atom back to the initial position. In the case of attractive interaction, these atoms attract the jumping atom to a new position and thus they enhance the diffusion.

The influence of  $v_2$  on  $D_{ch}$  is qualitatively the same, but more complicated. In the case of attractive interaction, the increase of the value  $v_2$  results in an increase of  $D_{ch}$  for higher coverages. In the case of repulsive interaction,  $D_{ch}$ , as a function of  $\Theta$ , shows a maximum, whose position depends on  $v_2$ . It is interesting that in the case of relatively small values of  $v_1$  and  $v_2$ , this maximum lies at  $\Theta = 0.5$  if  $v_1 + v_2 = 2$ . For higher values of this sum, the maximum of  $D_{ch}$  lies above  $\Theta = 0.5$ , and for lower values, the maximum is below half-coverage. Such results become intelligible if we expand the exponentials in (5) and (6) up to linear terms only. In this case we have

$$v_1 + v_2 = 1 + \frac{\delta E'}{k_B T} + \dots + 1 - \frac{\Delta E}{k_B T} + \dots = 2 + \frac{1}{k_B T}(\delta E' - \Delta E).$$

This means that the sum of  $v_1$  and  $v_2$  is equal to 2 if the decrease of the energy barrier to diffusion due to the change of equilibrium energy of the atom is compensated by the increase of the saddle-point energy,  $\delta E' - \Delta E = 0$ ; thus  $\delta E = 2 \Delta E$ . The maximum of  $D_{ch}$  is given by the maximum of the thermodynamic factor at  $\Theta = 0.5$ . If  $\delta E' > \Delta E$ , the effect of the decrease of the energy barrier is dominant, and the maximum of  $D_{ch}$  is observed at  $\Theta > 0.5$  (as was expected; see e.g. [13]). In the opposite case ( $\delta E' < \Delta E$ ), the influence of interaction at the saddle point is dominant, and the diffusion is suppressed at higher coverage. This is a less realistic situation, but interesting from the theoretical point of view.

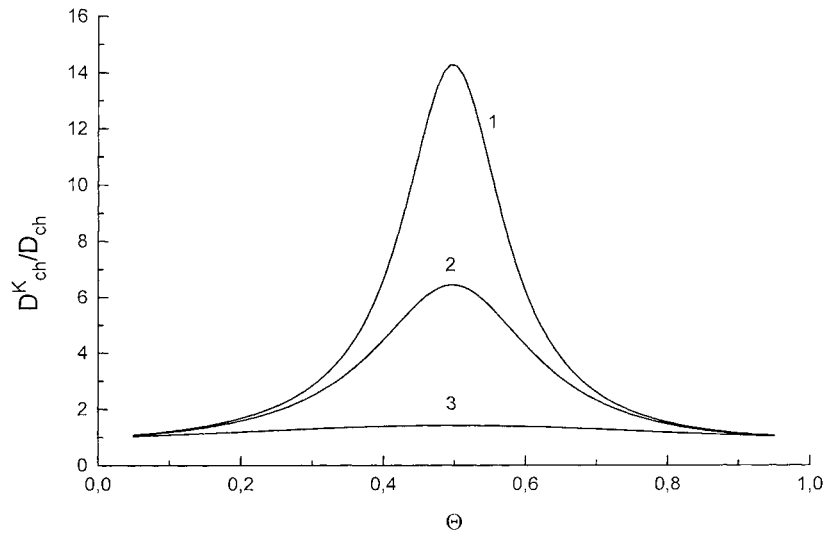
Now we return to the influence of  $\text{grad } \Theta$ . As was stated above, the tracer diffusion coefficient decreases proportionally to  $(\text{grad } \Theta)^2$ . This is demonstrated in figure 4. It is evident that the gradient of the coverage does not change the character of the coverage dependence of the tracer diffusion coefficient.

To estimate the influence of the deviation of the system from equilibrium on the dynamics of adatoms, we compare our results with the chemical diffusion coefficient calculated from the Green–Kubo formula within DMF theory (see appendix A) for the same model and approximations. For weak interaction or for higher temperatures we obtain practically identical results (see figure 6). The substantial deviations appear for strong interaction or low temperatures. This discrepancy is discussed in the following section.

## 8. Discussion and conclusions

This paper deals with the analysis of the influence of the gradient  $\text{grad } \Theta$  on the dynamic properties of adsorbed atoms on a surface. In the presence of the gradient  $\text{grad } \Theta$ , the jumps of atoms depend on its direction. This feature of the dynamics was studied as it relates to surface diffusion in [16], within the simple phenomenological model. It was shown that the diffusion coefficient contains a contribution from the anisotropy. We see the primary value of our model as lying in its paving the way for the determination of the diffusion coefficients within the microscopic model. It gives improved insight into the mechanisms of diffusion and the influence of interactions.

In our model we suppose  $\text{grad } \Theta$  to be constant and the temperature to be above the critical temperature of the phase transformation. An important feature is the specific influence of the interactions of adsorbed atoms on their dynamics. The presence of a coverage gradient breaks the symmetry of the adatoms jump and characterizes the deviation of the system from equilibrium. It has been demonstrated that the tracer diffusion coefficient decreases with  $(\text{grad } \Theta)^2$  independently of the kind of interaction experienced by the atoms. This can be interpreted as relating to the decrease of randomness in the dynamics of the adatoms with the increase of the drift of the centre of mass that is determined. This is an interesting result, which is in harmony with similar results from calculations of the long-range correlation of



**Figure 6.** The ratio of the chemical diffusion coefficient determined from the Green–Kubo formula,  $D_{ch}^K$ , and  $D_{ch}$  determined from equation (59) for different values of the interaction energy: curve 1:  $v_1 = 1.3$ ,  $v_2 = 0.8$ ; curve 2:  $v_1 = 1.1$ ,  $v_2 = 0.7$ ; curve 3:  $v_1 = 1.1$ ,  $v_2 = 0.9$ .

fluctuations in non-equilibrium systems; see e.g. [17, 18]. This correlation is found to be proportional to the square of the imposed gradient. Our results also impact on the analysis of experimental data. We must be careful if we are determining  $D_T$  from e.g. STM experiments performed on non-equilibrium systems to circumvent the time dependence of  $D_T$  and take the drift of the centre of mass into account.

Another situation arises in the case of the chemical diffusion coefficient  $D_{ch}$ . This coefficient is introduced in the linear non-equilibrium thermodynamics of the relaxation of the system to equilibrium, and it represents the coefficient of proportionality of the mass fluxes to the gradient of the chemical potential. So non-equilibrium conditions are automatically supposed. But our model enables us to determine  $D_{ch}$  within the microscopic model and to avoid the difficulties which we meet in the linear response theory. Determinations of the diffusion coefficient from the Green–Kubo formula usually neglect memory effects. This approximation is known as the dynamical mean-field (DMF) theory. Monte Carlo simulations of the diffusion [10] show considerable deviations in the diffusion coefficient from DMF theory for strongly interacting systems at temperatures at which ordered phases form. The memory effects can result in the increase of the effective energy barrier to diffusion near the phase boundary. Since our method is in some senses more general than the DMF one (the distribution of atoms is not homogeneous and detailed balance does not have to be observed), we compare the methods within a similar model. The comparison of our chemical diffusion coefficient with the one determined from the Green–Kubo formula in the DMF approximation exposes deviations in the case of strong interactions. But these deviations can be caused not only by the fact that the Green–Kubo formula is valid only near equilibrium, but also by the process of calculation of  $D_{ch}^K$  (see appendix A). As in [10], we observe a lower value of  $D_{ch}$  in comparison to the DMF approximation for lower temperatures near the coverage at which ordered phases form. Within the DMF theory, the chemical diffusion coefficient is calculated as a product of two terms. The first is the thermodynamic factor; the second represents the mean number of jumps per unit time. In the case of strong interactions, when an ordered



phase can form in the system, the thermodynamic factor reaches very high values while the mean number of jumps per unit time is very low. To obtain reasonable values of  $D_{ch}^K$ , we have to calculate both of these values very carefully. In the case of strong interactions, the DMF approximation ceases to be a good approximation for the description of collective diffusion in non-equilibrium conditions. The comparison of Monte Carlo simulations with DMF theory in [10] supports our results. Although both the Green–Kubo theory and our theory are linear, they are used differently in practice. It is very difficult to calculate memory effects (such as were introduced in [10]) using the Green–Kubo formula; our formalism does not need to accept such approximations or to introduce the dependence of the diffusion coefficient on the difference between the mean jump rate of atoms in the direction of  $\text{grad } \Theta$  and that in the opposite direction. This leads to the question of whether the differences between DMF and Monte Carlo simulations, explained in [10] as memory effects, are results of real memory effects or consequences of the presence of the coverage gradient in the system. This question will be addressed in future papers.

It has also been shown that the parameter  $v_2$  plays an important role and must be taken into account if we study interacting systems.  $v_2$  alone enhanced the breaking of the symmetry of the jump probability and substantially contributed to the influence of interactions. We must bear in mind that our theory is linear in  $\text{grad } \Theta$ , and we will need to deal with the influence of the second-order term and temperatures below the critical values for phase transitions.

As regards the maximum of  $D_{ch}(\Theta)$  for repulsive interactions, the analysis showed that the dynamics of adatoms characterized by  $v_2$  can influence the coverage dependence of  $D_{ch}$  more than the equilibrium properties given by the thermodynamic factor ( $S(0)^{-1}$ ), which depends only on the parameter  $v_0$ .

Concluding our analysis, we can state that our results contribute to the understanding of the complex dynamics of atoms on surfaces and to the interpretation of experiments which are often performed on systems far from equilibrium or during the formation of ordered phases (see e.g. [19]). Even though our method is linear, it is open to extension to non-linear approximations and for studying systems far from equilibrium.

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### Appendix

In this appendix we determine the chemical diffusion coefficient  $D_{ch}^K$  within the framework of the Green–Kubo formula [7, 20]:

$$D_{ch}^K = \pi \frac{1}{S(0)} \lim_{\omega \rightarrow 0} \omega^2 \left[ \lim_{q \rightarrow 0} \frac{1}{q^2} S(\vec{q}, \omega) \right] \quad (\text{A.1})$$

where  $S(\vec{q}, \omega)$  is the dynamic structure factor. The Green–Kubo formula determines the chemical diffusion coefficient in a system near the equilibrium state. We calculated the dynamic structure factor in the usual way. During the calculations, we neglect the memory matrix and use the quasi-chemical approximation, as we do throughout this paper. So we obtain the following results [7]:

$$S(\vec{q}, \omega) = \frac{1}{\pi} \frac{S(\vec{q})\Omega(\vec{q})}{\omega^2 + \Omega^2(\vec{q})} \quad (\text{A.2})$$

$$\Omega(\vec{q}) = \frac{\langle A(-\vec{q})LA(\vec{q}) \rangle}{NS(\vec{q})} \quad (\text{A.3})$$

where  $A(\vec{q})$  is the Fourier component of the fluctuations of the adatom density and  $L$  is the Lagrangian describing the dynamics of the adatoms. The microscopic model of the dynamics is described in section 2.  $N$  is the number of adsorbed atoms. Also,

$$A(\vec{q}) = \sum_{\vec{l}} (p_{\vec{l}} - \Theta) \exp(-i\vec{q} \cdot \vec{l}) \quad (\text{A.4})$$

$$Lp_{\vec{l}} = \sum_{\vec{a}}^{NN_{\vec{l}}} [p_{\vec{l}+\vec{a}}P_{\vec{l}+\vec{a} \rightarrow \vec{l}} - p_{\vec{l}}P_{\vec{l} \rightarrow \vec{l}+\vec{a}}]. \quad (\text{A.5})$$

$S(\vec{q})$  represents the static structure factor. Within our model, we obtain

$$S(\vec{q}) = (1 - \Theta) + \left( \frac{n_0}{\Theta} - \Theta \right) \sum_{\vec{a}}^{NN} \exp(-i\vec{q} \cdot \vec{a}) \quad (\text{A.6})$$

$$S(0) = (1 - \Theta) + 4 \left( \frac{n_0}{\Theta} - \Theta \right) \quad (\text{A.7})$$

$$\Omega(\vec{q}) = W_0 \bar{P}_0 \frac{4 - 2 \cos(qa \cos \beta) - 2 \cos(qa \sin \beta)}{\Theta(1 - \Theta) + 2(n_0 - \Theta^2)[\cos(qa \cos \beta) + \cos(qa \sin \beta)]} \quad (\text{A.8})$$

where  $\beta$  is the angle between the wave vector  $\vec{q}$  and the lattice vector  $\vec{a}$ . After some treatment, we obtain the final form of the chemical diffusion coefficient:

$$D_{ch}^K = W_0 a^2 \frac{\bar{P}_0}{(1 - \Theta) + 4(n_0/\Theta - \Theta)}. \quad (\text{A.9})$$

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