

Non-interacting dimer kinetics in hypercubic lattices

G. Costanza, S. Manzi ^{*}, V.D. Pereyra

Departamento de Física, Laboratorio de Ciencias de Superficie y Medios Porosos and Centro Latinoamericano de Estudios Ilya Prigogine, Universidad Nacional de San Luis, CONICET, Chacabuco 917, 5700 San Luis, Argentina

Received 12 May 2006; accepted for publication 1 July 2006
Available online 21 July 2006

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.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Kinetic lattice gas model; Dimer adsorption; Exact results

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 ($t \rightarrow \infty$).

^{*} Corresponding author. Tel./fax: +54 2652 4361 51.
E-mail address: smanzi@unsl.edu.ar (S. Manzi).

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 θ , as

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

where P_{ads} and P_{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 O_2 , N_2 , CO , 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 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 finding 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 associate 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 introduce 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 loose 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 distinguished 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 coor-

Download English Version:

<https://daneshyari.com/en/article/5426600>

Download Persian Version:

<https://daneshyari.com/article/5426600>

[Daneshyari.com](https://daneshyari.com)