

Study of adatoms diffusion through current density fluctuation functions

K. Saadouni^a, A. Hader^a, Y. Boughaleb^a, R. Nassif^{a,b} and A. Ayadi^c

^a *Laboratoire de Physique de la Matière Condensée, Université Hassan II- Mohammadia
Faculté des Sciences Ben M'sik Casablanca- Morocco*

^b *Laboratoire de Physique de la Matière Condensée, Université Chouaib Doukkali
Faculté des Sciences El Jadida- Morocco*

^c *Ecole nationale des Sciences appliquées Université Cadi Ayyad Marrakech- Morocco*

In this work, we investigate the diffusion process by using a mean field lattice gas dynamical model. The temporal correlation function of the current density is calculated in a probe area of radius R . The latter is considered to test if the developed formulation can be applied to reproduce STM experiments. The obtained results concerning the effective diffusion coefficient exhibit clearly the order disorder transition effect translated by two minima appearing respectively at $p=1/3$ and $p=2/3$. The effect of the ordering phase at $p=1/3$ requires a threshold size more precisely, the minimum size system where, the ordering phase effect begins, to appear here is $R=5$.

PACS:66.30.D;64.60.61.16.Ch;68.37Ef

I- INTRODUCTION

Interest in understanding the statistical mechanics of adsorbates diffusion on a surface has been stimulated by results obtained by several recently developed methods. Principal among these are the Monte Carlo simulation [1,2] and the fluctuation autocorrelation methods [3]. Hence, much research effort has been devoted to the study of the general aspects of the dynamics of first order phase transition in non-equilibrium systems [4]. In the case of repulsive interactions, the transitions are order-disorder transition with the appearance of order on sublattices. Not only the theorists which have been interested to the surface dynamics but also, the experimenters have devoted a lot effort to enrich the physics of surfaces. In this framework, the scanning tunneling microscopy (STM) technique has been developed and given rise to important results [5,6]. The diffusive behavior in two-dimensional systems is best described using the collective (or chemical) diffusion coefficient D_c , which is defined in terms of a concentration density relaxation in the Fick's equation. Typical experimental methods such scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) can be used to measure the autocorrelation function [7], and the constant of the diffusion can be extracted in consequence [8]. Indeed, for instance, X. Wang et al [9] have performed Monte Carlo calculations to measure the scanning tunneling microscopy tunneling-current fluctuations. This study has allowed to understand the effect of the electric field on the surface diffusion of adatoms. So far, the diffusion process The model is presented in some detail in [12]. Here, we only give a brief summary. We consider a triangular lattice of N sites, each site can be occupied or empty and $n_i = \{0,1\}$ denotes

can be studied beyond the simple picture of diffusion as a random walk in periodic potential, by using the sophisticated techniques. Generally, to treat the diffusive behavior, one has to distinguish the collective motion and the individual one, this latter concerns the proper single particle (or tracer) diffusion coefficient which is defined through the mean square displacement of the adatom at asymptotically long times. In fact, experiment measures of the tracer are not possible except in cases where the motion of single atoms can really be followed, e.g. in the field ion microscope, in radiotracer, or in incoherent neutron scattering experiments. Even if the tracer could be measured, the presence of other adsorbate particles would complicate the interpretation of transition frequency and diffusion activation energy because the adsorbate- adsorbate interacts between them.

In the present work, we investigate the diffusion process by modeling the scanning tunneling microscopy (STM) experiments. We calculate the diffusion coefficient by adopting the mean field approach within the lattice gas model for which the interaction between the adatoms is simply limited to nearest neighbor pairs. Our calculations are done in a small circular surface equivalent to the probe area in the (STM) experiments, centered on the global lattice. In order to confirm the validity of these results we have compared them with Monte Carlo simulation [1], quasi chemical and Darken's approximation [10,11], linear response theory [12] and Boltzmann matano's method [12].

2-LATTICEGASMODEL FORMULATION

2.1 The model

occupation ($n_i = 1$) or non occupation ($n_i = 0$) of site n_i . Let the configuration $\{n\}$ be the set of occupation numbers for each site that we note for a lattice with N sites as,

$$\{n\} = \{n_1, n_2, \dots, n_N\} \quad (1)$$

The Hamiltonian for given configuration $\{n\}$ is given by,

$$H = -\sum_{i>j} \epsilon_{ij} n_i n_j - \mu_0 \sum_i n_i \quad (2)$$

Where μ_0 is the bare chemical potential and ϵ_{ij} is the interaction energy between the site i and j .

The master equation is:

$$\frac{\partial P(\{n\}, t)}{\partial t} = \sum_{\{n'\}} \omega(\{n'\}, \{n\}) P(\{n'\}, t) - \omega(\{n\}, \{n'\}) P(\{n\}, t) \quad (3)$$

The rate of the configurations exchange is expressed by the transition frequency $\omega(\{n\}, \{n'\})$ which enclosed all physical information about the system considered.

The average concentration over all possible configurations is defined by,

$$p_k = \langle n_k \rangle = \sum_{\{n\}} n_k P(\{n\}, t) \quad (4)$$

The kinetic evolution of the average concentration $p_k = \langle n_k \rangle$ at site k , is governed by the general master equation

$$\frac{\partial p_k}{\partial t} = \frac{\partial}{\partial t} \langle n_k \rangle = \sum_j \langle \omega_{jk}(\{n\}) n_j (1 - n_k) - \omega_{jk}(\{n'\}_j) n_k (1 - n_j) \rangle \quad (5)$$

where $\omega_{jk}(\{n\})$ is the jump probability from site j to site k , depending on the local configuration.

The product $n_j (1 - n_k)$ imposes that the site j is filled while the site k is empty (the hard-core exclusion principle). We restrict the jumps to those between nearest neighbor sites k and $k + a$. Hence, it is convenient to introduce a current operator $J_{k, k+a} \{n\}$ along the bond $k \rightarrow k + a$. Equation (5) becomes then,

$$\frac{\partial p_k}{\partial t} = -\sum_a \langle J_{k, k+a} \{n\} \rangle \quad (6)$$

(where we have taken $j = k + a$ in equation (5))

The average current in the bond (i, j) is,

$$\langle J_{ij}(\{n\}) \rangle =$$

$$\langle \omega_{ij}(\{n\}) n_i (1 - n_j) \rangle - \langle \omega_{ji}(\{n\}) n_j (1 - n_i) \rangle \quad (7)$$

For systems of particles with repulsive interactions, an order-disorder transition rises at a critical temperature T_c . As a consequence, a symmetry breaking is present at low temperature. It is then convenient to distinguish the various sublattices by different "symbols". In the case of a triangular lattice, the ordered phase consists in ordering onto a checkerboard lattice formed with three sublattices with A, B and C . On each sublattice, a concentration can be defined and it is supposed by hypothesis to vary slowly in space, we taken into account the equation (6) then, we have three kinetic coupled equations as,

$$\frac{\partial p_i^\alpha}{\partial t} = \sum_{a=j-i} \langle J_{ij}^{\alpha\lambda}(\{n\}) \rangle \quad (8)$$

with $\langle J_{ij}^{\alpha\lambda} \rangle$ is given in equation (7)

The upper indexes $\alpha = A, B, C$ and $\alpha \neq \lambda$ are introduced to identify the sublattices.

The model is a hopping model in which the jumps are between nearest neighbor sites. The barrier that the particles have to overcome before making a jump, only depends on the depth of the initial site: the saddle point energy is insensitive to the environment and the energy of the final site has no influence on the jump probability. As the thermal energy is supposed small compared to the barrier heights, the jump probability follows an Arrhenius law. This leads to,

$$\omega_{ij}^{\alpha\lambda}(\{n\}) = \omega_0 \exp\left(-\frac{\epsilon}{k_B T} \sum_{a \neq j-i} n_{i+a}^\lambda\right) \quad (9)$$

where ω_0 is the isolated jump probability and ϵ denotes the interaction energy of the pair nearest neighbor particles. ϵ is taken negative in order to represent repulsive interaction.

2.2 Mean field approach

The mean field approximation is the simplest method that allows a primary understanding of the studied phenomenon by providing mathematical solutions although it cannot describe completely the physical reality. In our case, the consideration of the mean field approach consists in replacing all the occupation numbers n_k by their average concentration p_k [14]. Then, the general expression for the current in equations (8) for the mean field approach can be written,

$$J_{ik}^{\alpha\lambda} = \omega_{ik}^{\alpha\lambda} p_i^\alpha (1 - p_k^\lambda) - \omega_{ki}^{\lambda\alpha} p_k^\lambda (1 - p_i^\alpha) \quad (10)$$

$$\omega_{ik}^{\alpha\lambda}(\{n\}) = \omega_0 \exp(-\gamma \sum_{a \neq k-i} p_{i+a}^{\lambda}) \quad (11)$$

where $\gamma = -\varepsilon / k_B T$ denotes the reduced interaction energy.

So that, to model the scanning tunneling microscopy experiments, we choose a triangular lattice of size 39×39 sites. The particles are initially distributed with a concentration where represents the concentration of adsorbed particles in the experiment. The temporal correlation function is calculated within a circular area of radius R ($2R \ll 39$), centered on total surface its expression in the framework of lattice gas formulation is given by,

$$G(\tau) = 1/N_p \sum_{i,k}^N \langle J_i^{\alpha\lambda}(t) J_k^{\alpha\lambda}(t+\tau) \rangle_t \quad (12)$$

where N_p represents the number of sites in the probe area.

3. RESULTS AND DISCUSSIONS

Here, the temporal correlation function is an essential ingredient because all the calculation that follows depends on it.

We reported in Fig.1. The temporal correlation function of current density as function of the time for various interaction values above and below the critical interaction parameter γ_c .

We notice that when the interaction values increase, the correlation function decreases faster, then in the asymptotic regime, for all interactions range, the correlation function relaxes rapidly to its equilibrium value, this result is qualitatively in good agreement with the experiment and the Monte- Carlo Simulation one [7,9].

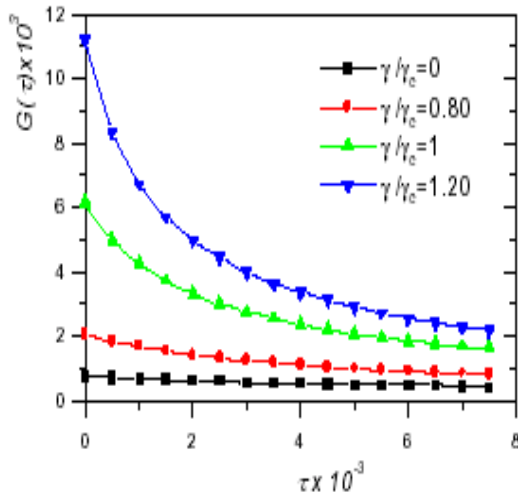


Figure.1 : The temporal correlation function of current density versus time for various interaction values

It's more useful to calculate the diffusion coefficient in order to investigate the diffusive behavior. The diffusion constant can be extracted by using the correlation function data. In this framework, the diffusion effective constant is proportional to the characteristic decay time τ_r like as: $D_c^{eff} \sim 1/\tau_r$ where τ_r is the characteristic time for which the correlation function has to drop to half its initial value [7]. Here, we adopted an other definition for τ_r since, for the long time, the correlation function follows an exponential law I.e. $G(\tau) = \exp(-t/\tau)$. Then, the characteristic time has been extracted easily from this formula. In fig.2. we report the average concentration evolution of the effective diffusion coefficient obtained by considering four different sizes R of probe area.

As R increases, the effective diffusion coefficient increases brusquely for all probe area sizes considered here. Thus, the different curves exhibit a minimum at $p=2/3$ indicating a blocking of the diffusion due to the establishment of the order-disorder transition effect at this concentration. In fact, we expected the same behavior at $p=1/3$ because this concentration corresponds also to the maximum ordering phase. Indeed, for $R \geq 5$ the curves exhibit the expected behavior but for all other system sizes no minimum has been appeared. So, we can conclude that the appearance of the minimum at $p=1/3$ requires a privileged size that we denote it by threshold value R_{th} i.e, the size from which the minimum begins to appear (here $R_{th} \approx 5$).

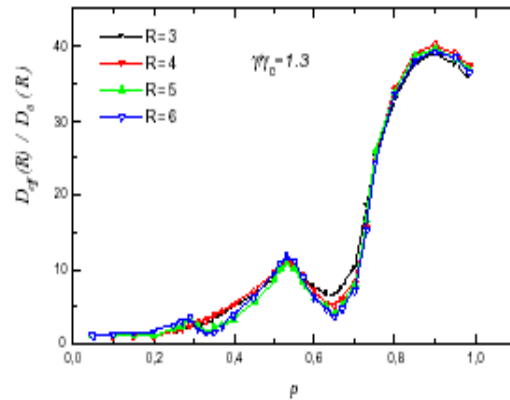


Figure.2 : The effective diffusion coefficient versus average concentration for different probe area sizes

These results are appeared strange but, they permit contrary to demonstrate the limits of the scanning tunneling microscopy (STM) experiments.

In order, to examine the minima dependence on the size, we plotted in fig.3 the effective collective diffusion coefficient values as a function of probe area size for two pertinent concentrations ($p=1/3$ and $p=2/3$). We remark that, the depth of the minima occurring respectively at ($p=1/3$ and $p=2/3$) increases with size up to a certain value

R_{sat} . This radius R_{sat} represents the value of R from which the diffusion coefficient for both concentrations does not change any more. One can explain this behavior by the fact that the dynamical behavior becomes insensitive to the probe area sizes (The horizontal regime presented in figure 3).

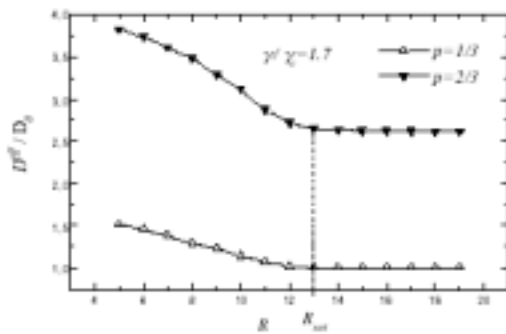


Figure.3 : The ratio between the effective diffusion coefficient D^{eff} and its zero coverage value D_0 as a function of the probe area sizes for two concentrations $p=1/3$ and $p=2/3$

In the figure below, we present the effective diffusion coefficient only for the probe area sizes which are bigger than the threshold value described in the precedent section ($R_{th} \approx 5$). The diffusion constant is plotted as a function of the mean concentration. Such as expected, the minima respectively at $p = 1/3$ and $p = 2/3$ are shown clearly. Their depths become more pronounced when the interaction value increases. The same behavior is found by [10,15].

The minima indicate the blocking of diffusion due to the ordering phase eventually established at these concentrations. However, the concentration $p = 1/3$ corresponds to the filling of one sublattice while the two other sublattices are empty, for the concentration $p=2/3$ the situation is reversed [16].

4 CONCLUDING REMARKS

We have seen how the mean field approach within the lattice gas model, allows a good modeling of the scanning tunneling microscopy (STM) experiments.

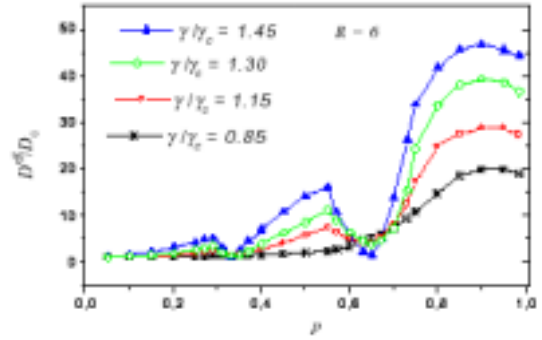


Figure.4 : Ratio between the effective diffusion coefficient D^{eff} and its zero coverage D_0 versus mean concentrations for different interaction parameters

We have also shown that the diffusive behavior included in the diffusion constant depends on the probe area sizes. However, the order-disorder phase effect occurs for the systems size upper the threshold value R_{th} . From our viewpoint this result constitutes one of the limits of the (STM) experiments although that it can measure the correlation function for a single site. We have thus, displayed that the minima depths, converge to the saturation value from which the dynamical behavior becomes, insensitive to the system size although, the diffusion coefficient is a macroscopic magnitude.

REFERENCES

- [1] R. Nassif, Y. Boughaleb, A. Hekkouri, J.F. Gouyet and M.Kolb; Eur Phys. J.B 1(1998) 453-464
- [2] C. Uebing and R. Gomer; J.Chem.Phys.95 (1991) 7626
- [3] R. Gomer; Rep. Prog phys. 53, 917 (1990)
- [4] G. Nicolis, I. Prigogine, *Self-organization in non-equilibrium systems* (Weiley Interscience, New-York, 1977; H. Haken, Synergetics (Springer-Verlag, , New-York, 1983; S.W. Koch, *Dynamics of first order phase transitions in Equilibrium and non-Equilibrium systems* (Springer- verlag, Berlin, 1984)
- [5] M. I. Larsson, M.C.Tringides, H. Pfnür, H. Frischat, K. Budde, M. Kammler and M. Henzler; Sur. Sci 411 (1998) 789-793
- [6] R. Van Gastel, E. Somfai, S. B. Van Albada, W. Van Saarloos and J. W. M. Franken (preprint)
- [7] E. H. Conrad, A. Menzel, S. Kiriukhin and M.C. Tringides; Phys. Lett. Rev 81(1998)3175-3178
- [8] Qiming Li and M.C.Tringides; Surf. Sci 365 (1996) 495-502
- [9] X.Wang, Qiming Li and M. C. Tringides Phys Rev B 57, 12 (1998) 7275

- [10] A. Danani, R. Ferrando, E. Scalas and M. Torri; Int. J. Mod. Phys B 11 (1997)2217
- [11] A. Danani, R. Ferrando, E. Scalas and M. Torri ; Surf. Sci. 409 (1998) 117
- [12] A.Memsouk, Y. Boughaleb, R. Nassif, and K. Saadouni; Physics letters A 279 (2001) 248-254
- [13] H. Ennamiri, R. Nassif and Y. Boughaleb; Physica A 238 (1997) 117
- [14] J. F. Gouyet; Physical Review E 51,3 (1995) 1695
- [15] K. Saadouni, A. Hader, Y. Boughaleb and A. Ayadi; M. J. Condensed Matter 4 (2001) 5-8
- [16] H. Ennamiri, R. Nassif, Y. Boughaleb and J. F. Gouyet ; M. J. Condensed Matter 1 (1997) 9