SURFACE DIFFUSION WITH A REALISTIC DAMPING COEFFICIENT

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Abstract. We study the diffusion of a particle in a two-dimensional external potential. Simulation results show that, in the underdamped limit, the average jump length $\langle\lambda\rangle$ scales with the damping coefficient η as $\langle\lambda\rangle \propto \eta^{-\sigma_\lambda}$ with $1/2 \leq \sigma_\lambda \leq 2/3$, so that the diffusion coefficient behaves as $D \propto \eta^{-\sigma}$ with $0 \leq \sigma \leq 1/3$. We then introduce a realistic friction coefficient for the phonon damping mechanism. The study of diffusion in this model shows that long jumps play an essential role for diffusing atoms of small masses, especially in two limiting cases: a large substrate Debye frequency, when the rate of phonon damping is low, and a small Debye frequency, when the one-phonon damping mechanism is ineffective. As an application, we consider the diffusion of a dimer adsorbed on the crystal surface.

1. Introduction

A variety of phenomena in physics and other fields can be modeled as Brownian motion in an external periodic potential [1, 2]. One particular example, the surface diffusion of atoms or small clusters, is of great fundamental and technological interest [3]. At low temperatures T, $k_BT \ll \varepsilon$, where k_B is the Boltzmann constant and ε is the height of the substrate potential, diffusion proceeds by uncorrelated thermally activated jumps over the barrier from one minimum of the external potential to another, and the diffusion coefficient takes the Arrhenius form, $D \propto A = \exp(-\varepsilon/k_BT)$. If the jump rate is known, the D can be found with the help of a lattice-gas model for any symmetry of the lattice [4]. Usually, it is assumed that atoms can jump only to nearest neighboring minima of the substrate potential. In this case

$$D = \frac{1}{2d} R\langle\lambda^2\rangle, \tag{1}$$

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where $d = 1$ or 2 for surface diffusion, R is the total rate of escape from a potential well, and the mean-square jump length $\langle\lambda^2\rangle$ coincides with the square of the lattice constant a^2. To find the rate of atomic jumps, one has to study the diffusional dynamics, either by molecular dynamics (MD) methods, or with the help of a more simple approach based on the Langevin equation

$$m\ddot{r} + m\eta\dot{r} + dV(r)/dr = \delta F(t), \tag{2}$$

where m is the atomic mass and $V(r)$ is the substrate potential. The energy exchange between the diffusing atom and the substrate is modeled by a viscous frictional force with the coefficient η and by the random force δF which corresponds to Gaussian white noise,

$$\langle\delta F(t)\,\delta F(t')\rangle = 2\eta m k_B T \delta(t - t'). \tag{3}$$

A rigorous expression for the diffusion coefficient is known only in the overdamped limit, $\eta \gg \omega_0$ [here $\omega_0 = (V''/m)^{1/2}$ is the frequency of atomic vibration at the minimum of the substrate potential], when the Fokker-Planck-Kramers (FPK) equation corresponding to Eqs. (2–3) reduces to a more simple Smoluchowski equation. An analytical solution is known for the one-dimensional (1D) substrate potential [5] and for the quasi-two-dimensional case of a channel with periodically varying width [6, 7]. An approximate solution was found also for a two-dimensional (2D) substrate potential [8, 9].

A typical situation in surface diffusion corresponds to the case of intermediate or low damping. For intermediate friction, $\eta \sim \omega_0$, the diffusion can be adequately described by transition state theory (TST), where the total escape rate is given by the Kramers expression [10] $R \approx \omega_0 A/\pi$ which does not depend on η, and $\lambda = a$. This case was studied in a number of papers [11]. Molecular dynamics predicts that atomic jumps longer than a unit lattice spacing ($\langle\lambda\rangle > a$) always exist, but the increase in the jump length is approximately compensated by the decrease in the escape rate R because of "backward" jumps, so that Eq. (1) still holds [11].

The present paper is devoted to the interesting case of low damping, $\eta \ll \omega_0$, when long jumps may play a dominant role. The problem of multiple jumps, or flights, has been discussed in a number of papers [12, 13, 14]. The escape rate at low damping is restricted by slow diffusion in energy space [10], $R \propto \eta$, but the probability of atomic jumps for many lattice constants is highly increased [13, 15], $\langle\lambda\rangle \propto \eta^{-1}$. Thus, the diffusion coefficient scales as $D \propto \eta^{-1}$ for low damping. Analytical results are known for the 1D case in the $\eta \to 0$ limit only [1].

Although experiments do demonstrate the existence of atomic jumps for several lattice constants [16], a corresponding theory has not yet been

developed. There are two factors that may significantly reduce the jump length. Firstly, in two dimensions (2D), the path connecting adjoining sites may not coincide with the direction of the easy crossing of the saddle point. This has to reduce the probability of long jumps [17, 18], so one could expect a dependence

$$\langle\lambda\rangle \propto \eta^{-\sigma_\lambda} \tag{4}$$

with $\sigma_\lambda < 1$. Since the escape rate in a multidimensional space should still behave as $R \propto \eta$ [19], we come to the dependence

$$D \propto \eta^{-\sigma} \tag{5}$$

with $\sigma = 2\sigma_\lambda - 1 < 1$. In particular, with the help of numerical simulation for the 2D substrate potential Chen *et al.* [20] found that $\sigma = 0.5$, which gives $\sigma_\lambda = 0.75$. Afterwards, Caratti et al [21] showed that σ is not universal but depends on the geometry of the substrate potential.

Secondly, long jumps may exist in the case of low damping only. Generally, there always exists the phonon damping mechanism due to excitation of phonons in the substrate, with the rate proportional to the density of phonon states in the substrate. Since the frequency associated with the adatom motion may be of the same order of magnitude as the maximum frequency of phonons in the substrate (the Debye frequency, ω_m), the phonon damping coefficient $\eta_{\rm ph}$ may strongly depend on the atomic velocity. In order to study this effect, we have to develop a corresponding technique, since the standard approach based on Langevin or FPK equations is not valid because it assumes that η is constant

The main goal of the present work is to find the conditions when long jumps play an essential role in surface diffusion. Throughout this paper we use a dimensionless system of units. The period of the substrate potential is taken as $a = 2\pi$, the energy barrier for activated diffusion is $\varepsilon = 2$, and the mass of the substrate atoms is $m_s = 1$. The temperature is measured in energy units ($k_B = 1$). In simulations we typically used $T = 1/3$, which corresponds to activated diffusion ($\varepsilon/T = 6$ so that $A \approx 2.48 \times 10^{-3}$, $R_{\rm TST} = \omega_0 A/\pi \approx 7.89 \times 10^{-4}$, and $D_{\rm TST} = \frac{1}{2} R_{\rm TST} a^2 \approx 1.56 \times 10^{-2}$), but allows us to achieve a reasonable accuracy. The diffusion coefficient is calculated as $D = \langle x^2(t)\rangle/2t$ by solving the Langevin equation (see details in Ref. [7]).

2. Diffusion in a 2D External Potential

Firstly, we study the role of the two-dimensionality of the substrate potential, assuming that the damping coefficient η in Eqs. (2–3) is constant. We considered several variants of the 2D potential (all potentials are characterized by the lattice spacing $a = 2\pi$ and the heigh $\varepsilon = 2$): (a) The potential

with a channel shape having a periodically varying width,

$$V(x,y) = (1-\cos x) + \tfrac{1}{2}\omega_1^2 y^2 + \tfrac{1}{4}(\omega_2^2 - \omega_1^2)(1-\cos x)y^2\,, \qquad (6)$$

where we put $\omega_1 = \omega_0 = 1$, so that atomic vibrations at the minimum of the substrate potential are symmetric, and the parameter $g = \omega_1^2 - \omega_2^2$ controls the coupling of the x (along the diffusion path) and y (the transverse direction) degrees of freedom; (b) A pure 2D substrate potential of square symmetry,

$$V(x,y) = (1-\cos x) + (1-\cos y) + \tfrac{1}{2}(\omega_2^2 - 1)(1-\cos x)(1-\cos y)\,. \quad (7)$$

Along a diffusion path this potential is similar to the "channel" potential, except that now both directions x and y are equivalent; (c) The "most isotropic" 2D substrate potential, with the triangular symmetry,

$$V(x,y) = \tfrac{1}{2}\left[1 - \cos x\,\cos y/\sqrt{3} + \tfrac{1}{2}\left(1-\cos 2y/\sqrt{3}\right)\right]\,; \qquad (8)$$

(d) The substrate potential with hexagonal symmetry, constructed as a product of two triangular potentials appropriately scaled and shifted with respect to one another. Contrary to the potentials (a)–(c), in the honeycomb lattice, the path connecting the next-nearest neighboring sites does not coincide with a straight line. Thus, ballistic motion corresponding to long jumps should be suppressed, and the average jump length may be strongly reduced.

Some of the simulation results for the dependence $D(\eta)$ for a wide interval of η ($10^{-3} \le \eta \le 5$) are presented in Fig. 1 [the diffusion coefficient D is normalized to the exact value for the diffusion in the one-dimensional (1D) sinusoidal potential in the overdamped limit, $D_{\mathrm{Smol1D}} = D_f I_0^{-2}(\varepsilon/2k_BT)$, where $D_f = k_BT/m\eta$ and I_0 is the modified Bessel function]. In the overdamped limit the coupling between the modes produces the entropy barriers [7]. In the case $\omega_1 > \omega_2$, the diffusional "channel" is wider at the saddle point than at the minimum, so that the entropy barrier is negative, which works against the energy barrier ε, and thus leads to an increase of the diffusivity. This effect remains approximately the same for intermediate frictions down to $\eta \ge 0.1$. At lower damping, $\eta < 0.1$, the 2D effects lead to a qualitatively different behavior. While the 1D diffusion coefficient slowly approaches the $\eta \to 0$ limit $D_{\mathrm{R}} = \pi D_f A/2$ (see [1]), so that $D/D_{\mathrm{Smol1D}} \propto \eta D$ tends to a plateau, in the 2D case, the value ηD continues to decrease with η. In Ref. [7] we found that the activated diffusion in the channel of varying width at small η can be fitted by the power law (5) with $\sigma = 1/3$ both for the case of wide barriers ($g = 0.99$) and the case of narrow barriers ($g = -0.99$). Figure 1 demonstrates that the same is

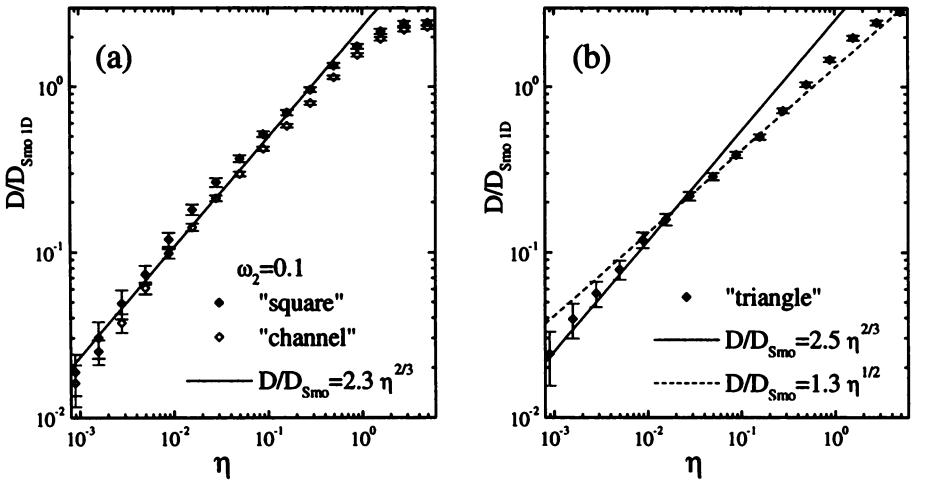

Figure 1. (a) $D(\eta)$ for the channel (open diamonds) and square (solid diamonds) substrate potentials for $\omega_1 = 1$ and $\omega_2 = 0.1$, and (b) the same for the triangular substrate potential. The lines show the low-damping fit $D \propto \eta^{-1/3}$. The dashed line in (b) describes the fit $D \propto \eta^{-1/2}$ of Chen *et al.* [20] for an interval of moderate damping.

true for square and triangular lattices. This leads to the scaling (4) of the jump length with the exponent $\sigma_\lambda = 2/3$. On the contrary, for the hexagonal lattice, the diffusion coefficient approaches a plateau, $D \propto \eta^0$ at small frictions, $\eta < 10^{-2}$.

From the simulation results it follows that the earlier results of Chen *et al.* [20] and Caratti *et al.* [21] do not correspond to the low-damping asymptotic behavior but to a crossover region of intermediate frictions. Calculating separately the escape rate R and the jump length λ, we found that they can be fitted by power laws $R(\eta) \propto \eta^{\sigma_R}$ and $\langle\lambda(\eta)\rangle \propto \eta^{-\sigma_\lambda}$ with the exponents σ_R and σ_λ. The escape rate exponent $\sigma_R \approx 0.9$ is close to the exact 1D value $\sigma_R = 1$. A small decrease of σ_R from 1 can be explained by the beginning of the crossover to the intermediate damping regime, where $\sigma_R = 0$. The results for the exponent σ_λ are, unfortunately, much less clear. The simulation leads to $\sigma_\lambda \sim 0.3 - 0.55$ for the 2D system, which is definitely lower than the value $\sigma_\lambda = 2/3 \approx 0.67$ predicted by the $D(\eta) \propto \eta^{-1/3}$ dependence.

In conclusion, the simulations predict that $0 \leq \sigma \leq 1/3$. The following speculations lead to the conjecture $\sigma_\lambda = 1/2$ for all 2D systems where the x and y degrees of freedom are coupled. Indeed, if the 2D external potential $V(x, y)$ is not separable, Newtonian motion in the conservative system should be stochastic in a general case [22]. For some initial conditions the

atomic trajectory is regular (e.g., the atom either oscillates in the same potential well, or it moves ballistically over the barriers), while for other initial conditions the motion is chaotic and corresponds to anomalous diffusion [22, 23], $\langle r^2 \rangle \propto t^{\nu}$. For the atoms that cross the barriers and have energies within a narrow "skin" layer close to $\varepsilon = 2$, the atomic trajectories are close to the separatrix trajectory in the $(x, \dot{x})$ phase space, so one could expect that these trajectories will be totally chaotic and the motion pure diffusional, $\nu \approx 1$. If we now include the external damping, then in the limit $\eta \to 0$ the jumping atoms all belong to a thin "skin" layer of width $\sim (\eta T)^{1/2}$ (e.g., see Refs. [1, 15]), so their trajectories should be close to the chaotic trajectories of the conservative system for times $t < \eta^{-1}$. Thus, one can predict that $\sigma_\lambda = 1/2$ and $\sigma = 0$ in the $\eta \to 0$ limit.

3. Diffusion of a Dimer

We now study the diffusion of a dimer in a 1D sinusoidal potential. Let x_1 and x_2 be the coordinates of two atoms coupled by an elastic spring with constant g and equilibrium distance $a_0 = 2\pi$. Introducing the coordinates $x = x_1 + x_2$ and $y = x_2 - x_1 - a_0$, the Hamiltonian can be written as

$$H = \tfrac{1}{2}m\left(\dot{x}^2 + \dot{y}^2\right) + \tfrac{1}{2}\varepsilon\left[1 - \cos\left(\tfrac{1}{2}x\right)\,\cos\left(\tfrac{1}{2}y\right)\right] + \tfrac{1}{2}\,g\,y^2, \qquad (9)$$

which describes the motion of one particle of mass $m = \frac{1}{2}m_a = \frac{1}{2}$ in the x-periodic potential of height $\varepsilon = 2\varepsilon_a = 4$ and period $a = 2a_s = 4\pi$.

The adiabatic trajectory for this system was studied in [24]. Its shape depends on a value of the elastic constant g. The points $(x, y) = (4\pi n, 0)$, where n is an integer, always correspond to the absolute minimum of the potential energy. Near the minimum, the potential energy has the expansion $V_N(x, y) \approx \frac{1}{2}m(\omega_{0x}^2 x^2 + \omega_{0y}^2 y^2)$ with $\omega_{0x} = 1$ and $\omega_{0y} = (2g + 1)^{1/2}$. For a strong spring, $g \geq 1/2$, there is only one saddle point at $(x_s, y_s) = (2\pi, 0)$ between two adjacent minima. Near the saddle, the potential energy has the expansion $V_N(x, y) \approx \varepsilon_s + \frac{1}{2}m[-\omega_{sx}^2(x - x_s)^2 + \omega_{sy}^2(y - y_s)^2]$ with $\varepsilon_s = 4$, $\omega_{sx} = 1$ and $\omega_{sy} = (2g - 1)^{1/2}$. Thus, dimer diffusion can be approximately described as the motion of one atom in a corrugated periodic potential with transverse frequencies $\omega_{1,2} = (2g \pm 1)^{1/2}$, i.e. it corresponds to the case of "wide" barriers studied above. Therefore, although the shape of the adiabatic trajectory does not depend on the elastic constant for $g \geq 1/2$, the diffusion coefficient does depend on g: it increases when $g \to 1/2$ due to the decrease of the transverse curvature at the saddle point. The simulation results show that close to the critical point $g = 1/2$, when anharmonicities of transverse vibrations at the saddle point are large, the entropy factor strongly depends on T, especially at low temperatures.

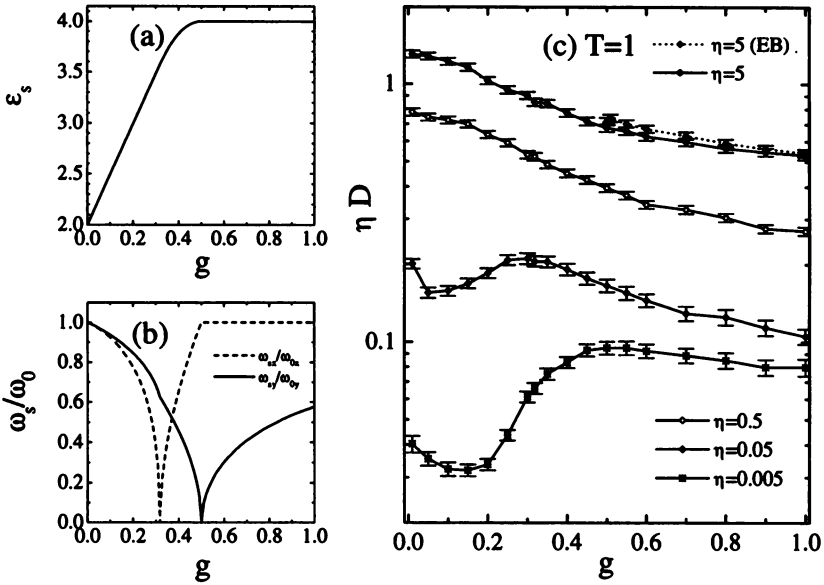

Figure 2. (a) The activation energy ε_s and (b) the ratio of frequencies at the saddle and minimum points as functions of the elastic constant g for dimer diffusion. (c) Dependence of the diffusion coefficient D (times η) on the elastic constant g at $T = 1$ for different values of the damping constant: $\eta = 5$ (dotted diamonds), $\eta = 0.5$ (open diamonds), $\eta = 0.05$ (solid diamonds), and $\eta = 0.005$ (crossed diamonds). The dotted curve and diamonds with plus signs show the simulation results for the "atom in channel" model with $\eta = 5$ and other parameters adjusted to the dimer case.

For intermediate values of the elastic constant, $1/\pi \leq g < 1/2$, the adiabatic trajectory still has only one saddle point $(2\pi, y_s)$ between the adjacent minima, which is characterized by the energy $\varepsilon_s(g) = \frac{1}{2}\varepsilon\,[1 + \cos(y_s/2)] + \frac{1}{2}gy_s^2$, so that $2 + \pi/2 < \varepsilon_s < 4$. Finally, for weak coupling between the atoms, $g < 1/\pi$, there are two saddle points between the adjacent minima, with a local minimum of the potential energy between these saddle points. The saddle points are characterized by the energy $\varepsilon_s(g) = \frac{1}{2}(\varepsilon + g\pi^2)$, so that $2 < \varepsilon_s < 2+\pi/2$. The dependence $\varepsilon_s(g)$ is shown in Fig. 2(a). The activation energy monotonically increases from the single-atom value $\varepsilon_s = 2$ at $g = 0$ to the rigid-dimer value $\varepsilon_s = 4$ at $g = 1/2$ and then remains constant. Thus, one could expect that the diffusion coefficient should monotonically decrease with increasing G. However, the simulation results show that often this is not true. The peculiarity in the transverse frequencies at the point $g = 1/2$, where the saddle transverse frequency reaches zero, leads to a maximum of the function $D(g)$ close to this point, if the damping is small, $\eta \leq 0.5$, and the temperature is not too low, $T \geq 1$ (recall that $\varepsilon = 4$). Thus, multi-dimensional effects may strongly affect dimer diffusivity.

4. Diffusion with Realistic Damping

The energy exchange between a moving atom and a substrate is caused by electromagnetic and electron-hole (e-h) mechanisms, which are approximately independent of the atomic velocity, and by phonon mechanisms, which strongly depend on this velocity. For small-amplitude vibrations of the atom at the bottom of the potential well, the damping mechanisms have been studied in detail theoretically as well as experimentally [25, 26]. The decay rate of the energy of an atom vibrating with a frequency ω due to one-phonon damping is

$$\eta_{\rm ph}(\omega) = \frac{\pi}{2}\frac{m}{m_s}\omega^2\rho(\omega). \tag{10}$$

The local density of phonon states $\rho(\omega)$ at the surface of a semi-infinite crystal can be approximated by [26] $\rho(\omega) = \frac{32}{\pi}\omega_m^{-6}\omega^2(\omega_m^2 - \omega^2)^{3/2}$, which has the correct behavior in the limits $\omega \to 0$ and $\omega \to \omega_m$. The one-phonon damping mechanism operates for frequencies lower than the maximum (Debye) frequency ω_m only, and its rate is small at small frequencies $\omega \ll \omega_m$, where $\eta_{\rm ph}(\omega) \propto \omega^4$. At $\omega > \omega_m$ the phonon damping is due to multi-phonon mechanisms and is characterized by a value [25, 26] $\eta_{\rm ph} \leq 10^{-2}\omega_0$.

Although Eq. (10) describes the rate of phonon damping for harmonic oscillations, one may expect that it will lead also to a reasonable accuracy for Brownian motion of atoms, if we use $\omega \sim \omega_0$ for the atoms vibrating close to the bottom of the potential well, and $\omega \sim \omega_{\rm wash} \equiv (2\pi/a)\langle v\rangle$ for the atoms moving over the barriers with an average velocity $\langle v\rangle$ when the velocity oscillates with the washboard frequency $\omega_{\rm wash}$. In the Langevin equation, however, we prefer to use a damping coefficient that depends on the instantaneous velocity of the atom [in a rigorous approach, based on the $\eta(\omega)$ dependence, the diffusion will be non-Markovian and the Langevin equation has to be replaced by a more complicated integro-differential stochastic equation, see [2] and references therein]. To couple the atomic velocity with the frequency in Eq. (10), we will use the relation $\omega = (2\pi/a)v$, so that the damping coefficient takes the form

$$\eta(v) = \eta_{\rm min} + \eta_{\rm ph}\,(2\pi v/a)\,, \tag{11}$$

where $\eta_{\rm min}$ describes the velocity-independent contribution to the external damping (the total action of the electromagnetic, e-h and multi-phonon damping mechanisms; in the simulation we used $\eta_{\rm min} = 0.01$), and $\eta_{\rm ph}(\omega)$ is given by Eq. (10).

One can show [27] that the random force $\delta F(t)$ in Eq. (2) in the case of a velocity-dependent friction coefficient has a correlator not given by Eq. (3), but by $\langle \delta F(t)\,\delta F(t')\rangle = 2\eta_R(v)mk_BT\delta(t-t')$, where the coefficient $\eta_R(v)$

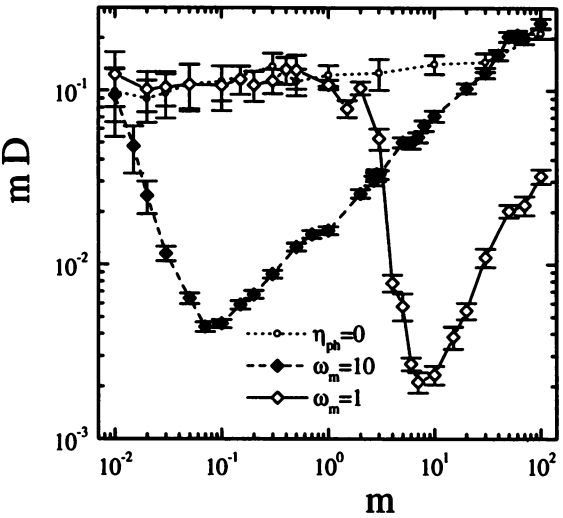

Figure 3. Diffusion coefficient D (times the atomic mass m) as a function of m for the 1D sinusoidal substrate potential with different Debye frequencies: $\omega_m = \infty$ (small open circles and dot curve), $\omega_m = 10$ (solid diamonds and dash curve), and $\omega_m = 1$ (open diamonds and solid curve).

is defined by the equation

$$\eta_R(v,T) = \int_0^\infty d\epsilon\, e^{-\epsilon}\eta\left(\tilde{v}(\epsilon)\right), \quad \tilde{v}^2(\epsilon) = v^2 + \frac{2k_BT}{m}\epsilon. \tag{12}$$

Calculations show that the deviation of $\eta_R(\omega)$ from $\eta(\omega)$ is more important at small frequencies and becomes relevant for $T > 10^{-2}\, m\omega_m^2 (a/2\pi)^2$.

The rate of phonon damping depends on the Debye frequency ω_m which is a characteristic of the substrate. To study the role of $\eta_{\rm ph}$, we made simulations for two values of ω_m, for a realistic (in our dimensionless units) value $\omega_m = 10$, and also for a quite small value $\omega_m = 1$ which may correspond to a soft substrate with low-frequency phonon spectrum, when the phonon damping could be very important. Because we fixed the mass of the substrate atoms in our dimensionless units ($m_s = 1$), now we will vary the mass of the diffusing atom in a wide range $m = 10^{-2} - 10^2$, so that the frequency $\omega_0 = m^{-1/2}$ changes from 10 to 0.1.

The dependences of the diffusion coefficient D on the mass m are presented in Fig. 3, where the functions $D(m)$ for $\omega_m = 1$ and $\omega_m = 10$ are compared to the case of no phonon damping. Due to phonon damping the total friction coefficient increases. This leads to an increase of the escape rate R, but the average jump length $\langle\lambda\rangle$ decreases, and the common action of both effects results in a decrease of the diffusion coefficient.

Let us first consider the case $\omega_m = 10$ (solid diamonds in Fig. 3). When the atom goes over the barrier, its energy is $\frac{1}{2}mv^2 \sim \varepsilon = 2$, so that $v \sim 2/\sqrt{m}$. Thus, for the lowest mass plotted in the figure ($m = 10^{-2}$), the characteristic atomic frequency, $\omega \sim 20$, is higher than the Debye frequency, $\omega_m = 10$, one-phonon damping is inoperative, the average jump length is large, $\langle\lambda\rangle > 10\,a$, and the diffusivity is high. Then, when the mass increases to $10^{-2} < m < 10^{-1}$, the velocity $v \sim 20 - 6$, so that the washboard frequency penetrates into the phonon zone, the one-phonon mechanism becomes operative, the damping sharply increases, goes through the largest value $\eta \sim 1.47\,m\omega_m \sim 1$ corresponding to the overdamped case, and then decreases to the intermediate friction regime. The jump length decreases to $\langle\lambda\rangle \sim a$, while the escape rate grows. Then, with the further increase of the mass to $10^{-1} < m < 10^2$, the total damping corresponds to the intermediate friction regime, so that the jump length remains small, $\langle\lambda\rangle \sim a$, and the escape rate and diffusion coefficient decrease, $D \propto R \propto \omega_0 \propto m^{-1/2}$. Note that, for large masses, $m > 10$, the phonon damping coefficient decreases to the small friction regime, since $\eta_{\mathrm{ph}} \propto v^4 \propto m^{-2}$, but long jumps are still suppressed due to the large mass of the atom. The "soft" substrate with $\omega_m = 1$ (open diamonds in Fig. 3) exhibits similar behavior. Now, the one-phonon damping mechanism comes into play at $m \approx \omega_m^{-1} = 1$. It is interesting that, around this point, $0.3 < m < 3$, the diffusion coefficient remains as high as for $\eta_{\mathrm{ph}} = 0$. Although the jump length decreases to $\langle\lambda\rangle \sim a$, the escape rate grows sharply and compensates this decrease.

Simulations for the 2D lattices lead to similar results. Thus, long jumps must exist for a diffusing atom with a small mass, $m < \omega_m^{-1}$, when the atom goes over the barriers so fast that the washboard frequency exceeds the maximum phonon frequency of the substrate, $v > a\omega_m/2\pi$, and one-phonon damping does not operate.

5. Conclusion

In the present work we have studied the role of long atomic jumps in activated surface diffusion. Firstly, simulation results predict that, in the underdamped limit, the diffusion coefficient behaves as $D \propto \eta^{-\sigma}$, where η is the coefficient of the viscous frictional force and $0 \leq \sigma \leq 1/3$. This allowed us to make the conjecture that the dependence $D \propto \eta^0$ should be universal in the $\eta \to 0$ limit for all nonseparable 2D substrate potentials.

Secondly, we proposed a realistic friction coefficient for the phonon damping mechanism that describes the energy exchange between the diffusing atom and the substrate. The simulation of diffusion in this model showed that long jumps (2–3 lattice spacings) do exist in the case of adatoms with small masses, $m < m_s$.

Finally, we would like to mention an interesting case of diffusion of adsorbed dimers [for example, the motion of Si_2 dimers on the Si(100) surface]. In this case the energy exchange between the vibrational, rotational and translational degrees of freedom may strongly affect the dimer diffusivity.

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References

1. Risken, H. (1996) *The Fokker-Planck Equation.* Springer, Berlin.
2. Hänggi, P., Talkner, P. and Borkovec, M. (1990) Reaction-rate theory: fifty years after Kramers, *Rev. Mod. Phys.* **62**, pp. 251–341.
3. Naumovets, A.G. and Vedula, Yu.S. (1985) Surface diffusion of adsorbates, *Surf. Sci. Rep.* **4**, pp. 365–434.
4. Braun, O.M. and Sholl, C.A. (1998) Diffusion in generalized lattice-gas models, *Phys. Rev. B* **58**, pp. 14870–14879.
5. Stratonovich, R.L. (1967) *Topics in the Theory of Random Noise.* Gordon and Breach, New York.
6. Zwanzig, R. (1983) Effective diffusion coefficient for a Brownian particle in a two-dimensional periodic channel, *Physica A* **117**, pp. 277–280.
7. Braun, O.M. (2001) Role of entropy barriers for diffusion in the periodic potential, *Phys. Rev. E* **63**, art. no. 011102.
8. Ala-Nissila, T. and Ying, S.C. (1992) Theory of classical surface diffusion, *Prog. Surf. Sci.* **39**, pp. 227–323.
9. Caratti, G., Ferrando, R., Spadacini, R. and G. E. Tommei, G.E. (1996) Noise-activated diffusion in the egg-carton potential, *Phys. Rev. E* **54**, pp. 4708–4721.
10. Kramers, H.A. (1940) Brownian motion in a field of force and the diffusion model of chemical reactions, *Physica* **7**, pp. 284–304.
11. Tully, J.C., Gilmer, G.H. and Shugard, J. (1979) Molecular dynamics of surface diffusion. I. The motion of adatoms and clusters, *J. Chem. Phys.* **71**, pp. 1630–1642; Doll, J.D. and McDowell, H.K. (1982) Theoretical studies of surface diffusion: Self-diffusion in the fcc (111) system, *J. Chem. Phys.* **77**, pp. 479–483; De Lorenzi, G. and Jacucci, G. (1985) The migration of point defects on bcc surfaces using a metallic pair potential, *Surf. Sci.* **164**, pp. 526–542.
12. Pollak, E., Bader, J., Berne, B.J. and Talkner, P. (1993) Theory of correlated hops in surface diffusion, *Phys. Rev. Lett.* **70**, pp. 3299–3302.
13. Ferrando, R., Spadacini, R. and Tommei, G.E. (1993) Kramers problem in periodic potentials: Jump rate and jump lengths, *Phys. Rev. E* **48**, pp. 2437–2451; Ferrando, R., Spadacini, R. and Tommei, G.E. (1995) Retrapping and velocity inversion in jump diffusion, *Phys. Rev. E* **51**, pp. 126–130.
14. Borromeo, M., Costantini, G. and Marchesoni, F. (1999) Critical hysteresis in a tilted washboard potential, *Phys. Rev. Lett.* **82**, pp. 2820–2823.
15. Borromeo, M. and Marchesoni, F. (2000) Backward-to-forward jump rates on a tilted periodic substrate, *Phys. Rev. Lett.* **84**, pp. 203–207.
16. Frenken, J.W.M., Hinch, B.J., Toennies, J.P. and Wöll, Ch. (1990) Anisotropic diffusion at a melting surface studied with He-atom scattering, *Phys. Rev. B* **41**, pp. 938–946; Ganz, E., Theiss, S.K., Hwang, I.S. and Golovchenko, J. (1992) Direct measurement of diffusion by hot tunneling microscopy: Activation energy, anisotropy, and long jumps, *Phys. Rev. Lett.* **68**, pp. 1567–1570; Ellis, J. and Toennies, J.P. (1993) Observation of jump diffusion of isolated sodium atoms on a Cu(001) surface by helium atom scattering, *Phys. Rev. Lett.* **70**, pp. 2118–2121; Senft, D.C. and Ehrlich, G. (1995) Long jumps in surface diffusion: One-dimensional migration of isolated adatoms, *Phys. Rev. Lett.* **74**, pp. 294–297.

17. Zhdanov, V.P. (1989) Dynamics of surface diffusion, *Surf. Sci.* **214**, pp. 289–303.
18. Haug, K., Wahnström, G. and Metiu, H. (1990) Hydrogen motion on a rigid Cu surface: The calculation of the site to site hopping rate by using fluxflux correlation functions, *J. Chem. Phys.* **92**, pp. 2083–2098.
19. Borkovec, M. and Berne, B.J. (1985) Reaction dynamics in the low pressure regime: The Kramers model and collisional models of molecules with many degrees of freedom, *J. Chem. Phys.* **82**, pp. 794–799; (1987) Activated barrier crossing for many degrees of freedom: Corrections to the low friction Kramers result, **86**, pp. 2444–2446; Straub, J.E., Borkovec, M. and Berne, B.J. (1987) Numerical simulation of rate constants for a two degree of freedom system in the weak collision limit, *J. Chem. Phys.* **86**, pp. 4296–4297.
20. Chen, L.Y., Baldan, M.R. and Ying, S.C. (1996) Surface diffusion in the low-friction limit: Occurrence of long jumps, *Phys. Rev. B* **54**, pp. 8856–8861.
21. Caratti, G., Ferrando, R., Spadacini, R. and Tommei, G.E. (1997) Underdamped diffusion in the egg-carton potential, *Phys. Rev. E* **55**, pp. 4810–4811.
22. Lichtenberg, A.J. and Lieberman, M.A. (1983) *Regular and Stochastic Motion.* Springer-Verlag, New York.
23. Geisel, T., Zacherl, A. and G. Radons, G. (1987) Generic $1/f$ noise in chaotic Hamiltonian dynamics, *Phys. Rev. Lett.* **59**, pp. 2503–2506; Geisel, T., Zacherl, A. and G. Radons, G. (1988) Chaotic diffusion and $1/f$ noise of particles in two-dimensional solids, *Z. Phys. B* **71**, pp. 117–127; Klafter, J. and Zumofen, G. (1994) Levy statistics in a Hamiltonian system, *Phys. Rev. E* **49**, pp. 4873–4877.
24. Braun, O.M. (1990) Adiabatic motion of an atomic chain in periodic potential, *Surf. Sci.* **230**, pp. 262–276.
25. Braun, O.M., Volokitin, A.I. and Zhdanov, V.P. (1989) Vibrational spectroscopy of adsorbates, *Usp. Fiz. Nauk* **158**, pp. 421–450. [*Sov. Phys. Usp.* **32** (1989) 605].
26. Braun, O.M. (1989) Energy exchange in adsorbed layers, *Surf. Sci.* **213**, pp. 336–358; Braun, O.M. and and Volokitin, A.I. (1986) Electron-hole mechanism of friction at chemisorbed atom vibrations, *Fiz. Tverd. Tela* **28**, pp. 1008–1014. [*Sov. Phys. – Solid State* **28** (1986) 564].
27. Gardiner, C.W. (1983) *Handbook of Stochastic Methods.* Springer-Verlag, Berlin.