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Nonlinear dynamics and surface diffusion of diatomic molecules

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The motion of molecules on solid surfaces is of interest for technological applications, but it is also a theoretical challenge. We study the deterministic and thermal diffusive dynamics of a dimer moving on a periodic substrate. The deterministic motion of the dimer displays strongly nonlinear features and chaotic behavior. The dimer thermal diffusive dynamics deviates from simple Arrhenius behavior, due to the coupling between vibrational and translational degrees of freedom. In the low-temperature limit the dimer diffusion can become orders of magnitude larger than that of a single atom, as also found experimentally. The relation between chaotic deterministic dynamics and stochastic thermal diffusion is discussed.

keywords: Surface, Molecules, Molecular Dynamics

I. INTRODUCTION

The surface diffusion of single adatoms has been intensively studied over the last decades, [1–3] due to its importance in thin film and crystal growth. [4] Once individual atoms are adsorbed on a surface they can meet, thus forming larger clusters. However, the diffusion of even the simplest cluster, a dimer, on a surface is by far not yet understood. [5–13] The diffusion dynamics can be strongly affected by the coupling of the intramolecular motion to the translational motion of the centre of mass (CM) of the cluster. [12–15] Herein, we present a simple, one-dimensional model for studying the Hamiltonian and diffusive dynamics of a dimer, which is relevant to systems where quasi-one-dimensional motion takes place. [16] The deterministic dynamics of this model is characterized by a complex behavior, dominated by non-linear effects, parametric resonances and chaotic features. At variance with the case of a single atom, at $T \neq 0$ the role of the internal degrees of freedom of the dimer is responsible for deviations from activated behavior of the diffusion coefficient. In Section II we briefly outline our model. In Sections III and IV we discuss the nonlinear deterministic and thermal dynamics, respectively, and compare the two situations in Section V. Concluding remarks are given in Section VI.

II. MODEL

We consider the deterministic and thermal dynamics of a dimer moving on a periodic one-dimensional substrate. The particle-substrate interaction is a sinusoidal function of amplitude $2U_0$ and period a, and the interparticle interaction is given by a harmonic potential with spring constant K and equilibrium length l. We use Langevin dynamics to deal with finite temperature T. The equations of motion for the two atoms of mass m and of coordinates x_1 and x_2 composing the dimer are given by Equation (1):

$$\begin{cases} m\ddot{x}_1 + m\eta\dot{x}_1 = K(x_2 - x_1 - l) - \frac{2\pi U_0}{a}\sin\left(\frac{2\pi x_1}{a}\right) + f_1 \\ m\ddot{x}_2 + m\eta\dot{x}_2 = K(x_1 - x_2 + l) - \frac{2\pi U_0}{a}\sin\left(\frac{2\pi x_2}{a}\right) + f_2 \end{cases}$$

$$(1)$$

where the effect of finite temperature T is taken into account by the stochastically fluctuating forces f_i, satisfying the conditions $< f_i(t) >= 0$ and $< f_i(t)f_j(0) >= 2m\eta k_B T\delta_{ij}\delta(t)$, and by the damping term $m\eta\dot{x}_i$. In the following, we will use representative values of the parameters, $a = 0.25$ nm, $U_0 = 0.2$ eV, $m = 5 \times 10^{-26}$ kg, $\eta = 0.7$ ps^{-1}. The values of K and l will be given in the caption of each figure. We performed molecular dynamics (MD) simulations, integrating the equations of motion using a velocity-Verlet algorithm, with a time step $\Delta = 10^{-16}$ s and averaging the trajectories over several thousands of realizations in the case of thermal diffusion, in order to reduce the statistical noise.

III. HAMILTONIAN DYNAMICS

First we consider the Hamiltonian dynamics ($f_i = 0$ and $\eta = 0$ in Equation (1)). It is convenient to rewrite Equation (1) in terms of the CM coordinate $x_{CM} = (x_1 + x_2)/2$ and of the deviations from equilibrium of the internal coordinate $x_r = x_2 - x_1 - l$, obtaining Equation (2):

$$\begin{cases} m\ddot{x}_{CM} = -\frac{2\pi U_0}{a}\sin\left(\frac{2\pi x_{CM}}{a}\right)\cos\left[\frac{\pi}{a}(x_r + l)\right] \\ m\ddot{x}_r = -2Kx_r - \frac{2\pi U_0}{a}\cos\left(\frac{2\pi x_{CM}}{a}\right)\sin\left[\frac{\pi}{a}(x_r + l)\right] \end{cases}$$

$$(2)$$

We have considered the case of a commensurate dimer ($l = a$) starting at equilibrium with a given initial kinetic energy E_{kin}^0, a case which allows some analytical results for the initial phase of the motion, showing the role of internal vibrations on the dynamics, to be obtained. [12] In fact, for a rigid dimer with $\dot{x}_1(0) = \dot{x}_2(0) = v_0$, the minimum kinetic energy for the CM to overcome the potential barrier is $E_{kin}^0 = mv_0^2 = 4U_0$. Hence, for $v_0 < \sqrt{4U_0/m}$, the motion of the CM is oscillatory, while a drift regime is attained for $v_0 > \sqrt{4U_0/m}$. Conversely, when the dimer is allowed to vibrate, the coupling between the CM and the internal motion makes it possible for the CM of the dimer to overcome the potential barrier $4U_0$ for values of v_0 below the threshold $\sqrt{4U_0/m}$. In fact, if the internal motion is excited, it can happen that one particle remains in the minimum and the other reaches the nearest maximum. From the energy balance, Equation (3) follows:

$$E_{kin}^0 = 2U_0 + \frac{1}{2}K(a/2)^2 \qquad (3)$$

If K is sufficiently small, the right-hand side of Equation (3) can be smaller than $4U_0$. This is the situation shown in Figure 1, where the CM motion is rather irregular, behaving in a chaotic fashion.
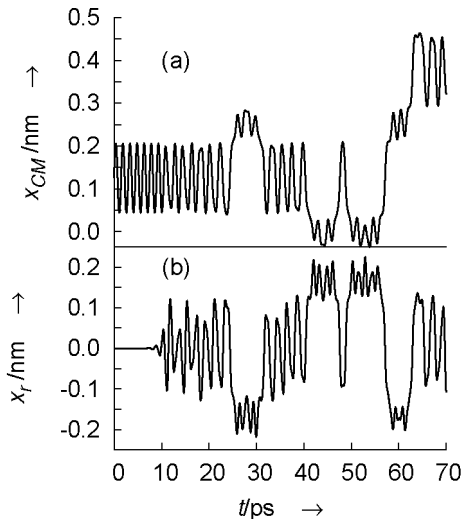

FIG. 1. Dynamics given by Equation (2) for $K = 0.2\ \mathrm{Nm}^{-1}$ and $v_0 = 380\ \mathrm{ms}^{-1}$, $f_i = 0$ and $\eta = 0$. (a) The CM motion is plotted; (b) the deviations from equilibrium of the internal coordinate are plotted.

This chaotic regime occurs for weakly bound dimers in a velocity window around the threshold $\sqrt{4U_0}$, and can be characterized by Lyapunov exponents and power spectra. [12] We have also shown that, for larger values of K, the drift motion of the CM may excite the internal vibrations by a parametric resonance in a velocity window around twice the natural stretching frequency of the dimer $\omega_0 = \sqrt{2K/m}$.

IV. THERMAL DIFFUSION

The thermal diffusive behavior of the dimer is characterized by computing the diffusion coefficient D from the mean square displacement $< x_{CM}^2(t) >$, as in Equation (4):

$$D = \lim_{t \to \infty} \frac{< x_{CM}^2(t) >}{2t}. \qquad (4)$$

For temperatures that are small compared to the energy barrier, Kramer's theory [17] predicts an activated Arrhenius behavior of diffusion, given by Equation (5):

$$D = D_0 \exp(-E_a/k_B T), \qquad (5)$$

where the activation energy E_a and the prefactor D_0 do not depend on T. In the limit of vanishing energy barrier, the adatom diffusion coefficient obeys the Einstein relation and is given by $D = k_B T/(m\eta)$, twice the value of the dimer $D = k_B T/(2m\eta)$. The diffusion coefficient of a single adatom shown in Figure 2 has an activation energy corresponding to the energy barrier $2U_0 = 0.4$ eV, except at very high temperatures owing to finite barrier effects. [18]

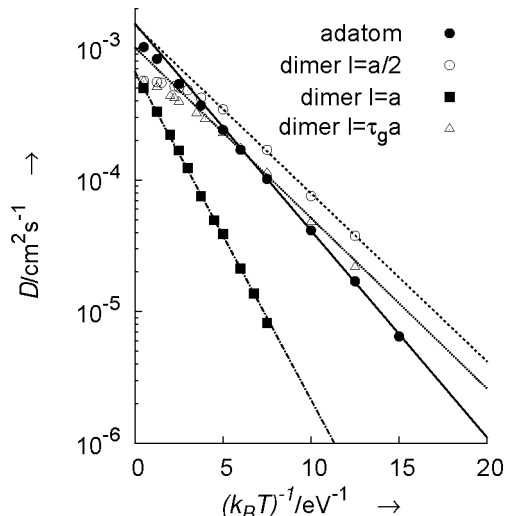FIG. 2. Diffusion coefficient D as a function of $1/(k_B T)$ for the adatom and the dimers with different values of l and $K = 2\ \mathrm{Nm}^{-1}$. The points are the result of the simulations and the lines represent fits to the data in the low-temperature regime.

For a rigid dimer, $E_a = 4U_0$ for $l = a$ down to $E_a = 0$ for $l = a/2$. If the dimer is not rigid, the activation energy is a non trivial function of the equilibrium length and elastic constant. In Figure 2, we show the diffusion coefficient for non rigid dimers with different values of l. We find $E_a = 0.6$ eV for $l = a$, $E_a = 0.3$ eV for $l = a/2$ and $E_a = 0.34$ eV for the incommensurate case $l = \tau_g a$, where $\tau_g = (1 + \sqrt{5})/2$ is the golden mean. The finite-barrier

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corrections to the Arrhenius behavior at high temperatures ($k_B T > 2U_0$) are rather pronounced for $l \neq a$. Deviations from the Arrhenius law due to incommensurability are also found for larger clusters. [19]

It has been suggested that non-Arrhenius behavior can result also from dynamical effects related to the internal motion of the dimer. [13,15] The role of the internal vibrations on the diffusive behavior is illustrated in Figure 3(a), where we compare the diffusion coefficient of the rigid and non rigid incommensurate dimer ($l = \tau_g a$).
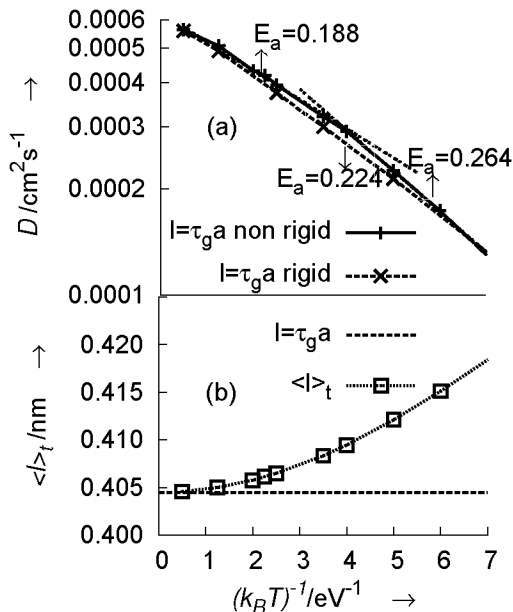
FIG. 3. (a) Diffusion coefficient as a function of $1/(k_B T)$ for the incommensurate dimer with $l = \tau_g a$ and $K = 2\,\mathrm{Nm}^{-1}$. The intramolecular length was kept fixed or not fixed, as indicated by the labels. Fitted activation energies [eV] are also reported. (b) Dynamical equilibrium length $< l >_t$ as a function of $1/(k_B T)$.

It is clear that we can define a unique value of E_a for the rigid dimer, whereas the activation energy is, in general, temperature dependent when the dimer is allowed to vibrate. The temperature dependence of E_a is linked to a temperature dependent misfit $< l >_t$, induced by the dynamics, as shown in Figure 3(b).

Moreover, the dimer can even diffuse faster than the adatom, at least for $l \neq a$ and low temperatures. Enhanced diffusivity of dimers and small clusters is also found by theoretical studies of $1D$ diffusion in molecular sieves [20] and in zeolite crystals. [21] Mitsui et al. [22] measured water diffusion on Pd(111) at low temperature ($T \simeq 40$ K), finding the mobility of dimers and larger clusters to be $3 - 4$ orders of magnitude larger than that of adatoms. This experimental result is compatible with our findings. In fact, extrapolation to low temperature of our results of Figure 2 shows that the dimer diffusion for $l \neq a$ can be orders of magnitude higher than for the

adatom. pin

V. RELATION BETWEEN DETERMINISTIC AND THERMAL DIFFUSION

We find that the chaotic dynamics discussed in Section III can give rise to a diffusive behavior, even in the absence of thermal fluctuations. The role of the heat bath is played by the exchange between translational and internal motion which, owing to the nonlinearity of the system, can occur in a random manner. Figure 4 shows a comparison between the deterministic and the thermal mean square displacements.
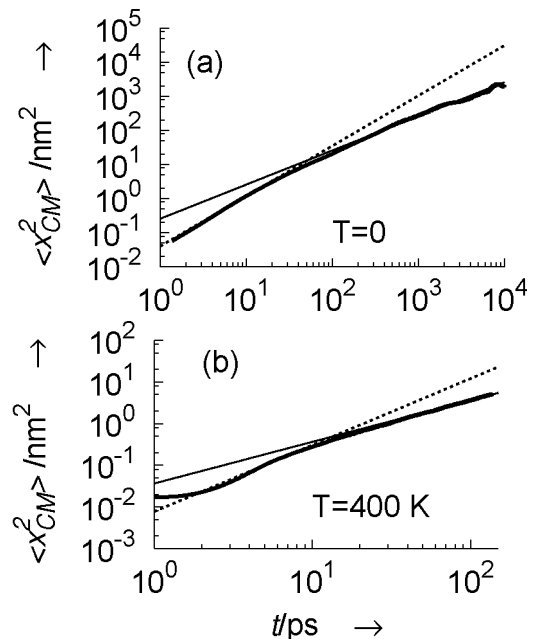
FIG. 4. Mean-square displacement for (a) the deterministic and (b) the thermal motion for $l = a$ (thick solid lines). (a) $K = 0.1\,\mathrm{Nm}^{-1}$, $v_0 = 475\,\mathrm{ms}^{-1}$, $\eta = 0$. (b) $K = 0.2\,\mathrm{Nm}^{-1}$. The thin solid lines are linear fits for large t; the dotted lines are power-law fits with exponent ~ 1.5 for small t. The data plotted in (b) were obtained by averaging the trajectory over 3000 realizations.

In the deterministic case $< x_{CM}^2 >$ represents a time averaging taken by displacing the time origin, [23] whereas at $T \neq 0$ it is an average over realizations. The long-time behavior is linear (diffusive) even for the Hamiltonian dynamics in the chaotic regime. In both cases we also find a transient superdiffusive regime ($< x_{CM}^2 > \propto t^\alpha$, with $\alpha \simeq 1.5$). Anomalous diffusion with $\alpha \simeq 7/5$ has also been observed in a model of adatom surface diffusion in two dimensions. [24] Anomalous diffusion might be related to long jumps of the dimer, that is to trajectories that move over multiple surface minima, [24,25] which do occur during our simulations. Furthermore, it has been claimed that a deterministic diffusive behavior leads to a

non-Arrhenius dependence of the thermal diffusion coefficient, [26] which is compatible with our results.

VI. CONCLUSIONS

We have presented a one-dimensional model to describe the diffusive dynamics of dimers on periodic surfaces. We have shown that the coupling between translational and vibrational degrees of freedom can lead to Hamiltonian chaotic motion and to non-Arrhenius behavior of thermal diffusion. We have also pointed out the relation between deterministic and thermal diffusion. It would be interesting to enhance the complexity of the system by considering orientational degrees of freedom in two dimensions and anharmonic intramolecular potentials.

ACKNOWLEDGEMENTS

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