

# Study Of Inertia And Stoichiometric Effect On Surface Diffusion By Monte Carlo Method

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In this work, we investigate the inertia and stoichiometric effect on surface diffusion of adsorbates particles. The study is done by means of Monte-Carlo simulation in the framework of the lattice gas model. Only first neighboring repulsive pair interaction is considered. We concentrate on the behaviour of the tracer diffusion coefficient  $D_t(\theta)$ , as a function of surface coverage  $\theta$  in the case where two type of particles A and B are adsorbed. A and B are only different by their mass. The results shows that  $\theta$ , ordering phenomenon is not strongly influenced. However the diffusion process is decreased by inclusion of heavy particles.

## I. INTRODUCTION

Surface diffusion plays a fundamental role in various physically and technological important processes, such as adsoption, desorption, melting, roughening, crystal and film growth, catalysis and corrosion [1-10]. More effort has been directed toward understanding the physical laws of nature that govern the diffusion of adatoms on solid surfaces. Due to all these activities, it is fair to say that many of the prominent features of surface diffusion under ideal conditions in equilibrium are now well understood.

The situation becomes much more complicated, however, when the system is no longer ideal but containing particles with different mass and concentrations. In this work we investigate inertia and stoichiometric effect on diffusion of adsorbate particles. We consider a particularly occupied bidimensional lattice with two type of particles A and B. We carry out Monte Carlo simulations for a lattice-gas model with repulsive interactions between nearest neighbor particles. We expect the behaviour of the tracer diffusion coefficient,  $D_t$ , versus the ratio mass and concentrations.

In the section 2 we present the lattice gas model, in section 3 we define the tracer and diffusion coefficients. In section. 4 we will describe the simulation and discuss the results obtained.

## II. THE MODEL

We consider a lattice a gas system of N particles on square lattice with nearest neighbor interaction. Thermodynamical state of the adparticle system at

The transition frequency  $\omega(\{n\}, \{n'\})$  from configuration  $\{n\}$  to  $\{n'\}$  is supposed to satisfy the detailed balance condition that insures the equivalence of transitions between the system equilibrium states:

instant time, is completely described by configuration  $\{n\}$ :

$$\{n\} = \{n_1, n_2, \dots, n_i, \dots, n_{N-1}, n_N\}$$

where  $n_i$  is an occupation number

The Hamiltonien for this model is given by:

$$H = J/2 \sum_{\langle ij \rangle} n_i n_j - \mu_0 \sum_i n_i \quad (1)$$

where the interaction constant J is positive for repulsive and negative for attractive interactions. for each site "i", we define an occupation number  $n_i$  which is equal to unity if site "i" is occupied by one particle and zero otherwise. Double occupation of a same site is forbidden.

The notation  $\langle i, j \rangle$  implies the summation in **eq(1)** over each pair of particles in nearest neighboring sites.

The diffusion process of the particles is assured by the change of the occupation numbers of the lattice sites. In the lattice gas formulation this can be seen as the change of the lattice configuration. The dynamics of the lattice is governed by the phenomenological master equation [11,12] which describes the evolution in time of the probability  $P(\{n\}, t)$  of the configuration  $\{n\}$ .

$$\frac{\partial P(\{n\}, t)}{\partial t} = \sum_{\{n'\}} \omega(\{n'\}, \{n\}) P(\{n'\}, t) - \omega(\{n\}, \{n'\}) P(\{n\}, t). \quad (2)$$

$$\omega(\{n\}, \{n'\}) P_{eq}(\{n\}) = \omega(\{n'\}, \{n\}) P_{eq}(\{n'\}) \quad (3)$$

## III. The tracer and jump diffusion coefficients:

For the quantitative description of diffusion we briefly recall two concepts, which describe the adparticle migration. Conceptually the simplest diffusion

coefficient,  $D_t$  which addresses the random walk of individual tagged particles on two – :[dimensionnal lattice.  $D_t$  is defined as[13

$$D_t = \lim_{t \rightarrow \infty} \frac{1}{2 N d t} \sum_i^N \langle |\Delta r_i(t)|^2 \rangle \quad (4)$$

(Where  $d$  is the system dimension ( $d=2$ ))  
 $\hat{r}_i(t) \equiv r_i(t + \tilde{t}_m) - r_i(\tilde{t}_m)$  : denotes the shift of the  $i$ th adparticle during time  $t$ . The brackets  $\langle \dots \rangle$  denote ensemble averaging.

The jump diffusion coefficient,  $D_j$ , is a many particle diffusion coefficient describing the asymptotical behaviour of the mean square displacement of the center of mass of the adparticles.  
 $D_j$  is define as [13,14]

$$D_j = \lim_{t \rightarrow \infty} \frac{1}{4 N t} \left\langle \left( \sum_i^N \hat{r}_i(t) \right)^2 \right\rangle \quad (5)$$

The corresponding relation between the two coefficients is given by :

$$D_j = D_t \left( 1 + \frac{\sum_{i \neq j} \langle \hat{r}_i(t) \hat{r}_j(t) \rangle}{\sum_i \langle [\hat{r}_i(t)]^2 \rangle} \right) \equiv D_t f \quad (6)$$

where  $f$  is the so- called correlation factor

#### IV. Simulation and Results

The Monte Carlo technique is probably one of the most reliable methods which can be used to study adparticle diffusion on different lattices and for various sets of the interaction [15-17]. Our 2D system consists on a square lattice with  $L \times L$  sites and periodic boundary conditions. The probability of obtaining a given configuration will be given by the corresponding Boltzmann factor:

$$P = C \exp(-\hat{J} / 2 \sum_{\langle ij \rangle} n_i n_j) \quad (7)$$

With  $C$  is a normalisation factor. We are interested to investigate the influence of inertia on surface diffusion. Initial lattice gas configurations concern surface coverage  $\theta$  with different proportion of A and B particles and for many ratio of their mass.

We are carried out MC Metropolis algorithm [18]:

1. first, we select a tagged particle of the lattice .
2. then an adjacent final site "j" is randomly chosen
3. if the destination is vacant, a jump can occur with the probability  $P_{i \rightarrow j}$ , otherwise no jump occurs.

$$P_{i \rightarrow j} = C_{i \rightarrow j} \exp(-\hat{J} \hat{H}) \quad (8)$$

$C_a = 1$  if the particle is of mass  $M_a$

$C_a = \lambda$  if the particle is of mass  $M_b$

$\lambda$  defines the mass ratio of particles A and B.

$\hat{H}$ : denotes the activation energy for such jump, it is calculated as the difference between final and initial energy:  $\hat{H} = H_f - H_i$

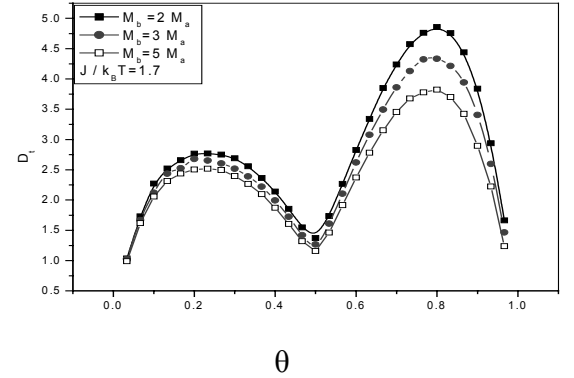


Fig.1. The tracer diffusion coefficient versus concentration for  $N_a = 2N_b$

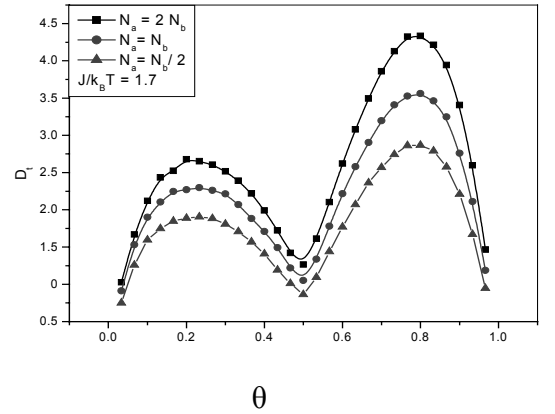


Fig. 2. the tracer diffusion versus concentration at rate of inertia  $M_b / M_a = 3$

Before starting the diffusion runs the equilibration of the system is performed for  $10^4$  MCS. The lattice size is  $L=30$ .

In the MC method the tracer diffusion and the jump diffusion coefficient respectively  $D_t$  and  $D_j$  can be easily determined from measurements of the mean square displacements of particles according to eq(7) and eq(8).

The displacements  $\hat{r}_i(t)$  are expressed in units of the lattice constant  $a_0$ .

The calculations are done in the case where interaction regime favors the appearance of order. In fig I, we report the variation of the  $D_t$  versus the surface concentration  $\theta$  with a fixed proportion of the adsorbate particles and for different mass ratio. The figure shows that in the limit of dilute system, the diffusion process is not affected. When the coverage exceeds 0.2 value, diffusion is reduced with increasing ratio  $M_b / M_a$ .

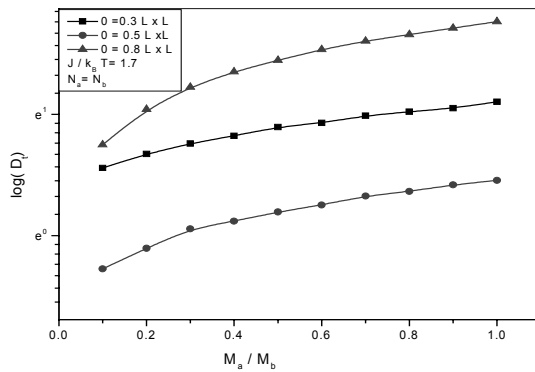


Fig. 3a. The tracer coefficient versus the rate of inertia at  $N_a=N_b$

In order to expect the influence of stoichiometric, we calculate the  $D_t$  for different proportions of light and heavy particles. Fig II shows that inclusion of heavy particles reduces the diffusion. No influence on ordering is observed. To get a better understanding of inertia effect, we report the dependency of  $D_t$  on  $M_a/M_b$  for different concentration regimes. This figure III shows that the usual dependency of  $D_t$  on mass is valid only for light density limit.

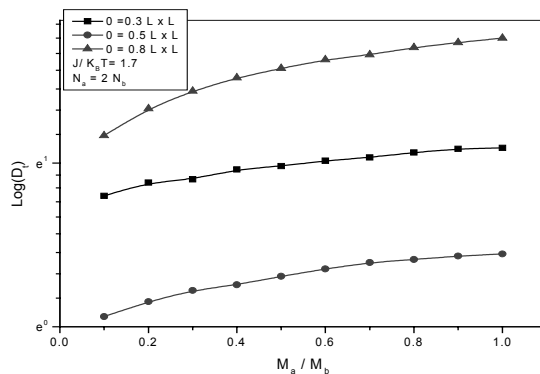


Fig. 3a. The tracer coefficient versus the rate of inertia at  $N_a=N_b$

## V. Conclusion

The present work deals with adsorbates diffusion on surface systems. We showed that adsorption of two different elements that interaction repulsively does not affect the ordering phenomenon. Diffusion process is found to be reduced by introducing heavy particles.

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