

# Non-interacting dimer kinetics in hypercubic lattices

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## Abstract

The exact formulation of the kinetic of dimer in hypercubic lattices is developed in the framework of the kinetic lattice gas model. The so-called local evolution rules are used to obtain the hierarchy of equation of motion for the correlation functions where processes like adsorption and desorption are included. The hierarchy of equations are truncated using a mean field  $(m, n)$  closures which allows the analytical treatment of the system. A general expression for non-interacting dimer isotherm and two particle correlation functions are obtained in hypercubic lattices.

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## 1. Introduction

The theory of the adsorption–desorption kinetics on surfaces is of fundamental interest in surface science, particularly, due to the relevance in those processes like gas separation or heterogeneous catalysis [1–3]. To understand time dependent phenomena at surfaces like adsorption and desorption, different methods can be used. One of these methods is the kinetic lattice gas model (KLG) applied to the adsorbed layer [4–6]. The approach is based on the non-equilibrium statistical mechanics involving time-dependent distribution functions and it was set up in close analogy to the time dependent Ising model for magnetic systems, which has been originally introduced by Glauber [7,8]. Both models are based on the master equation approach. In the KLG, adsorption, desorption, diffusion and reactions are introduced as Markovian processes throughout transition probabilities, which must satisfy the detailed balance principle. Different methods like matrix diagonalization, renormalization group or perturbation approach, were used to solve the master equation in

order to obtain the time evolution of the different moments related to the distribution of the adsorbed particles on the surface. In other formalisms one first derives directly a hierarchy of equations of motion for  $n$ -site correlation functions, which must be truncated using some closure scheme, like Kirkwood approximation, to obtain a set of finite coupled differential equations [9,10]. This method is effective if the adsorbate remains homogeneously distributed on the lattice, then with the coverage and some correlation functions one can describe the kinetics of the process. Alternatively, one can treat the evolution of the system analyzing the time behavior of one site of the lattice and obtain a set of evolution rules depending on the state of the site and its neighborhood, these are the so-called local evolution rules. This technique has been used to analyze irreversible growth models, particularly, to derive the Langevin equations in  $(1 + 1)$ -dimensional systems [11–14].

On the other hand, the kinetics involve questions of energy transfer, however, from the time behavior of the observable, one can obtain the equilibrium properties of the system which are associated to the minimum of the free energy. In fact, one can derive the adsorption isotherm of a given system calculating the time dependence of the observables and taking the limiting value for large times ( $t \rightarrow \infty$ ).

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Alternatively, one can obtain the coupled differential equations of motion for the observables in a given system and in the equilibrium they must be set equal to zero. This methodology has been used to obtain the kinetics of adsorption–desorption of particles in a one-dimensional lattice, particularly, the equilibrium properties, where an exact expression for the adsorption isotherms and two particle correlation functions for interacting particles are obtained [16]. Extension to two-dimension is treated in Ref. [17] where, from the kinetics equation, the authors have been reported the quasichemical approximation.

The non-interacting case, for simple site occupation (where there are one particle per adsorption site) can be straightforwardly derived from the rate equation for the coverage  $\theta$ , as

$$\frac{d\theta}{dt} = P_{\text{ads}}(1 - \theta) - P_{\text{des}}\theta, \quad (1)$$

where  $P_{\text{ads}}$  and  $P_{\text{des}}$  are the probability of adsorption and desorption respectively. Solving Eq. (1), one can obtain the very well known Langmuir isotherms.

Generalization of Eq. (1) to multisite occupation is not straightforward, however, most adsorbates, except noble gases, are polyatomic. Furthermore, surfaces generally present inhomogeneities due to irregular arrangement of surface and bulk atoms, the presence of various chemical species, etc., which can significantly affect the entropic contribution to the adsorbate's free energy. Typical examples are  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  adsorbed in carbon and zeolite molecular sieves [18–20] and oligomers in activated carbon [21,22]. On the other hand, extensive experimental studies have been performed confirming the multisite adsorption on different adsorbate–substrate system, such as ethane on graphite [23,24]. Recently, direct observation of dioxygen molecules physisorbed in the nanochannels of a microporous copper coordination polymer by the maximum entropy/Rietveld method, using in situ high-resolution synchrotron X-ray powder diffraction measurements, has been reported [25]. The obtained MEM electron density revealed that van der Waals dimers of physisorbed  $\text{O}_2$  locate in the middle of nanochannels and form a one-dimensional ladder structure aligned to the host channel structure. This new technique was also used to observe hydrogen molecules adsorbed in similar substrate [26]. These experimental findings represent clear evidence of one-dimensional adsorbed systems with multisite occupation (dimers).

The difficulties in the analysis of the multisite adsorption–desorption kinetics are mainly associated to three factors: (i) no statistical equivalence exists between particles and vacancies; (ii) the occupation of a given lattice site ensures that at least one of its nearest-neighbor sites is also occupied; (iii) an isolated vacancy cannot serve to determine whether that site can ever become occupied. For these reasons, it has been difficult to formulate, in an analytical way, the statistic (and kinetics) of occupation for correlated particles such as dimers, even without lateral interactions. Very recently, it has been demonstrated that  $k$ -mers

adsorption can be described in the framework of a fractional statistics, where particles behave like objects which occupied partially an adsorption site [27]. This formulation allows, the exact calculation of the adsorption isotherms with lateral interaction in one-dimensional space, as is shown in Refs. [27–29]. However, for dimension  $d \geq 2$ , a simple expression for the adsorption isotherms can not be derived up to now, even for the simplest non-interacting case (Langmuir isotherm).

In view of these difficulties, the purpose of this work is the calculation of a close expression for the Langmuir isotherm and two particle correlation functions for non-interacting dimers in hypercubic lattices. The analytical formulation is based on the Local Evolution Rules introduced in Refs. [30–32]. One starts with the definitions concerning the lattice gas model and the calculation of the correlation functions. Next one introduces the so-called local evolution rules. Then one can write explicitly the hierarchy of coupled differential equations and proceed to truncate via a mean-field closure approximation. Equating to zero the differential equations, the equilibrium solution can be obtained. A general expression for the Langmuir isotherms and two particle correlation functions in  $d$ -dimensional hypercubic lattices can be postulated. The analytical results are compared to those obtained by Monte Carlo simulation. The last section, contains the conclusions.

## 2. Lattice gas model with multisite occupation and the local evolution rules

### 2.1. Definitions

A  $d$ -dimensional hypercubic lattice with periodic boundary conditions and  $N_k$  sites in the  $k$ th-dimension will be considered. The total number of sites amounts to  $N = (N_k)^d$  if all  $N_k$  are equals. The diatomic molecule adsorbed on different surfaces is modeled as two interaction centers at a fixed separation, which equals the lattice constant  $a$  and will be set equal to one without loss of generality. In the model, one considered that the dimer is adsorbed when both parts of the molecule are attached to the surface. The components of the dimer are labeled depending on orientation in the lattice, say, the tail  $T$  and the head  $H$ . This nomenclature introduced by Ben-Avraham and Köhler (see Ref. [9]) is necessary to distinguish the dimer–dimer correlation function from the components of a given dimer. In the framework of the model, a given site located at the coordinates  $(i_1, i_2, \dots, i_d)$  of the lattice can be empty  $E$  or occupied by one component of the dimer, say,  $T$  (or  $H$ ). Let us introduce the occupation numbers  $H^{(r)}(i_1, i_2, \dots, i_d; t_n)$  which can take the values “1”, if site with coordinates  $(i_1, i_2, \dots, i_d)$  in the generic realization  $r$  at time  $t_n$  is occupied by the head of a dimer, and “0”, if it is not occupied by the head of a dimer. Equivalently, the occupation numbers  $T^{(r)}(i_1, i_2, \dots, i_d; t_n)$  describe the occupation state of the generic site with coordinates

ordinates  $(i_1, i_2, \dots, i_d)$  in the generic realization  $r$  at time  $t_n$ , by the tail of a dimer. The variable  $E^{(r)}(i_1, i_2, \dots, i_d; t_n)$  describing the “emptiness” of a site with coordinates  $(i_1, i_2, \dots, i_d)$  is defined as:

$$\begin{aligned} E^{(r)}(i_1, i_2, \dots, i_d; t_n) = & 1 - T^{(r)}(i_1, i_2, \dots, i_d; t_n)H^{(r)}(i_1 + 1, i_2, \dots, i_d; t_n) \\ & - T^{(r)}(i_1 - 1, i_2, \dots, i_d; t_n)H^{(r)}(i_1, i_2, \dots, i_d; t_n) \\ & - T^{(r)}(i_1, i_2, \dots, i_d; t_n)H^{(r)}(i_1, i_2 + 1, \dots, i_d; t_n) \\ & - T^{(r)}(i_1, i_2 - 1, \dots, i_d; t_n)H^{(r)}(i_1, i_2, \dots, i_d; t_n) \\ & \vdots \\ & - T^{(r)}(i_1, i_2, \dots, i_d; t_n)H^{(r)}(i_1, i_2, \dots, i_d + 1; t_n) \\ & - T^{(r)}(i_1, i_2, \dots, i_d - 1; t_n)H^{(r)}(i_1, i_2, \dots, i_d; t_n). \end{aligned} \quad (2)$$

The  $E^{(r)}(i_1, i_2, \dots, i_d; t_n) = 1$  means that the site  $(i_1, i_2, \dots, i_d)$  in the generic realization  $r$  at time  $t_n$  is empty. Note that the definition of a dimer implies that a site with coordinate  $(i_1, i_2, \dots, i_d; t_n)$  cannot be occupied by different occupation numbers. In other words, products like  $T^{(r)}(i_1, i_2, \dots, i_d; t_n)H^{(r)}(i_1, i_2, \dots, i_d; t_n)$ ,  $T^{(r)}(i_1, i_2, \dots, i_d; t_n)E^{(r)}(i_1, i_2, \dots, i_d; t_n)$ ,  $H^{(r)}(i_1, i_2, \dots, i_d; t_n)E^{(r)}(i_1, i_2, \dots, i_d; t_n)$ , etc., are forbidden and consequently must be set equal to zero.

Denoting with  $P(c'; t)$  the probability that the system is found in the configuration  $c' = \{T(i_1, i_2, \dots, i_d), \{H(i_1, i_2, \dots, i_d)\}\}$  at time  $t$ , let us define (following the usual definition of statistical mechanics) the average occupation numbers as

$$\begin{aligned} \overline{T(i_1, i_2, \dots, i_d)} &= \lim_{N_s \rightarrow \infty} \frac{1}{N_s} \sum_{r=1}^{N_s} T^{(r)}(i_1, i_2, \dots, i_d; t_n) \\ &= \sum_{c'} T(i_1, i_2, \dots, i_d; t)P(c'; t), \end{aligned} \quad (3)$$

$$\begin{aligned} \overline{H(i_1, i_2, \dots, i_d)} &= \lim_{N_s \rightarrow \infty} \frac{1}{N_s} \sum_{r=1}^{N_s} H^{(r)}(i_1, i_2, \dots, i_d; t_n) \\ &= \sum_{c'} H(i_1, i_2, \dots, i_d; t)P(c'; t) \end{aligned} \quad (4)$$

and the correlation in the  $k$ th coordinate as

$$\begin{aligned} &\overline{T(i_1, \dots, i_k, \dots, i_d)H(i_1, \dots, i_k + 1, \dots, i_d)} \\ &= \lim_{N_s \rightarrow \infty} \frac{1}{N_s} \sum_{r=1}^{N_s} T^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n) \\ &\quad \times H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n) \\ &= \sum_{c'} T(i_1, \dots, i_k, \dots, i_d; t) \\ &\quad \times H(i_1, \dots, i_k + 1, \dots, i_d; t)P(c'; t), \end{aligned} \quad (5)$$

where  $N_s$  is the number of realizations. In the second relation in Eqs. (2)–(5) it was defined  $t = t_n$  and the sum runs over all microscopic configurations  $c'$  with each  $T(i_1, \dots, i_k, \dots, i_d; t) = 0, 1$  and  $H(i_1, \dots, i_k, \dots, i_d; t) = 0, 1$ . Note that  $T(i_1, \dots, i_k, \dots, i_d; t)$ ,  $H(i_1, \dots, i_k, \dots, i_d; t)$  and  $H(i_1, \dots, i_k + 1, \dots, i_d; t)$  are the different values that  $T^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)$ ,  $H^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)$  and

$H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n)$  can take at time  $t$ . It is not difficult to see that the above three moments are identical. In the same way it is possible to calculate higher order moments. In order to save printing the following definition was also used in the left hand side in Eqs. (2)–(4):

$$\begin{aligned} X^{(r)}(i_1, i_2, \dots, i_d; t_n) &= X(i_1, i_2, \dots, i_d) \\ \text{for } X &= T, H \text{ or } E. \end{aligned} \quad (6)$$

Performing the average over the sites it is possible to obtain the coverage and the higher moments as

$$\langle T(i_1, i_2, \dots, i_d) \rangle = \frac{1}{N} \sum_{\{i\}} \overline{T(i_1, i_2, \dots, i_d)}, \quad (7)$$

$$\langle H(i_1, i_2, \dots, i_d) \rangle = \frac{1}{N} \sum_{\{i\}} \overline{H(i_1, i_2, \dots, i_d)} \quad (8)$$

and

$$\begin{aligned} &\langle T(i_1, \dots, i_k, \dots, i_d)H(i_1, \dots, i_k + 1, \dots, i_d) \rangle \\ &= \frac{1}{N} \sum_{\{i\}} \overline{T(i_1, \dots, i_k, \dots, i_d)H(i_1, \dots, i_k + 1, \dots, i_d)}, \end{aligned} \quad (9)$$

where  $\{i\}$  are the set of sites of the lattice.

## 2.2. The local evolution rules

The usual way to describe the kinetic lattice gas model is the master equation approach (MEA). However, in case of multisite occupation (even in the simplest one) the MEA is rather cumbersome. Alternatively, the local evolution rules (LER) has been used successfully in the description of the one-dimensional dimer kinetics [30], as well as in the analysis of the irreversible growth models, particularly to derive the Langevin equations in (1 + 1)-dimensional systems [14,15]. The method is rather simple and consist in monitoring the time evolution of a chosen site, through the following procedure:

- (i) In order to specify the coordinate of the head of the dimer in the generic realization  $r$  at time  $t_n$ , a set of  $d$  dummy indexes  $(j_1, j_2, \dots, j_d)$  is chosen at random among  $(N_1, N_2, \dots, N_d)$  integer numbers respectively. To locate the tail of the dimer, one choose at random one of the  $d$  directions, say  $l$ . Then the chosen index  $j_l$  must be increased in one ( $j_l + 1$ ).
- (ii) For dimers, one needs to specify the evolution of two sites simultaneously, say site  $(i_1, \dots, i_l, \dots, i_d)$  and  $(i_1, \dots, i_l + 1, \dots, i_d)$ , corresponding to the head and tail of the dimer adsorbed or desorbed on the lattice at time  $t_{n+1} = t_n + \tau_0$  (here  $\tau_0$  is the elemental time step between two successive events at any site of the lattice).

Then, one needs two evolution equations, one for the tail and another for the head of the dimer,

$$\begin{aligned}
T^{(r)}(i_1, \dots, i_k, \dots, i_d; t_{n+1}) \\
&= T^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n) \\
&\quad + G^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)|_{\text{ads}} \\
&\quad + G^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)|_{\text{des}}
\end{aligned} \tag{10}$$

and

$$\begin{aligned}
H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_{n+1}) \\
&= H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n) \\
&\quad + G^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n)|_{\text{ads}} \\
&\quad + G^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n)|_{\text{des}},
\end{aligned} \tag{11}$$

where  $G^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)|_{\text{ads}}$  and  $G^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)|_{\text{des}}$  are the local evolution rules that represent the adsorption and desorption events for the site  $(i_1, \dots, i_k, \dots, i_d)$  (a similar set of equation is given for the site  $(i_1, \dots, i_k + 1, \dots, i_d)$ ). Note that, Eqs. (10) and (11) give the state  $T^{(r)}(i_1, \dots, i_k, \dots, i_d; t_{n+1})$  and  $H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_{n+1})$  at time  $t_{n+1}$  as a function of the state  $T^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)$ ,  $H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n)$  and the corresponding neighboring sites at the previous time  $t_n$ .

Explicitly, one can write,

$$\begin{aligned}
G^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)|_{\text{ads}} &= \Theta_{\text{ads}}^{(r)} \delta(k, l) \prod_{p=1}^d \delta(i_p, j_p) \\
&\quad \times E^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n) \\
&\quad \times E^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n)
\end{aligned} \tag{12}$$

and

$$\begin{aligned}
G^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n)|_{\text{des}} &= \Theta_{\text{des}}^{(r)} \delta(k, l) \prod_{p=1}^d \delta(i_p, j_p) \\
&\quad \times T^{(r)}(i_1, \dots, i_k, \dots, i_d; t_n) \\
&\quad \times H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t_n).
\end{aligned} \tag{13}$$

In the above equations  $\Theta_{\text{ads}}^{(r)}$  and  $\Theta_{\text{des}}^{(r)}$  are defined as,

$$\Theta_{\text{ads}}^{(r)} = \Theta(P_{\text{ads}} - \xi_n^{(r)}) \tag{14}$$

and

$$\Theta_{\text{des}}^{(r)} = \Theta(P_{\text{des}} - \xi_n^{(r)}), \tag{15}$$

where  $\delta(k, l)$ ,  $\delta(i_p, j_p)$  are Kronecker deltas and  $\Theta^{(r)}(z)$  is the well known step function defined as 1 for  $z \geq 1$  and 0 otherwise. In the argument of the Kronecker deltas  $l$  and  $j_p$  are obtained in the generic realization  $r$  at time  $t_n$ . The randomly chosen number  $\xi_n^{(r)}$  is uniformly distributed in  $[0, 1]$ . Following the definitions of Ref. [29]  $P_{\text{ads}}$  and  $P_{\text{des}}$  (the probability of adsorption and desorption at vanishing lateral interaction ( $V=0$ )) are given by

$$P_{\text{ads}} = dN\tau_0 W_0 \tag{16}$$

and

$$P_{\text{des}} = dN\tau_0 W_0 C_0, \tag{17}$$

where

$$C_0 = \exp(\beta(V_s - \mu)). \tag{18}$$

The constant  $V_s$  is the adsorption energy site and  $\mu$  is the chemical potential. On the other hand

$$W_0 = S_0 a_s \frac{P\beta^{1/2}}{(2\pi m)^{1/2}}, \tag{19}$$

where  $S_0$  is the sticking coefficient at vanishing coverage,  $a_s$  is the adsorption area for a dimer of mass  $m$ ,  $P$  is the pressure and  $\beta$  is the inverse of the temperature parameter. In the rest of the paper one considers  $V_s = 0$  without loss of generality.

To obtain the equations of motion for the coverage and correlations from the local evolution rules one can use the following procedure. For example, let us consider the evolution equation corresponding to the one particle correlation. Taking the average on both sides of Eq. (10), using the approximation

$$\begin{aligned}
\langle T(i_1, i_2, \dots, i_d; t_{n+1}) \rangle - \langle T(i_1, i_2, \dots, i_d; t_n) \rangle \\
\approx \tau_0 \frac{d\langle T(i_1, i_2, \dots, i_d; t_n) \rangle}{dt_n}
\end{aligned} \tag{20}$$

and letting  $t_n = t$  in Eq. (19) the differential equation for  $\langle T(i_1, i_2, \dots, i_d; t) \rangle$  becomes,

$$\begin{aligned}
\tau_0 \frac{d\langle T(i_1, i_2, \dots, i_d; t) \rangle}{dt} &= \left\langle \Theta_{\text{ads}}^{(r)} \delta(k, l) \prod_{p=1}^d \delta(i_p, j_p) \right. \\
&\quad \times E^{(r)}(i_1, \dots, i_k, \dots, i_d; t) \\
&\quad \times E^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t) \left. \right\rangle \\
&\quad - \left\langle \Theta_{\text{des}}^{(r)} \delta(k, l) \prod_{p=1}^d \delta(i_p, j_p) \right. \\
&\quad \times T^{(r)}(i_1, \dots, i_k, \dots, i_d; t) \\
&\quad \times H^{(r)}(i_1, \dots, i_k + 1, \dots, i_d; t) \left. \right\rangle.
\end{aligned} \tag{21}$$

Similarly, for  $\langle H(i_1, i_2, \dots, i_d; t) \rangle$ ,  $\langle T(i_1, \dots, i_k, \dots, i_d; t) \rangle$ ,  $\langle H(i_1, \dots, i_k + 1, \dots, i_d; t) \rangle$ , etc., after performing the products of the dynamic variables in the required sequence and taken the average on both sides, the equations of motion are constructed. Details of such procedure can be found in Ref. [30]. Next, one can obtain the set of evolution equations for one, two and three-dimensional lattices for non-interacting dimer adsorption–desorption kinetics.

### 3. Dimer isotherms and two particle correlation function in one-, two- and three-dimensional lattices

In this section, we will derive the first (coverage) and second moments (two particle correlation function) for dimers in hypercubic lattices with  $d = 1, 2, 3$ . This moments are enough to obtain the Langmuir isotherms (non-interacting dimers) in all cases.

### 3.1. One-dimensional lattice

The evolution equation for the first moment is given by

$$\frac{d\langle T(i_1)H(i_1+1) \rangle}{dt} = W_0\langle E(i_1)E(i_1+1) \rangle - W_0C_0\langle T(i_1)H(i_1+1) \rangle. \quad (22)$$

The corresponding to the second moment or two-particle correlation function can be written as

$$\begin{aligned} \frac{d\langle T(i_1)H(i_1+1)T(i_1+2)H(i_1+3) \rangle}{dt} \\ = 2W_0\langle T(i_1)H(i_1+1)E(i_1+2)E(i_1+3) \rangle \\ - 2W_0C_0\langle T(i_1)H(i_1+1)T(i_1+2)H(i_1+3) \rangle. \end{aligned} \quad (23)$$

In order to simplify the notation in the last two equations  $t$  was eliminated in the arguments of the dynamical variables  $T$ ,  $H$  and  $E$ . To solve the above set of equations it is necessary to use the following (2,1) mean field closure:

$$\begin{aligned} \langle T(i_1)H(i_1+1)E(i_1+2)E(i_1+3) \rangle \\ = \frac{\langle T(i_1)H(i_1+1)E(i_1+2) \rangle \langle E(i_1+2)E(i_1+3) \rangle}{\langle E(i_1+2) \rangle}, \end{aligned} \quad (24)$$

where

$$\begin{aligned} \langle E(i_1)E(i_1+1) \rangle = 1 - 3\langle T(i_1)H(i_1+1) \rangle \\ + \langle T(i_1)H(i_1+1)T(i_1+2)H(i_1+3) \rangle. \end{aligned} \quad (25)$$

To obtain the equilibrium solution of the adsorption–desorption kinetics, it is necessary to equate the lefthand side of Eqs. (22) and (23) to zero. After that, the solution for the Langmuir isotherm and the two particle correlation function for dimers in 1D are obtained as,

$$\theta = \frac{1 + 4e^{\beta\mu} - \sqrt{1 + 4e^{\beta\mu}}}{1 + 4e^{\beta\mu}} \quad (26)$$

and

$$X_{11} = \frac{(\theta/2)^2}{1 - (\theta/2)}, \quad (27)$$

where  $X_{11} = \langle T(i_1)H(i_1+1)T(i_1+2)H(i_1+3) \rangle$  and  $\theta = 2\langle T(i_1)H(i_1+1) \rangle$ .

As is very well known, in one-dimensional space, the knowledge of the coverage and correlation between two consecutive site (pairs correlation function) is enough to obtain the complete statistical description of the system [33]. In fact, it is demonstrated that quasicheical approximation with  $z = 2$  (where  $z$  is the coordination number) is the exact solution for the one-dimensional lattice gas with nearest-neighbor interaction.

The expression for coverage and pairs correlation function for interacting dimers in one-dimension lattice have been reported in Ref. [30], where (2,1) mean field closure scheme have been used to obtain a system of differential equations which is exactly solved. These expressions coin-

cide with those obtained by statistical mechanics [28]. Eqs. (26) and (27) are particular cases of such expressions.

Next, the two-dimensional case will be considered.

### 3.2. Two-dimensional lattice

Following the same procedure as in the one-dimensional case one can obtained the evolution equation for the first two correlation functions. Due to the cumbersome notation let us define the correlation functions in the simplified version as:

$$\begin{aligned} X_0 &= \langle E(i_1, i_2) \rangle, \\ X_1 &= \langle T(i_1, i_2)H(i_1+1, i_2) \rangle, \\ X_{00} &= \langle E(i_1, i_2)E(i_1+1, i_2) \rangle, \\ X_{10} &= \langle T(i_1, i_2)H(i_1+1, i_2)E(i_1, i_2-1)E(i_1+1, i_2-1) \rangle, \\ X_{11} &= \langle T(i_1, i_2)H(i_1+1, i_2)T(i_1, i_2-1)H(i_1+1, i_2-1) \rangle, \\ X_{20} &= \langle T(i_1, i_2)H(i_1+1, i_2)E(i_1+1, i_2-1)E(i_1+2, i_2-1) \rangle, \\ X_{21} &= \langle T(i_1, i_2)H(i_1+1, i_2)T(i_1+1, i_2-1)H(i_1+2, i_2-1) \rangle, \\ X_{30} &= \langle T(i_1, i_2)H(i_1+1, i_2)E(i_1+2, i_2)E(i_1+3, i_2) \rangle, \\ X_{31} &= \langle T(i_1, i_2)H(i_1+1, i_2)T(i_1+2, i_2)H(i_1+3, i_2) \rangle, \\ X_{40} &= \langle T(i_1, i_2)H(i_1+1, i_2)E(i_1+2, i_2)E(i_1+2, i_2+1) \\ &\quad + E(i_1, i_2)E(i_1+1, i_2)T(i_1+2, i_2)H(i_1+2, i_2+1) \rangle, \\ X_{41} &= \langle T(i_1, i_2)H(i_1+1, i_2)T(i_1+2, i_2)H(i_1+2, i_2+1) \rangle, \end{aligned} \quad (28)$$

where the following relations can be established,

$$X_0 = \langle E(i_1, i_2) \rangle = 1 - 4X_1. \quad (29)$$

and

$$X_{00} = 1 - 7X_1 + 2X_{11} + 2X_{21} + X_{31} + 4X_{41}. \quad (30)$$

With these definitions one can write the evolution equation for the first moment as

$$\frac{dX_1}{dt} = W_0X_{00} - W_0C_0X_1. \quad (31)$$

Due that there are four different two particle correlation functions, see Fig. 1(a), the corresponding set of differential equations are:

$$\begin{aligned} \frac{dX_{11}}{dt} &= 2W_0X_{10} - 2W_0C_0X_{11}, \\ \frac{dX_{21}}{dt} &= 2W_0X_{20} - 2W_0C_0X_{21}, \\ \frac{dX_{31}}{dt} &= 2W_0X_{30} - 2W_0C_0X_{31}, \\ \frac{dX_{41}}{dt} &= W_0X_{40} - 2W_0C_0X_{41}. \end{aligned} \quad (32)$$

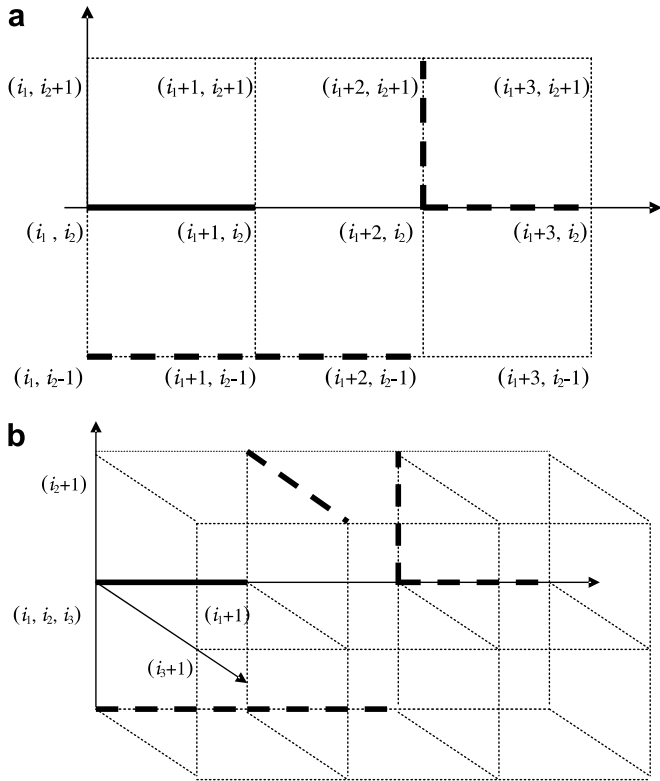


Fig. 1. Schematic representation of a generic pair of sites (filled line), surrounding by the different pair of sites which generates all the possible two particle correlations (dashed lines): (a) two-dimensional square lattice and (b) three-dimensional cubic lattice.

Using the following (2,1) mean field closures:

$$\begin{aligned}
 X_{10} &= \frac{(X_1 - X_{11} - X_{21} - X_{41})X_{00}}{X_0}, \\
 X_{20} &= X_{10}, \\
 X_{30} &= \frac{(X_1 - X_{31} - 2X_{41})X_{00}}{X_0}, \\
 X_{40} &= \frac{(X_1 - X_{11} - X_{21} - X_{41})X_{00}}{X_0} \\
 &\quad + \frac{(X_1 - X_{31} - 2X_{41})X_{00}}{X_0}
 \end{aligned}
 \tag{33}$$

one can obtain the Langmuir isotherm equating the left-hand side of Eqs. (31) and (32) to zero and solving the resulting algebraic system. The final expression for the coverage is

$$\theta = 2 \frac{1 + 8e^{\beta\mu} - \sqrt{1 + 12e^{\beta\mu}}}{1 + 16e^{\beta\mu}},
 \tag{34}$$

where  $\theta = 4X_1$ . Similarly for the two particle correlation functions one get

$$X_{Z1} = \frac{(\theta/4)^2}{1 - (\theta/4)} \quad \text{for } Z = 1, \dots, 4.
 \tag{35}$$

Note that this solution is not exact as in the one-dimensional lattice, however it provide the first approximation level for the problem.

### 3.3. Three-dimensional lattice

Following the same procedure as in the previous cases, the evolution equation for the first and second correlation functions can be obtained without a considerably effort. In this case just an additional equation is necessary. As above let us define the following correlations

$$\begin{aligned}
 X_0 &= \langle E(i_1, i_2, i_3) \rangle, \\
 X_1 &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \rangle, \\
 X_{00} &= \langle E(i_1, i_2, i_3)E(i_1 + 1, i_2, i_3) \rangle, \\
 X_{10} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times E(i_1, i_2 - 1, i_3)E(i_1 + 1, i_2 - 1, i_3) \rangle, \\
 X_{11} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times T(i_1, i_2 - 1, i_3)H(i_1 + 1, i_2 - 1, i_3) \rangle, \\
 X_{20} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times E(i_1 + 1, i_2 - 1, i_3)E(i_1 + 2, i_2 - 1, i_3) \rangle, \\
 X_{21} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times T(i_1 + 1, i_2 - 1, i_3)H(i_1 + 2, i_2 - 1, i_3) \rangle, \\
 X_{30} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times E(i_1 + 2, i_2, i_3)E(i_1 + 3, i_2, i_3) \rangle, \\
 X_{31} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times T(i_1 + 2, i_2, i_3)H(i_1 + 3, i_2, i_3) \rangle, \\
 X_{40} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times E(i_1 + 2, i_2, i_3)E(i_1 + 2, i_2 + 1, i_3) \\
 &\quad + E(i_1, i_2, i_3)E(i_1 + 1, i_2, i_3)T(i_1 + 2, i_2, i_3) \\
 &\quad \times H(i_1 + 2, i_2 + 1, i_3) \rangle, \\
 X_{41} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times T(i_1 + 2, i_2, i_3)H(i_1 + 2, i_2 + 1, i_3) \rangle, \\
 X_{50} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times E(i_1 + 1, i_2 + 1, i_3)E(i_1 + 1, i_2 + 1, i_3 + 1) \rangle, \\
 X_{51} &= \langle T(i_1, i_2, i_3)H(i_1 + 1, i_2, i_3) \\
 &\quad \times T(i_1 + 1, i_2 + 1, i_3)H(i_1 + 1, i_2 + 1, i_3 + 1) \rangle,
 \end{aligned}
 \tag{36}$$

where the following relations are introduced:

$$X_0 = 1 - 6X_1
 \tag{37}$$

and

$$X_{00} = 1 - 11X_1 + 3X_{11} + 3X_{21} + X_{31} + 8X_{41} + 8X_{51}.
 \tag{38}$$

With these definitions one can write the evolution equation for the one particle correlation functions as

$$\frac{dX_1}{dt} = W_0 X_{00} - W_0 C_0 X_1. \tag{39}$$

There are five different two particle correlation functions (see Fig. 1(b)), then the corresponding differential equations are:

$$\begin{aligned} \frac{dX_{11}}{dt} &= 2W_0 X_{10} - 2W_0 C_0 X_{11}, \\ \frac{dX_{21}}{dt} &= 2W_0 X_{20} - 2W_0 C_0 X_{21}, \\ \frac{dX_{31}}{dt} &= 2W_0 X_{30} - 2W_0 C_0 X_{31}, \\ \frac{dX_{41}}{dt} &= W_0 X_{40} - 2W_0 C_0 X_{41}, \\ \frac{dX_{51}}{dt} &= 2W_0 X_{50} - 2W_0 C_0 X_{51}. \end{aligned} \tag{40}$$

Using the following (2,1) mean field closures:

$$\begin{aligned} X_{10} &= \frac{(X_1 - X_{11} - X_{21} - X_{41} - 2X_{51})X_{00}}{X_0}, \\ X_{20} &= X_{10}, \\ X_{30} &= \frac{(X_1 - X_{31} - 4X_{41})X_{00}}{X_0}, \\ X_{40} &= \frac{(X_1 - X_{11} - X_{21} - X_{41} - 2X_{51})X_{00}}{X_0} \\ &\quad + \frac{(X_1 - X_{31} - 4X_{41})X_{00}}{X_0}, \\ X_{50} &= X_{10} \end{aligned} \tag{41}$$

one can proceed as in the other cases. After equating to zero the lefthand side of Eqs. (39) and (40) and solving the system, the expression for Langmuir isotherm can be written as

$$\theta = 3 \frac{1 + 12e^{\beta\mu} - \sqrt{1 + 20e^{\beta\mu}}}{1 + 36e^{\beta\mu}}, \tag{42}$$

where  $\theta = 6X_1$ . Equivalently for the two particles correlation functions,

$$X_{Z1} = \frac{(\theta/6)^2}{1 - (\theta/6)} \quad \text{for } Z = 1, \dots, 5. \tag{43}$$

In such way, we can write the general expression for the coverage as a function of the chemical potential and the two particle correlation functions as

$$\theta = d \frac{1 + 4de^{\beta\mu} - \sqrt{1 + 4(2d - 1)e^{\beta\mu}}}{1 + 4d^2e^{\beta\mu}} \tag{44}$$

and

$$X_{Z1} = \frac{(\theta/2d)^2}{1 - (\theta/2d)} \quad \forall Z. \tag{45}$$

with  $d = 1, 2, 3$ .

In Fig. 2 one can observe a comparison between the previous results and Monte Carlo simulations. As is shown in the figure, the difference between the numerical experi-

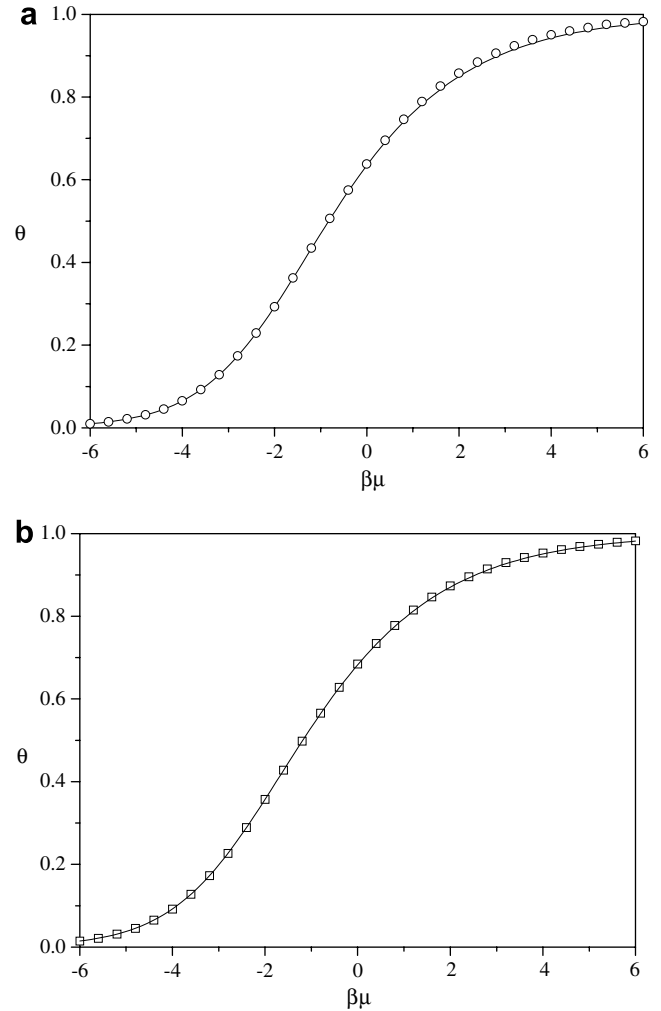


Fig. 2. Comparison between the theoretical results given in Eq. (44) (line) and Monte Carlo simulation (symbol): (a) two-dimensional square lattice and (b) three-dimensional cubic lattice.

ments and the analytical model is rather small, particularly in three-dimension.

#### 4. Conclusions

In this paper, closed expressions for the non-interacting dimer isotherms and the two particle correlation functions in hypercubic lattices (with  $d = 1, 2, 3$ ) are obtained. The local evolution rules are implemented in order to obtain the evolution equations for the coverage and higher correlations. After a truncation and using a (2,1) mean-field closure approximations, the system can be exactly solved in one-, two- and three-dimensional hypercubic lattices and a general expression for the Langmuir adsorption isotherms and the two particle correlation functions for dimers are postulated. The one-dimensional results coincide with the exact solution obtained by statistical mechanical methods (combinatorial analysis, transfer matrix calculations, etc.). In higher-dimension the (2,1) mean field closure provide a close expression for the adsorption isotherms and

two particles correlation function. Beside that the analytical isotherms are in good agreement with Monte Carlo simulations. Although the method seems to be rather complicated concerning the notation, presents various advantages as compared to the Master equation formulation, where an explicit expression for the Hamiltonian is necessary. On the contrary, in the local evolution approach, it is only needed the interactions between particles. In the last years new experimental techniques have been developed to analyze the behavior of simple dimer molecules adsorbed in quasi one-dimensional structures [25,26]. The analytical expression for the adsorption isotherms with multisite adsorption, with and without lateral interaction, can help to understand the behavior of the adsorbed phase, not only in one but in higher-dimensions.

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