Study of quenched impurities effect on order-disorder phase transition by Monte-Carlo method

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We investigate the effect of quenched impurities on phase transition of layer particles. The study is done by means of Monte-Carlo technique on a fixed square lattice in the framework of the lattice gas model. The considered interactions are restricted to first neighboring particles and are of repulsive nature between diffusing particles. Attractive interactions between mobiles particles and impurities are considered. We focus on the behavior of the tracer diffusion coefficient, D^*, and the mean square fluctuation of adsorbates particles number $<(\delta N)^2>/<N>$. Our results show that the parameter controlling of phase transition are strongly influenced by the presence of the quenched impurities

Keywords: Monte Carlo, order-parameter, tracer diffusion coefficient

I. INTRODUCTION

The transport of adsorbate particles on solid surface is related to many physical and chemical phenomena such as adsorption, desorption, crystal, film growth, catalytic reaction [1-4]. Experimental studies of the surface diffusion focus on scanning tunneling microscopy (STM) and field ion microscopy (FIM) in order to measure the number of particles fluctuations [5] and the single adatom motion [6] respectively. Up to now, there is no theoretical model, exactly soluble, that allows the calculation of the above mentioned physical quantities. In addition, all studies carried out, to our knowledge, are limited to ideal case. So, the numerical calculation by Monte-Carlo technique has been intensively used to investigate the kinetic properties of surface diffusion and has provided to shed light in understanding of the dynamics of mobile adparticles. However, the most studies are devoted only perfect systems. It has been shown that the diffusion of particles on a square lattice gas with nearest-neighbor repulsive interactions for temperature below T_c, ($T \le T_c$), yields to C (2x2) the order-disorder phase transition ordering that the motion of particles [7]. The aim of the present work is to study a more realistic system by considering the presence of impurities. We limit ourselves to the case of quenched impurities and shows that the dynamics of diffusion process as well as the order-disorder phase transition are affected. Our Monte-Carlo (MC) simulations are performed for lattice-gas for the case of nearest-neighbor repulsive interactions. We show that for attractive interaction between the quenched impurities and the mobile particles, the tracer diffusion coefficient increase and the long-range of the ordered structures is broken. The outline of this work is as the follows: in section 2, we define the lattice gas model. In section 3, a description of Monte Carlo is given. Finally, section 4, is devoted to MC results and discussion.

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II. THE MODEL

We consider a lattice gas system of N_A particles on a square lattice with nearest-neighbor interactions. We assume that N_I adsorbate sites are randomly occupied by quenched impurities.
The hamiltonian for this model is given by:

$$H=-1/2\sum_{\langle ij\rangle} V_{AA} n_i^A n_j^A - 1/2\sum_{\langle ij\rangle} V_{AI} n_i^A n_j^I - \mu \sum_i n_i^A, \quad (1)$$

where V_{AA} and V_{AI} are interaction energies between particle-particle and impurity-particle respectively. n_i^α is an occupation number for each site $'i'$ which is equal to unity if the site is occupied by one particle of specie α (with α=A or I) and zero otherwise. Double occupation of a same site is forbidden.
The notation $\langle ij \rangle$ implies the summation in eq (1) over each pair of particles in nearest-neighbor sites.
Impurity-impurity interaction V_{II} is supposed null.

When the particle jump from full site to empty one, the probability $P(\{n\},t)$ of having the configuration

{n} at time t is given by the following phenomenological Master equation [8].

$$\frac{\partial P(\{n\},t)}{\partial t} = \sum_{\{n'\}} [\omega(\{n'\} \to \{n\}) P(\{n'\},t) - \omega(\{n\} \to \{n'\})\, P(\{n\},t)], \qquad (2)$$

where $\omega(\{n\} \to \{n'\})$ is the transition probability from {n} to $\{n'\}$ configurations.

The model used in this work is a happing model in which the jumps are between nearest- neighbor sites. The jump rate at temperature T, which leads to Arrhenius behavior and the Boltzmann equilibrium distribution [9], is given by:

$$\omega_{ij}^{A}\{n\} = \omega_0^A \exp\left(-\frac{V_{AA}}{K_B T} \sum_a n_{i+a}^A - \frac{V_{AI}}{K_B T} \sum_a n_{i+a}^I \right), \qquad (3)$$

where ω_0^A is the jump frequency of an isolated A-particle.

III. MONTE CARLO SIMULATION.

Our system consists on a square lattice of the size $L = 50$ with periodic boundary conditions. Initial lattice gas configurations are generated by throwing at random N_A diffusion particles and C impurities. We define the coverage θ_A by:

$$\theta_A = \frac{N_A}{L^2 - C}. \qquad (4)$$

We carry out two procedures. First, it's sufficient to use the Metropolis Algorithm [10] for thermodynamical equilibrium. Second, the diffusion of particles depend the jump probability P_i via the interaction energy.

$$P_i \propto \exp(-\Delta E_i^A / K_B T), \qquad (5)$$

Where ΔE_i^A is given by:

$$\Delta E_i^A = \sum_j V_{AA} n_j + \sum_j V_{AI} n_j . \qquad (6)$$

For each filled site $'i'$, an adjacent final site $'j'$ is randomly chosen. If the destination is vacant, a jump can occur with the probability P_i, otherwise no jump occur. The jump probability is compared with a random number η between 0 and 1 and allowing a jump if $P_i \le \eta$. For calculating the mean square fluctuation of adsorbates number particles we use the grand canonical ensemble with μ and T treated as independent thermodynamical variables [11]. Then the single-site energy is:

$$\varepsilon_i^A = n_i^A \left(\sum_{j \neq i} V_{AA} n_j + \sum_{k \neq i} V_{AI} n_j - \mu \right) \qquad (7)$$

Here, the flip probability P_f of a randomly selected occupation variable n_i^A is given by:

$$P_f = \exp\left(\frac{\varepsilon_i^{Af} - \varepsilon_i^{Ai}}{k_B T} \right), \qquad (8)$$

where ε_i^{Af} and ε_i^{Ai} denote single-site energies for the final and initial state.

IV. RESULTS AND DISCUSSION.

Our calculations concern physical quantities attached to phase transition. In this paper, we restrict ourselves to tracer D^*, and mean square fluctuations of adsorbates particles number.

4.1. Order parameter

As one can distinguish, the presence of impurities reduces the order range. In fact, Fig. 1. (c) and (d) show antiphase domains at the concentration $\theta_A = 0.5$. There are only ordered clusters rather than an order extended to the whole lattice size.

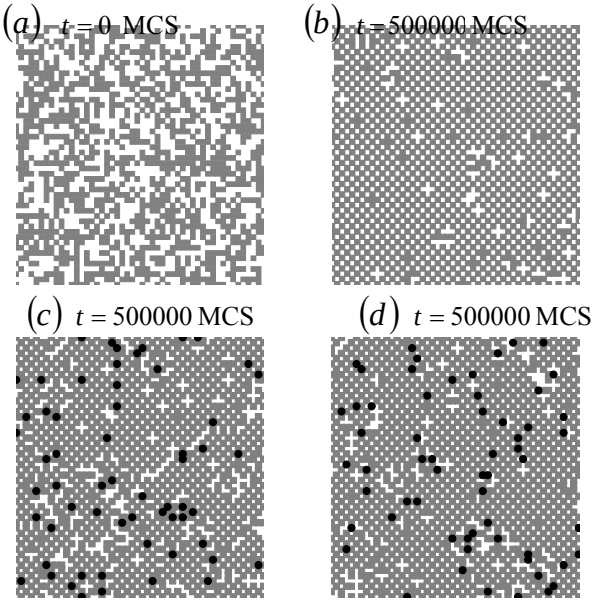

FIG.1. Representative Snapshots for lattice- gas model at, V_{AA} / K_BT=2 with θ_A =0.5. Filled squares represent diffusin particles while the filled circles are immobile impurities. (a); (b); (c); (d) correspond to initial lattice – gas configuration; C=0; V_{AI}/V_{AA}=0, C=0.024 ; V_{AI}/V_{AA}=-2 , C=0.024 respectively.

In order to explain these findings, we expected the order parameter versus the coverage at low temperature. The results shown in Fig. 2, indicate clearly the decrease of the order parameter at each coverage.

The decrease is more pronounced at the half full system. In addition the Fig. 2 shows that consideration of attractive interactions between diffusive and impurities lead to a loss of the order.

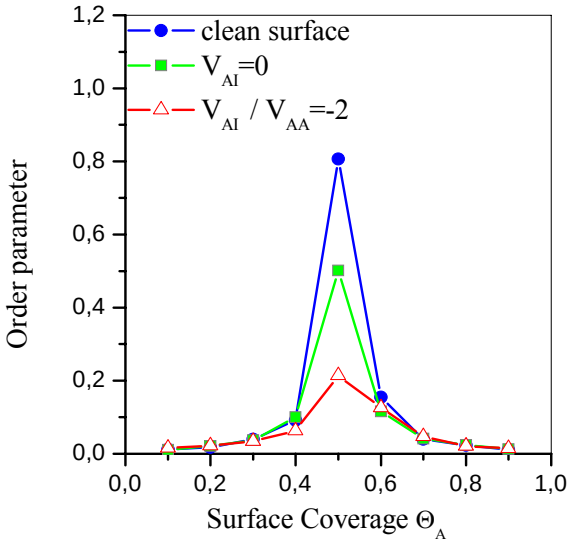

FIG. 2. Order parameter versus coverage θ_A at $V_{AA}/K_BT=2$, for C=0.024 and clean surface.

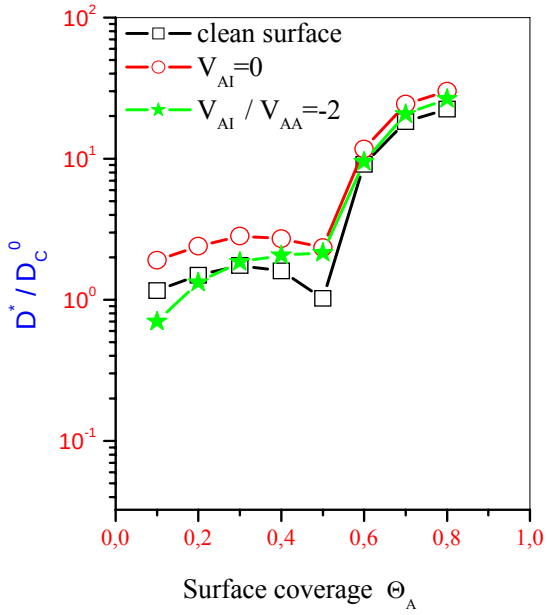

FIG.3. D^*/D_c^0 versus coverage θ_A at $V_{AA}/K_BT=2$, for c=0.024 and clean surface.

4.2. Tracer diffusion coefficient

The tracer diffusion coefficient, D^* describes the random walk of individual tagged particles on two-dimensional lattice for long time through the mean square displacement. D^*, is defined by [12],

$$D^* = \lim_{t\to\infty} \frac{1}{2Ndt} \sum_i^{N_A} \left\langle \left| \Delta r_i(t)^2 \right| \right\rangle, \qquad (9)$$

where d is the system dimension $(d=2)$, t is the elapsed time expressed in units of MC step, consisting of 50X50 random interrogations of lattice sites.

Fig. 3 shows the normalized tracer diffusion coefficient, D^*/D_c^* as a function of the coverage θ_A at $V_{AA}/K_BT=2$, we can see that the presence of impurities, influences the behavior of the diffusion coefficient. The case where $V_{AI}=0$ shows that the diffusion process increases. However there is a signature of establishment of ordered regime at $\theta_A=0.5$ with a dip less pronounced than the case of clean surface. The presence of particle-impurities interaction $(V_{AI}\neq 0)$ leads to a complete disappearance of ordered

4.3 Mean square fluctuations.

In the grand canonical ensemble, mean square fluctuation $\left\langle (\delta N)^2 \right\rangle / \left\langle N \right\rangle$ at equilibrium can be obtained from the slope of the isotherms of μ/k_BT as versus of mean coverage [13],

$$\left(\frac{\partial \mu / k_B T}{\partial \ln(\theta_A)}\right)^{-1} = \frac{\left\langle (\delta N)^2 \right\rangle}{\left\langle N \right\rangle} \qquad (10)$$

Equation (10) is also useful to show the order-disorder phase transition: since $\left\langle (\delta N)^2 \right\rangle$ can diverge (for an infinite system) at T_C.

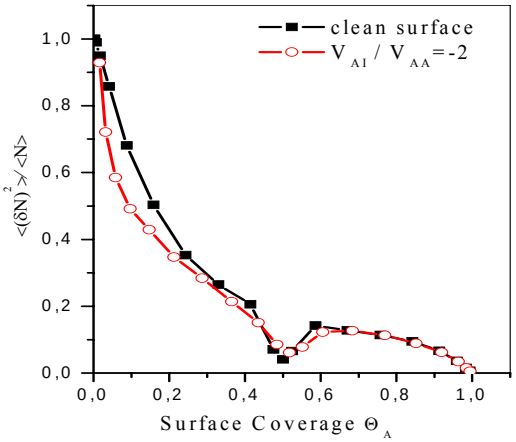

FIG. 4. $<(\delta N)^2>/<N>$ versus coverage θ_A at $V_{AA}/K_BT=2$, for c=0.024 and clean surface.

Fig. 4 shows the normalized mean square fluctuation $<(\delta N)^2>/<N>$ as function coverage θ_A for c=0 and c=0.024 at temperature T, $T \leq Tc$. $< (\delta N)^2>/<N>$ exhibits a minimum at θ_A=0.52 rather than at θ=0.5 corresponding to a clear surface. This finding shows that study of ordering in this case needs to introduce local order parameter rather than the global one considered here.

V. CONCLUSIONS

In this work, we have examined the effect of quenched impurities on the ordering and the tracer diffusion coefficient of system in the framework of lattice-gas model. We have concluded that the presence of impurities has broken the long-range of the ordered structures at low temperature and increase the motion of single-particle in a lattice. Furthermore, the establishment of the order clusters of particles requires introducing the local order parameter rather than the global order parameter.

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