Study of surface diffusion by Langevin Dynamics simulation

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We investigate the dynamic properties of Brownian interacting particles subject to a two-dimensional periodic potential. By employing the Langevin dynamics simulation, we calculate the collective diffusion coefficient in different situations corresponding to different densities. On the other hand, our numerical studies show that the collective diffusion coefficient depends not only on the shape of adsorbed potential but also on the coupling between particles.
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I. INTRODUCTION

The diffusion of atoms, particles or molecules in two-dimensional periodic potentials is a subject of great interest in many fields in physics, biology and chemistry [1-6]. In general, the diffusion is treated as a Brownian motion, which can be described by some form of the Langevin equation. Its use for a wide class of problems, make it a popular equation both for Theoreticians and for experimentalists. Theoretical aspects of the Langevin equations stimulated by new experimental findings are still under intensive studies. On the other hand, a variety of new experimental phenomena, some anticipated by theory, have been found to be well described by the Langevin equation. This synergism between experiment and theory,
coupled with ever-increasing computer power has spurred intensive efforts to obtain accurate numerical solutions of the Langevin equation efficiently.
In the existing literature, the problem of the diffusion in periodic potentials has been thoroughly investigated in the case of one-dimensional systems [1-10]. In these systems, exact numerical result concerning the diffusion coefficient, the escape rate and the probability Distribution of jumps length is available in the literature. Moreover, accurate analytical approximations have been developed.
In the contrary, much less is known about the diffusion in two-dimensional systems. The study of these systems is necessary when trying to develop realistic mode of diffusion on surfaces and in Superionic conductors. Indeed, diffusion in multidimensional systems can display qualitative difference compared to diffusion in one dimension; for example, in two dimensions, localization may occur in conservatives systems also at energies higher than the saddle-point energies, and this has deep consequences on diffusion. On the other hand, systems with high density of interacting particles are of special interest. They are equally treated within the lattice-gas approximations, which allow calculating more easily the collective diffusion coefficient. However it is important to go beyond such approximation, which is valid only at low temperature, and it is not able to describe incommensurate layers in any case.
In this paper, we use a Langevin dynamic simulation for interacting particles. We will study the collective diffusion coefficient in an arbitrary 2D adsorption potential, in many different situations. The main goal of this study is to give the influence of coupling on the collective diffusion coefficient *Dcoll* and taking account of interactions between the particles. This problem is more interesting and would be closer to physical reality than the single-particle case.
This paper is organized as follows. In section II, we describe briefly the two-dimensional Langevin dynamics simulations (LDS) and the potentials used in this numerical calculation.
Section III, contains the description of effective potential *Veff (r)*. In section IV and V, we present same results concerning the collective diffusion coefficient *Dcoll* . The conclusions are outlined in Section VI.

II- TWO-DIMENSIONAL LANGEVIN DYNAMICS SIMULATIONS (LDS)

In this section, we present Langevin dynamic simulation, which is particularly well suited for the low friction regime, thus making it complementary to the matrix continued-friction expansion approach [11-12-13], which works well in the high to intermediate friction regime.
The Langevin dynamic simulation is carried out by solving numerically the set of *2N* coupled Langevin equations:

$$\begin{cases} m_i \dfrac{d^2x_i}{dt^2} = -m\gamma_i \dfrac{dx_i}{dt} - \dfrac{\partial V_{tot}(x_1,x_2,....,x_N)}{\partial x_i} + \zeta_i(t) \\ \\ m_i \dfrac{d^2y_i}{dt^2} = -m\gamma_i \dfrac{dy_i}{dt} - \dfrac{\partial V_{tot}(y_1,y_2,....,y_N)}{\partial y_i} + \zeta_i(t) \end{cases} \quad i = 1,2,....,N \qquad (1)$$

where *xi* , *yi* and *m*i are, respectively, the positions and the mass of the ion *i*. The damping coefficient ã and the random force *(t) i* æ both arise from the interaction of the mobile ion with the thermal vibrations of the rigid framework and are related by the fluctuation dissipation theorem:

$$\begin{cases} < \zeta_i(t) >= 0 \\ \\ < \zeta_i(t)\zeta_j(t') >= 2mk_B T\delta_{ij}\delta(t-t') \end{cases} \qquad (2)$$

These equations, which are phenomenological in nature, are then solved numerically. These are reasonable assumptions when the mass of the diffusing particle is larger than its neighbours (bath particle), because even on a short time-scale the motion will be determined by a very large number of essentially uncorrelated collisions (in this case the particle performs a Brownian motion; its velocity is slightly modified by single collision and thermalisation occurs because of the large number of this even). When all particles have the same mass the assumptions are less well justified and a generalization is required. Assuming pair interaction the total potential energy *Vtot* may be written as

$$V_{tot}(r) = \sum_{i}^{N} V_1(r_i) + \sum_{i>j} V_2(r_i - r_j) \qquad (3)$$

where *V1 (r)* denotes the square egg-carton potential obtained by considering only the lowest order terms of the Fourier expansion of the periodic potential given by Eq.(4)

$$V_1 = G_1\left[\cos(\frac{2\pi}{a}x) + \cos(\frac{2\pi}{a}y)\right] + G_2\cos(\frac{2\pi}{a}x)\cos(\frac{2\pi}{a}y) \qquad (4)$$

where the lattice constant *a* is chosen to be the same in the *xx* and *yy* directions (the positions of these sites form a square lattice). The parameters *G1* and *G2* give the amplitudes of the decoupled and coupled part respectively. This potential has the form of an egg-carton as is shown in Fig.1. It has potential minima in the centres of the cells, potential maxima at the four corners, and the saddle points at midpoints of the edges, with energy barriers *V0=2(G2- G1)*. The coupling term *G2* is responsible for the energy transfer between the *x* and *y* degrees of freedom and leads to qualitatively new dynamical features in the case of Hamiltonian systems. This simple form of potential has been largely used as a model periodic potential in theoretical studies of many different problems, such as the non-linear conservative dynamics of a classical particle [14], the collective diffusion of particles in Superionic conductors [15] and the noise-actived diffusion of a classical particle [16].

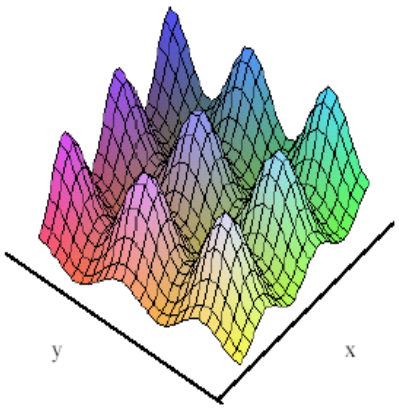

Fig.1: The 2D coupled "egg-carton" potential. G_1=0.02eV, G_2=0.01eV

Interactions between particles introduce new times scales, which leads in general too more complicated phenomena. One of the simplest interaction type which is widely used in the context of two dimensional systems [17], is the well known Yukawa pair potential:

$$V_2(r) = \frac{Q^2}{r} exp(-\frac{r}{r_D}) \qquad (5)$$

Where *Q* is the effective charge and *rD* is the screening length, which is taken to be equal to *L/2*, where *L* represents the length of the system. The parameters: friction, temperature and density were varied for each simulation. Initially, *N* particle are placed randomly in a squared lattice array enclosed in a square box length *L*. The particles are then allowed to move according to Eq. (1) until equilibrium is reach. The time step is assumed to be short enough and was taken to be 3x10-14s. By varying the density of diffusing ions, we can go from configuration where both potential *V1* and *V 2* assume their minimum for a given spacing to a competing state . One distinguishes the former as a commensurate (cooperating) state with *c-1*integer and the latter as incommensurate (or competing) state with *c-1* non-integer (here *c* is the concentration measured in particle per site); incommensurate structure generally

shows up in system with competing periodicities. In solid state system of the periods is that of the basic lattice. The other period *b* may be that of another lattice. Commensurate situations can arise in the sense that the interparticle distances favoured by short-range order is close to the lattice periodicity (*b=na*, where *n* is an integer). By varying the density commensurate situation can change into incommensurate or high order commensurate ones where the lattice spacing *b* is a simple rational fraction of the period a (*b* , *na*). Recently [18] a new type of incommensurate–commensurate transition in overlayers via domain wall evaporation has been found. This type of transition can take place when the commensurate lattice has a large number of sublattice. Depending on the system parameters, this transition can be either first or second order. In both cases we expect pronounced hysteresis effects due to the large barrier for point defect formation in the domain wall phase. Here we investigate different (complementary) situations where the structure of the 2D system is incommensurate or commensurate; the following numerical computations were performed in square lattice using the potentials given by Eqs. (2) and (5).

III. EFFECTIVE POTENTIAL *Veff(r)*

The stochastic Langevin dynamics technique has proved to be very useful in studying transport properties in solid. However, determination of the bulk properties of interacting particle systems whose dimensionality is greater than one requires large computer resource. This problem can be alleviated if the many body dynamics is replaced by a single particle effective potential, which contains the effects of the other mobile particles. In analogy to systems without pair interactions, the one particle density defined by:

$$\rho(r) = \sum_i < \delta(r - r_i) > \qquad (6)$$

$$\rho(r) = cte \times exp(-V_{eff}/k_B T) \qquad (7)$$

These equations define the effective potential *Veff(r)*, which includes the effects of both potentials *V1* and *V2* in a static way. It is independent of the friction and contains no memory effects, which arise essentially from the fluctuation of the pair interactions. Moreover, the barrier height of *Veff(r)* can be very useful in interpreting the transport properties of the system. By comparing *Veff(r)* with the bare single particle potential *V1* originating from the host ions only, *one* can deduce quantitative information on the role of the commensurability effect, i.e. on the degree of competition between correlation among the mobile ions and the ion-host interaction. Langevin dynamics simulation provides trajectories to calculate *) r (* for any given pair interaction and thus obtain *Veff(r)* directly. The rest of this section is devoted to the discussion of some results concerning *Veff(r)* of the two-dimensional Brownian model, for a Yukawa pair interaction.

In Fig.2, we have reported the variation of the *Veff(r)* along the two directions of space for incommensurate concentration *c=2/3*. The analysis of this figure show that in the *xx* direction, the barrier height (dash-dotted line) increases compared with the one corresponding to non– interacting particles (full line) *V0*.

On the other hand, the barrier height (dotted line) is reduced with respect to *V0* in the *yy*-direction.

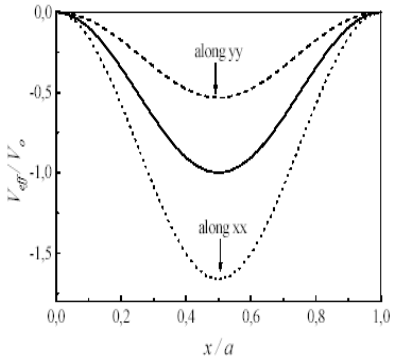

Fig.2: Effective potential V_{eff} obtained from the simulation with Yukawa potential; it is evaluated

IV- COLLECTIVE DIFFUSION COEFFICIENT *Dcoll*

The collective diffusion coefficient, which is the relevant quantity for studying
commensurability effects, is given by the linear part of the mean square displacement [12]:

$$D = \lim_{t \to +\infty} \frac{1}{2Ndt} \sum_{i,j} \left\langle \left(r_i(t) - r_j(0) \right)^2 \right\rangle \qquad (8)$$

where the angle brackets < > means average over the initial conditions and over the stochastic trajectories obtained by numerically integrating the Langevin equation, *N* is a number of particles and d is the dimensionality of the space. One may notice that the diffusion coefficient relates to the temperature, the coupling strength and the concentration. In particular, the dependence on the coupling strength and the density does not happen for the single-particle case.

Studies of their dependences are very interesting and significant.

separately along each direction of space incommensurate for concentration *c=2/3* in two dimensional system. *V0=0.1eV ,T = 400K* and *Q2=0.5 a.u*

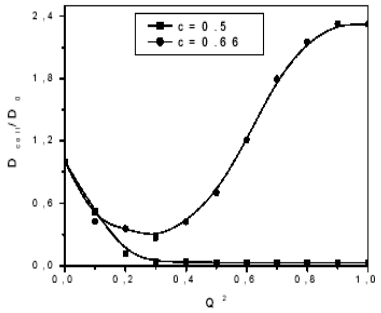

Fig.3. Collective diffusion coefficient as function of Q^2 for fixed concentration *c=2 3*and *c=1 2.*

For *c=2/3* (full circles), the first phenomena we observe is that the relation between the diffusion coefficient and the coupling strength is not monotonic. For weak strengths (*Q2<0.25)* the diffusion coefficient decreases with the coupling. When *Q2>0.25* the diffusion coefficient begins to increase as one increases the coupling strength. While for *Q2>0.7. Dcoll* begins exceeding the single-particle value (*Q2 =0.*). So, the results indicate clearly that if one introduces some interactions between the particles, then a higher diffusion rate than noninteracting particles can be achieved in the range of high coupling between particles. In much realistic application one hopes that the diffusion process can be improved as quickly as possible. Our explorations indicate that for the incommensurate case, the coupling between particles may enhance the diffusion process.

For commensurate concentration *c=1/2* (full squares), the shape of *Dcoll* decreases with increasing *Q2* , this indicates contrary to incommensurate case, that the diffusion is suppressed by introducing the coupling among particles. In this simulation, coupling between particles act as an additional source of dissipation, as for incommensurate case for weak strengths of interactions ($Q^2<0.25$)

V- INFLUENCE OF COUPLING ON THE COLLECTIVE DIFFUSION COEFFICIENT

In this section we will present the results concerning the influence of coupling term in the host periodic potential on the collective diffusion coefficient *Dcoll* . Recently, by using different method of calculation Ferrando et al [ ] have studied the influence of the coupling term on the diffusion process for the single – particle case. In the following we will generalize their results

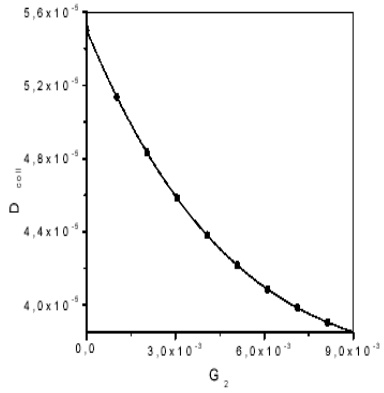

Fig.4: Collective diffusion coefficient as function of G_2 in the *cases* of noninteracting particles

by introducing interactions among particles, which are of fundamental importance in understanding many physical systems. In Fig.4. We have reported the variation of *Dcoll* as a function *G2* in the case of noninteracting particles (*Q²=0*). Our LDS for this case recovers the results of previous studies using the matrix continued fraction expansion method. The diffusion coefficient decreases with the coupling term *G2*. This behaviour can be well explained by that in the presence of coupling, the width of the channel is narrower at the saddle point positions than at the minimum. Consequently, the particles find it more difficult to overcome the barrier. Additionally, the coupling allows the energy transfer between the *x* and *y* degrees of freedom; because of that, it may be difficult for the diffusing particle to perform long and straight inertial trajectories.

In Fig.5, we have taking into account of interaction *(Q2 =0.3a.u*). In this situation, we find qualitatively the same behaviour, i.e. *Dcoll* decreases normally with the coupling term *G2*. But, the only difference between the two cases, as visible in this figure, is the saturation of the *Dcol* for a value of *G2* much lower than the noninteracting particles case.

Thus, we can confirm explicitly that the behaviour of *Dcoll* as a function of the coupling term for interacting particles is quantitatively different from the one corresponding to noninteracting case.

Let us now consider a different situation, which can be found when the potential wells are transformed into a grid of minima lines as in Fig.6. This situation represents the extreme case of very strong *x-y* coupling (*G1=G2*), the energy barriers vanish and a

network of flat channels connects the minima. In Fig .7, we have reported the variation of the *Dcoll* with the coupling term *G2* in the maximum coupling case (*G2= G1*). As found above, the collective diffusion coefficient has qualitatively the same behaviour, as in the situation of the

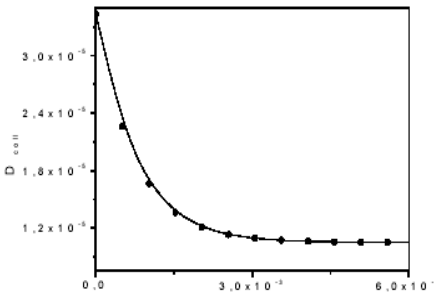

Fig.5: Collective diffusion coefficient as function of G_2 for $Q^2=0.3$ *u.a.*

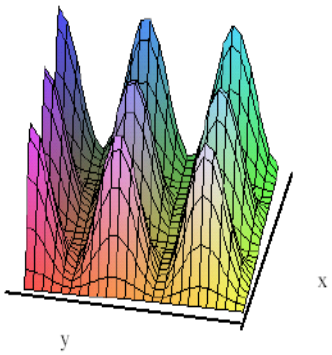

Fig.6: The 2D coupled "egg-carton" potential. $G_1=0.01eV$, $G_2=0.01eV$ (flat channel.)

noninteracting particles(*Dcoll* decrease normally with the coupling term), but not the same dependence on the coupling term. Thus, inclusion of interactions between diffusing particles affect clearly the dependence of the collective diffusion coefficient with the coupling term.

VI- CONCLUSION

In this paper, we have used the Langevin dynamic simulation for studying the collective transport behaviour in two-dimensional systems. Our numerical calculations predict that the collective diffusion coefficient depends sensitively on the pair interaction potential as well as on the details of adsorption potential. These results reported here should be valuable for application in many physical cases, such as intercalation compounds, Superionic conductors,
etc. In future work we will study the dependence of the collective diffusion coefficient on the friction in the low friction regime. Our aim is to extend the earlier results obtained by different groups and by different methods, which predict an "anomalous" behaviour of the diffusion coefficient in the under damped regime. These studies along this line are currently in progress.

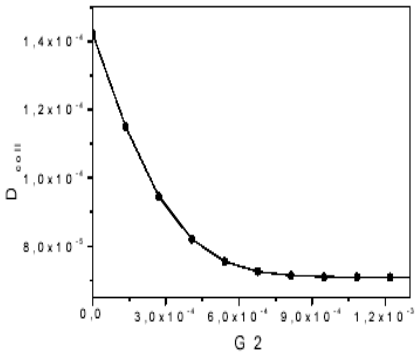

Fig.7: Collective diffusion coefficient as function of G_2 for fixed concentration $c=2/3$ and $Q^2=0.3$ *u.a.* In case $G_1=G_2$

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