

Role of entropy barriers for diffusion in the periodic potential

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Diffusion of a particle in the N -dimensional external potential which is periodic in one dimension and unbounded in the other $N-1$ dimensions is investigated. We find an analytical expression for the overdamped diffusion and study numerically the cases of moderate and low damping. We show that in the underdamped limit, the multidimensional effects lead to a reduction (compared to the one-dimensional motion) in the jump lengths between subsequent trappings of the atom at the minima of the external periodic potential. As an application, we consider the diffusion of a dimer adsorbed on the crystal surface.

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I. INTRODUCTION

A variety of phenomena in physics and other fields can be modeled as Brownian motion in an external periodic potential [1–3]. One particular example, the surface diffusion of atoms or small clusters, is of great fundamental and technological interest [4]. During crystal growth, the deposited atoms diffuse over the surface until they become incorporated into the lattice. On the semiconductor Si(100) or Ge(100) surface, most of the deposited Si or Ge atoms combine to form dimers, and the diffusion of such dimers has recently been studied experimentally by scanning tunneling microscopy [5]. Moreover, atoms adsorbed on metal surfaces in some cases form closely packed islands that diffuse as a whole [6,7].

Theoretically, the problem of diffusion can be described by a Langevin equation for the atom(s) or, equivalently, a Fokker-Planck-Kramers equation for the distribution function in the phase space [1,2]. In the trivial case of Brownian motion without the external potential, the diffusion coefficient is equal to $D = D_f \equiv k_B T / m \eta$, where k_B is the Boltzmann constant, T is the temperature, m is the particle mass, and η is the viscous damping coefficient that models the energy exchange with the substrate (thermostat). For a single atom in the one-dimensional (1D) sinusoidal external (substrate) potential, the value of diffusion coefficient is well known as summarized in the Risken monograph [1]. Exact results exist for the overdamped (Smoluchowski) case, $\eta \rightarrow \infty$, when [8]

$$D = D_f J_0^{-2}(h), \quad (1)$$

where $h \equiv \varepsilon / 2k_B T$, ε is the (total) height of the substrate potential, and $I_0(h)$ is the modified Bessel function, and in the underdamped limit, $\eta \rightarrow 0$ when [1]

$$D = D_f G(h), \quad (2)$$

where

$$G(h) = (h/2\pi)^{1/2} e^h I_0^{-1}(h) J(h),$$

$J(h) = \int_0^1 du u^{-3/2} e^{-2h/u} \mathbf{E}^{-1}(u)$, and $\mathbf{E}(u)$ is the complete elliptic integral of the second kind. At low temperatures, $k_B T \ll \varepsilon$, both expressions (1) and (2) take the Arrhenius form, $D = \bar{D} A$ with $A = \exp(-\varepsilon/k_B T)$ and $\bar{D} \approx \omega_0^2 a^2 / 2\pi \eta$ in the high-friction case [here a is the period of the substrate potential and $\omega_0 = (2\pi/a)(\varepsilon/2m)^{1/2}$ is the frequency of oscillation at its minimum], and $\bar{D} \approx \pi D_f / 2$ in the low-friction limit. In general, the diffusion coefficient can be found numerically with practically any desired accuracy using the matrix continued-fraction-expansion method [1].

At low temperatures, $k_B T \ll \varepsilon$, when the diffusion proceeds by uncorrelated thermally activated jumps over the barrier from one minimum of the external potential to another, the diffusion coefficient may be presented as $D = RA \langle \lambda^2 \rangle$, where RA is the rate of escape from a minimum of the external potential and $\langle \lambda^2 \rangle$ is the mean-square jump length. For moderate or large damping, $\eta \gtrsim \omega_0$, when only jumps for one period a of the external potential are possible, one should take $\lambda = a$ and $R = R_{\text{TST}} B(\eta)$, where $R_{\text{TST}} = \omega_0 / 2\pi$ is the escape rate given by the transition state theory (TST) [2,9], and the factor $B(\eta) = (z^2 + 1)^{1/2} - z$ with $z = \eta / 2\omega_s$ provides an interpolation between the TST and overdamped limits, as was found by Kramers [10] [here ω_s is the ‘‘saddle’’ frequency at the saddle point $x = x_s$, near which the external potential has the form $V(x) \approx \varepsilon - \frac{1}{2} m \omega_s^2 (x - x_s)^2$; for the sinusoidal potential $\omega_s = \omega_0$]. The underdamped limit, $\eta \ll \omega_0$, is qualitatively different: in this case $R \approx 2\eta \varepsilon / \pi k_B T \propto \eta$, as was found first by Kramers [10], but the average jump length diverges as $\lambda \propto \eta^{-1}$. Thus, this again leads to the dependence $R \lambda^2 \propto \eta^{-1}$, similarly to the overdamped case. The occurrence of long jumps, $\lambda > a$, has been observed in a number of experiments on surface diffusion [4,11]. The interval from low to moderate friction is covered by the Mel’nikov-Meshkov formula [12]

$$R_{\text{MM}} \approx R_{\text{TST}} \exp \left(\frac{1}{\pi} \int_0^\infty du \frac{\ln \left\{ 1 - \exp \left[-\Delta \left(u^2 + \frac{1}{4} \right) \right] \right\}}{u^2 + \frac{1}{4}} \right), \quad (3)$$

where $\Delta = 8h\eta/\omega_0$. Thus, the whole interval of frictions may be described by the interpolation formula R

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$\approx R_{\text{MM}}B(\eta)$, which was checked numerically in [13]. Combining this expression for R with the numerically calculated values of D , one can find the distribution of jump lengths [14]. Note that the widely used TST expression $D \approx R_{\text{TST}}Aa^2$, where the diffusion coefficient does not depend on the damping coefficient, operates in fact for a narrow interval of friction close to the point $\eta \sim \omega_0$ only (which, fortunately, often corresponds to experimental situations).

Although the results described above for one-dimensional diffusion are very important and often lead to reasonable estimations for experimentally measured diffusion coefficients, in real systems the motion always takes place in a $N > 1$ configurational space. Indeed, even for diffusion of a single atom adsorbed on a crystal surface, $N=2$ at least. Besides, the diffusing object may have internal degrees of freedom. Multidimensional effects modify both the escape rate R and the jump length λ . The escape rate can be presented as $R = R_{\text{1D}}F$, where the coefficient F is known as the ‘‘entropy factor’’ [15]. The value of F can be found with the help of transition state theory [9], which yields $F \approx (\prod_i \omega_{0,i}) / (\prod_i \omega_{s,i})$, where $\omega_{0,i}$ are the frequencies at the minimum and $\omega_{s,i}$ are the saddle frequencies for all degrees of freedom i except the one given along the diffusion path. In this approach, F can be interpreted as $F = \exp(\Delta S/k_B)$, where ΔS is the difference in entropy between the saddle and minimum-energy configurations. The entropy factor is often used to explain the ‘‘compensation effect’’ [4], when during an experiment one observes that a decrease in the activation energy (calculated as a slope of the Arrhenius plot of $\ln D$ versus T^{-1}) is compensated by a decreasing of the prefactor. As for the jump length, while for $\eta \gtrsim \omega_0$ it still is given by $\lambda = a$, in the underdamped limit it is modified qualitatively compared with the one-dimensional case. In multidimensional space, the path connecting adjoining minima of the external potential may not coincide with the direction of easy crossing at the saddle point. Therefore, the probability of deactivation during long jumps is enhanced, leading to a reduction in the jump length, $\lambda < \lambda_{\text{1D}}$ [16–18]. In particular, for the 2D-periodic substrate potential with square symmetry, it was found numerically [18] that $D \propto \eta^{-0.5}$, which gives $\lambda \propto \eta^{-0.75}$.

The multidimensional effects are also important in the diffusion of molecules or small clusters: even for diffusion in the 1D periodic potential (e.g., along ‘‘channels’’ on furrowed or stepped surfaces) one has, for the diffusion of the dimer, $N=2$ at least. Diffusion of the dimer was studied numerically by Vollmer [19] with the help of the matrix continued-fraction-expansion technique. The adiabatically slow motion of a linear molecule in the 1D sinusoidal potential was analyzed in [20], where the adiabatic trajectory was found for a general case. This made it possible to find the activation barriers and the minimum-energy and saddle-state frequencies and then to estimate the diffusion coefficient.

The aim of the present paper is to study the multidimensional effects in the diffusion processes. We consider two typical examples: motion of a single atom in a channel that is periodic in one dimension and parabolic in others, and diffusion of a dimer (two-atom molecule) in the 1D sinusoidal potential. We find an analytical solution for the overdamped

case and analyze numerically the dependence of diffusion coefficient on the damping constant η . The numerical results were obtained with the Verlet algorithm by calculating the trajectory $x(t)$ and then splitting it into N_{tr} pieces, each with a time duration τ . The diffusion coefficient was then calculated as $D = \langle \Delta x^2 \rangle / 2\tau$.

The paper is organized as follows. In Sec. II we obtain the analytical expression for the diffusion coefficient in the overdamped limit. In Sec. III A we analyze the case of pure entropic barriers. In Sec. III B the activated diffusion of a single atom is studied. In Sec. III C the diffusion of a dimer is described. Finally, Sec. IV concludes the paper.

II. OVERDAMPED LIMIT

Consider a particle moving in the N -dimensional external potential $V_N(x, y_1, \dots, y_{N-1})$ which is periodic in the x direction,

$$V_N(x+a, \dots) = V_N(x, \dots), \quad (4)$$

and grows unboundedly in the other $N-1$ dimensions,

$$V_N(x, y_1, \dots, y_{N-1}) \rightarrow \frac{1}{2} \omega_i^2(x) y_i^2 \quad \text{if } y_i \rightarrow \pm \infty, \quad (5)$$

where $\omega_i(x) > 0$ for all x .

In the presence of viscous friction, the particle motion should be diffusive on long time scales. The diffusion coefficient D can be found with the Einstein relation $D = T\mu$, where the mobility μ describes the proportionality between the linear current j and the infinitesimal external dc force f which causes this current, $j = \mu f$. Therefore, we have to consider the particle motion in the external potential,

$$V_f(x, y_1, \dots, y_{N-1}) = V_N - fx, \quad (6)$$

and then take the limit $f \rightarrow 0$.

In the overdamped case, when the friction coefficient η is much larger than the characteristic system frequencies, the motion of the particle is described by the Smoluchowski equation

$$\frac{\partial W}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0, \quad \vec{J} = -\eta^{-1} (W \vec{\nabla} V_f + T \vec{\nabla} W), \quad (7)$$

where $W(x, y_1, \dots, y_{N-1}; t)$ is the distribution function, $\vec{J}(x, y_1, \dots, y_{N-1}; t)$ is the density of the particle’s current, and the particle mass and Boltzmann constant are put to unity, $m=1$ and $k_B=1$.

For a steady state, Eq. (7) takes the form

$$T \frac{\partial W}{\partial x} + W \frac{\partial V_f}{\partial x} = -\eta J_x \quad (8)$$

for the x component, and a similar form for other degrees of freedom. The density \vec{J} of the current should satisfy the equation

$$\frac{\partial J_x}{\partial x} + \sum_{i=1}^N \frac{\partial J_{y_i}}{\partial y_i} = 0. \quad (9)$$

To reduce notation, below we consider the case of $N=2$ only; generalization to the $N>2$ case is simple. Let us introduce the one-dimensional density and current as

$$\rho(x) = \int_{-\infty}^{+\infty} dy W(x,y), \quad (10)$$

$$j(x) = \int_{-\infty}^{+\infty} dy J_x(x,y). \quad (11)$$

Owing to condition (5), the current $j(x)$ does not depend on x ,

$$\frac{dj(x)}{dx} = -J_y(x, +\infty) + J_y(x, -\infty) = 0, \quad (12)$$

where we have used Eq. (9). Thus, integrating both parts of Eq. (8) over y , we obtain the one-dimensional equation

$$T \frac{d\rho(x)}{dx} + \rho(x) \frac{dV_F(x)}{dx} = -\eta j, \quad (13)$$

where we introduce the potential $V_F(x)$ defined by the equation

$$\frac{dV_F(x)}{dx} = [\rho(x)]^{-1} \int_{-\infty}^{+\infty} dy W(x,y) \frac{\partial V_f(x,y)}{\partial x}. \quad (14)$$

Now, if $V_F(x)$ may be presented in the form

$$V_F(x) = V_N(x;f) - fx, \quad (15)$$

where $V_N(x;f)$ is a periodic function of x , Eq. (13) takes the form studied in [8], and the diffusion coefficient can be calculated as

$$D = D_f (I_+ I_-)^{-1}, \quad I_{\pm}(T) = (2\pi)^{-1} \int_0^{2\pi} dx e^{\pm V_{\text{eff}}(x)/T}, \quad (16)$$

where $D_f = T/\eta$ and $V_{\text{eff}}(x) = \lim_{f \rightarrow 0} V_N(x;f)$. Thus, the diffusion coefficient D is determined by the one-dimensional function $V_N(x;0)$. In the limit $f \rightarrow 0$ we may substitute the equilibrium distribution function $W = W_{\text{eq}} \propto \exp(-V_N/T)$ into Eq. (14), thus obtaining

$$\frac{dV_{\text{eff}}(x)}{dx} = \frac{\int_{-\infty}^{+\infty} dy e^{-V_N(x,y)/T} \partial V_N(x,y) / \partial x}{\int_{-\infty}^{+\infty} dy e^{-V_N(x,y)/T}}. \quad (17)$$

We emphasize that this is the key approximation which is rigorous in the overdamped limit only. For the underdamped case, $\eta \rightarrow 0$, a similar multiplicative separation in the

Fokker-Planck-Kramers equation, $W(x,y,v_x,v_y,f) \propto W(x,v_x,f) W_{\text{eq}}(y,v_y)$, does not work even in the $f \rightarrow 0$ limit.

Let $V_N(x,y)$ take the form

$$V_N(x,y) = V(x) + U(y) + v(x,y), \quad (18)$$

where the function $v(x,y)$ describes the coupling between the two degrees of freedom. Then the effective potential $V_{\text{eff}}(x)$ can be presented in the form

$$V_{\text{eff}}(x) = V(x) - TS(x,T), \quad (19)$$

where the ‘‘entropy potential’’ $S(x,T)$ is defined by the expression

$$S(x,T) = \ln \int_{-\infty}^{+\infty} dy \exp\{-[U(y) + v(x,y)]/T\}. \quad (20)$$

Notice that $S(x)$ does not depend on $V(x)$.

III. APPLICATIONS

A. Pure entropy barriers

Let $V(x) = 0$ in Eq. (18),

$$U(y) = \frac{1}{2} m \omega_1^2 y^2, \quad (21)$$

and

$$v(x,y) = \frac{1}{4} m (\omega_2^2 - \omega_1^2) (1 - \cos x) y^2, \quad (22)$$

so that the atomic motion is inactivated in the x direction, but the frequency of transverse oscillation depends on x , $\omega = \omega_1$ at $x=0$, and $\omega = \omega_2$ at $x=\pi$. Then the integral in Eq. (20) can be easily evaluated analytically, and the entropy potential is given by the expression

$$S(x) = -\frac{1}{2} \ln \left\{ 1 + \frac{1}{2} \left[\left(\frac{\omega_2}{\omega_1} \right)^2 - 1 \right] (1 - \cos x) \right\}. \quad (23)$$

Notice that the entropy potential (23) does not depend on temperature, because both potentials (21) and (22) depend on y in the same way ($\propto y^2$). The function $S(x)$ is shown in Fig. 1. It is periodic with the period $a=2\pi$ and the height $\varepsilon_S = |\ln(\omega_2/\omega_1)|$. The diffusion coefficient is given by $D = D_f F$, where the entropy factor F depends on the ratio of frequencies $z = \omega_2/\omega_1$ only,

$$F(z) = [I_+(z) I_-(z)]^{-1}, \quad (24)$$

where

$$I_{\pm}(z) = \pi^{-1} \int_0^{\pi} dx \left[1 + \frac{1}{2} (z^2 - 1) (1 - \cos x) \right]^{\pm 1/2}. \quad (25)$$

Equations (24,25) yield

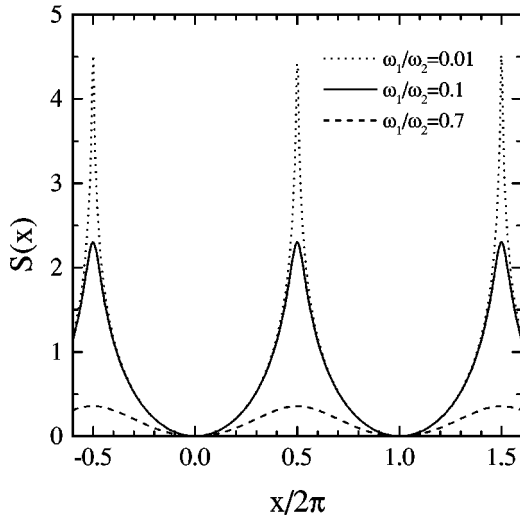


FIG. 1. Entropy potential $S(x)$ for pure entropic barriers with $\omega_1/\omega_2=0.01$ (dotted curve), $\omega_1/\omega_2=0.1$ (solid curve), and $\omega_1/\omega_2=0.7$ (dashed curve) respectively.

$$F(z) = (\pi/2)^2 \mathbf{K}^{-1}(\sqrt{1-z^2}) \mathbf{E}^{-1}(\sqrt{1-z^2}),$$

where \mathbf{K} is the complete elliptic integral of the first kind. Near $z \approx 1$ the function $F(z)$ has the expansion $F(z) \approx 1 - \frac{1}{8}(1-z)^2$, while at $z \rightarrow 0$ it behaves as $F(z) \approx (\pi/2)^2 \ln^{-1}(4/z)$. The function $F(z)$ is presented in Fig. 2. One can see that in the overdamped limit, the effect of entropy barriers is not very strong, in particular, even for $\omega_1/\omega_2=0.1$ the diffusion coefficient decreases compared with the free-diffusion value by a factor of $F(0.1) \approx 0.66$ only. Indeed, although the height ε_S tends to infinity at $z \rightarrow 0$, the widths of the barriers become very narrow and thus cannot exert much influence on the diffusion coefficient.

Conversely, in the underdamped case the role of the entropy barriers is essential. The dependence of the diffusion coefficient on the damping constant η was obtained numerically and shown in Fig. 3. One can see that the function

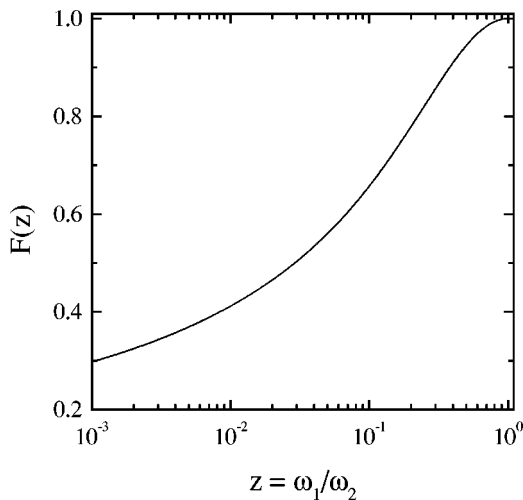


FIG. 2. Entropy factor $F(\omega_1/\omega_2)$ for pure entropy barriers in the overdamped limit.

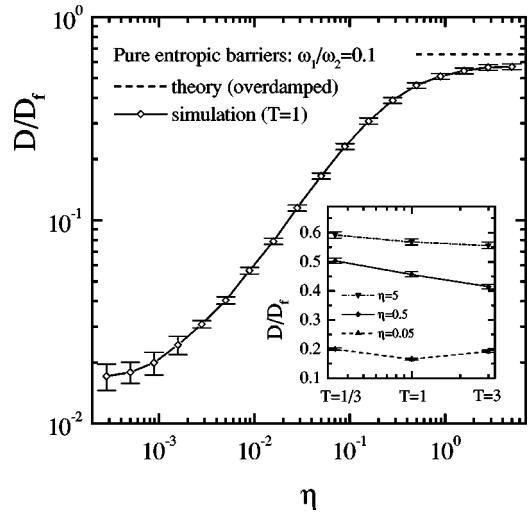


FIG. 3. Diffusion coefficient D/D_f (where $D_f = k_B T/m \eta$) as a function of the friction coefficient η for pure entropic barriers with $\omega_1=0.1$ and $\omega_2=1$ at $T=1$. Inset: dependence on temperature ($T=1/3, 1$, and 3) for $\eta=0.05$ (up triangles), 0.5 (diamonds), and 5 (down triangles).

$D(\eta)$ exhibits a typical behavior of activated diffusion ($D \propto \eta^{-1}$ at small and large frictions with a crossover between the limits) as might be expected from the shape of the entropy potential $S(x)$ of Fig. 1. In the overdamped limit the average jump length is equal to the period of the potential $S(x)$, $\lambda \approx 2\pi$, while in the underdamped limit long jumps with $\lambda/2\pi \gg 1$ play the dominant role as shown in Fig. 4 (in these simulations we assumed that the atom is trapped in a given well if it has sojourned in this well for a time period not shorter than $(2\eta)^{-1}$ [1,21]). The effect of entropy barriers

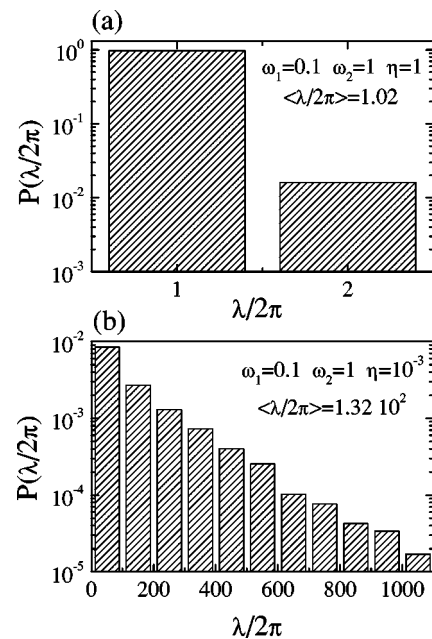


FIG. 4. Distribution of jump length for pure entropic barriers with $\omega_1=0.1$ and $\omega_2=1$ at $T=1$ for (a) the overdamped case ($\eta=1$) and (b) the underdamped limit ($\eta=10^{-3}$).

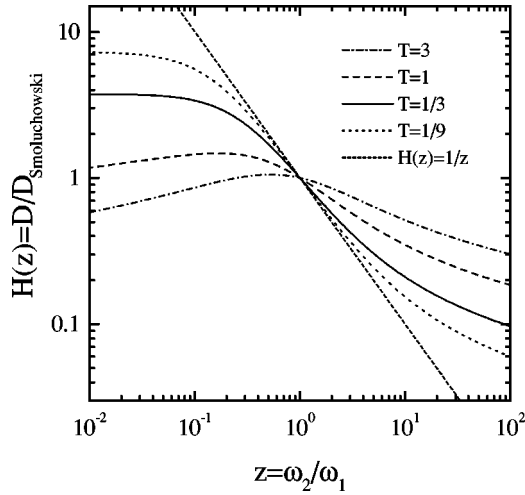


FIG. 5. Activated diffusion with barrier $\varepsilon = 2$: D [normalized on the Smoluchowski value (1)] versus the ratio of transverse frequencies $z = \omega_2/\omega_1$ in the overdamped limit for temperatures $T = 3$ (dot-dashed curve), $T = 1$ (dashed curve), $T = 1/3$ (solid curve), and $T = 1/9$ (dotted curve). The short-dashed line shows the TST approximation.

ers is even stronger than might be expected from the analogy with the energy barriers of the same height. For example, for the frequencies $\omega_1/\omega_2 = 0.1$ used in the simulation, the height of the barrier is $\varepsilon_S = S(\pi) \approx 2.3$, which would yield the ratio $D(\eta \rightarrow \infty)/D(\eta \rightarrow 0) \approx 2\varepsilon_S/k_B T \approx 4.6$ for the $T = 1$ case, while the simulation leads to the ratio $D(\eta \rightarrow \infty)/D(\eta \rightarrow 0) > 33$. From Fig. 4(b) one can see that $\langle \lambda/2\pi \rangle \approx 10^2$ for the case of $\eta = 10^{-3}$, while for the one-dimensional diffusion it should be $\langle \lambda/2\pi \rangle \sim \eta^{-1} = 10^3$. Thus, multidimensional effects result in a significant reduction of the jump length in the underdamped limit, which leads to a decrease in the diffusion coefficient compared with the 1D motion. Note also that the dependence on temperature (shown in inset of Fig. 3) is almost negligible, as should to be expected for the entropy potential.

B. Atom in a corrugated channel

Allow now that the dependence of the external potential $V_N(x, y)$ on y is still given by Eqs. (21) and (22), but motion in the x direction is activated,

$$V(x) = \frac{1}{2} \varepsilon (1 - \cos x), \quad (26)$$

where ε is the height of the external potential. At the minima of the potential (26), the transverse vibrations are characterized by the frequency ω_1 , while at the saddle points, they are characterized by the frequency ω_2 . In the one-dimensional case, as well as for the 2D case with $\omega_1 = \omega_2$, in the overdamped limit we have, according to Eq. (1), $D_{\text{Smoluchowski}} = D_f I_0^{-2}(\varepsilon/2T)$. Because the entropy potential $S(x)$ does not depend on the function $V(x)$, it is still given by Eq. (23), and the integral (16) can be easily evaluated. The results for the overdamped limit are shown in Fig. 5, which can be compared with the simulation results for different degrees of

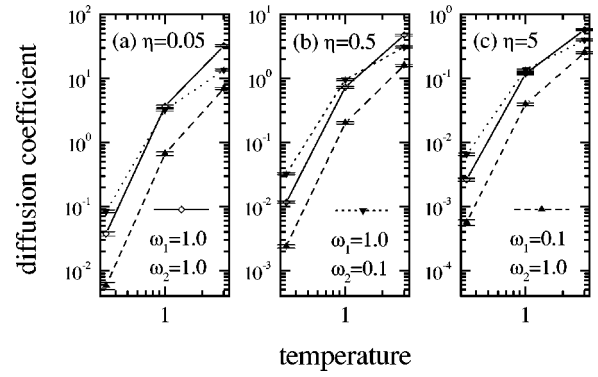


FIG. 6. D versus T for activated motion with barrier $\varepsilon = 2$ for three values of transverse frequency (open diamonds and solid curves for $\omega_1 = \omega_2 = 1.0$, down triangles and dotted curves for wide barriers with $\omega_1 = 1.0$ and $\omega_2 = 0.1$, and up triangles and dashed curves for narrow barriers with $\omega_1 = 0.1$ and $\omega_2 = 1.0$) for three values of external damping: (a) $\eta = 0.05$, (b) $\eta = 0.5$, and (c) $\eta = 5$.

friction presented in Figs. 6 and 7. From the $D(T)$ dependence of Figs. 5 and 6, one can see that at high temperatures, when the motion is deactivated, the $\omega_1 = \omega_2$ case leads to the maximum of the diffusion coefficient, similarly to the case with pure entropic barriers. With decreasing temperature, the energy barriers and the entropy barriers play “in phase” for the narrow-barriers case of $\omega_1 < \omega_2$, and “in antiphase” for the wide-barriers case of $\omega_1 > \omega_2$. At low temperatures $D > D_{\text{1D}}$ for the case of $\omega_1 > \omega_2$ at high and moderate degrees of friction, in agreement with predictions of the TST approach. The effect, however, is smaller than the TST predicts: in our simulation, we found that the diffusion coefficient changes only three times when the ratio of frequencies is equal to ten. At very low

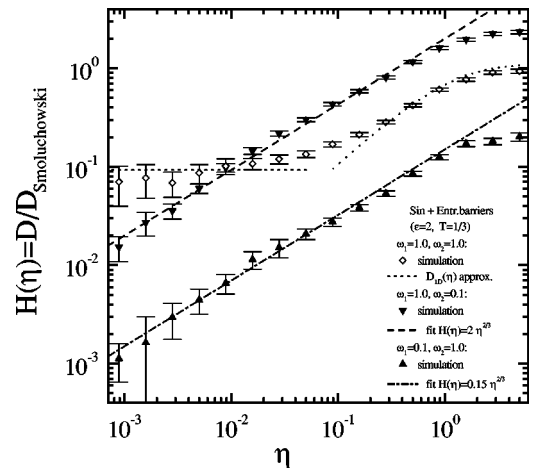


FIG. 7. Diffusion coefficient D [normalized on the Smoluchowski value (1)] as a function of friction coefficient η for activated motion with barrier $\varepsilon = 2$ at $T = 1/3$ for three values of transverse frequency: (1) $\omega_1 = \omega_2 = 1.0$ [open diamonds; the dotted curves show the 1D approximate values $D \approx (\omega_0/2\pi)Aa^2B(\eta)$ and $D \approx \pi D_f A/2$ at high and low friction, respectively], (2) $\omega_1 = 1.0$ and $\omega_2 = 0.1$ (down triangles, wide barriers), and (3) $\omega_1 = 0.1$ and $\omega_2 = 1.0$ (up triangles, narrow barriers). The dashed lines show the fit $D(\eta) \propto \eta^{-1/3}$.

friction (e.g., $\eta < 10^{-2}$ in Fig. 7), the entropy barriers become more important than the energy barriers, and the diffusion coefficient again becomes smaller than the 1D one for all cases of $\omega_1 \neq \omega_2$, as it was for the case of pure entropic barriers. For moderate and low friction the simulation results of Fig. 7 can be fitted by a dependence $D(\eta) \propto \eta^{-1/3}$. Because the escape rate R is still proportional to η in the multidimensional case [22], we may conclude that in the present case, the average jump length scales as $\langle \lambda \rangle \propto \eta^{-2/3}$, which is in agreement with the results for pure entropic barriers presented in the preceding subsection, and also may be compared with the 1D law $\langle \lambda \rangle \propto \eta^{-1}$ and the 2D simulation result [18] $\langle \lambda \rangle \propto \eta^{-3/4}$. Thus, in the underdamped limit, multidimensional effects lead to decreasing diffusivity (compared with the 1D case) due to a reduction in jump length, which scales as $\langle \lambda \rangle \propto \eta^{-2/3}$ instead of the 1D scaling law $\langle \lambda \rangle \propto \eta^{-1}$.

C. Diffusion of the dimer

Now we can study diffusion of a dimer in the 1D sinusoidal potential. Let x_1 and x_2 be the coordinates of two atoms coupled by the elastic spring with the constant g , and a_0 be the equilibrium distance ($0 \leq a_0 \leq \pi$). Then the Hamiltonian of the system takes the form

$$H = \frac{1}{2} m_a \dot{x}_1^2 + \frac{1}{2} m_a \dot{x}_2^2 + \frac{1}{2} \varepsilon_s (1 - \cos 2\pi x_1 / a_s) + \frac{1}{2} \varepsilon_s (1 - \cos 2\pi x_2 / a_s) + \frac{1}{2} g (x_2 - x_1 - a_0)^2. \quad (27)$$

In what follows, we put $\varepsilon_s = 2$, $m_a = 1$, $a_s = 2\pi$, and in the present paper we consider the case of $a_0 = 0$ only. Introducing the coordinates $x = x_1 + x_2$ and $y = x_2 - x_1$, the Hamiltonian (27) can be rewritten as

$$H = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2) + V_N(x, y);$$

$$V_N(x, y) = \frac{1}{2} \varepsilon \left(1 - \cos \frac{x}{2} \cos \frac{y}{2} \right) + \frac{1}{2} g y^2, \quad (28)$$

which describes the motion of one particle of mass $m = m_a/2 = 1/2$ 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 [20]. 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 $(0, 0)$ and $(4\pi, 0)$. Near the saddle, the potential energy has the expansion

$$V_N(x, y) \approx \varepsilon_s + \frac{1}{2} m [-\omega_{sx}^2 (x - x_s)^2 + \omega_{sy}^2 (y - y_s)^2], \quad (29)$$

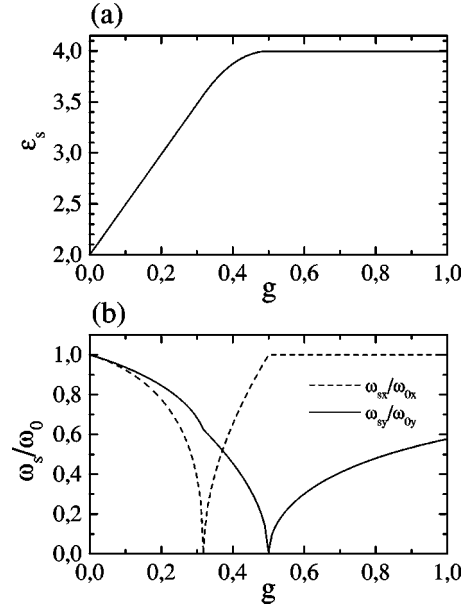


FIG. 8. (a) Activation energy ε_s and (b) ratio of frequencies at the saddle and minimum points as functions of the elastic constant g for dimer diffusion.

with $\omega_{sx} = 1$ and $\omega_{sy} = (2g - 1)^{1/2}$, so that the activation energy for dimer motion is equal to $\varepsilon_s = \varepsilon = 4$ (see Fig. 8). Therefore, dimer diffusion can be roughly described as the motion of one atom in the corrugated periodic potential with the transverse frequencies $\omega_{1,2} = (2g \pm 1)^{1/2}$, i.e., it corresponds to the case of wide barriers studied in the preceding subsection. Thus, although the shape of adiabatic trajectory does not depend on the elastic constant for the case of strong coupling, the diffusion coefficient does depend on g ; it increases when $g \rightarrow 1/2$ due to the decreasing of the transverse curvature at the saddle point. The simulation results of Fig. 9

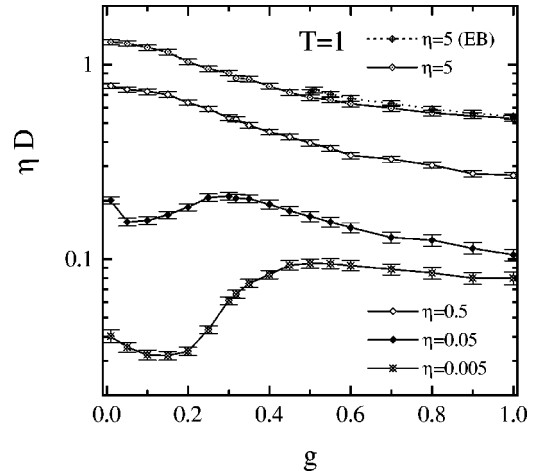


FIG. 9. Dependence of diffusion coefficient D (times η) on the elastic constant g at $T=1$ for different values of the damping constant: $\eta=5$ (dotted diamonds), $\eta=0.5$ (open diamonds), $\eta=0.05$ (solid diamonds), and $\eta=0.005$ (crossed diamonds). The dotted curve and cross-hatched diamonds show the simulation results for the “atom in channel” model with $\eta=5$ and other parameters adjusted to the dimer case.

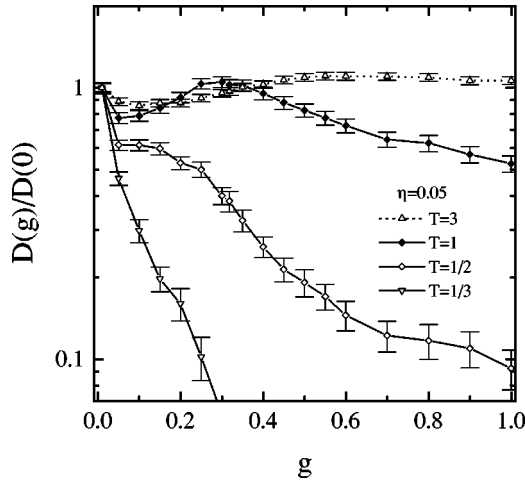


FIG. 10. Ration $D(g)/D(0)$ as a function of the elastic constant g for the dimer diffusion at $\eta=0.05$ and different temperatures $T = 3, 1/2, 1/3$.

show that the harmonic approximation describes the $D(g)$ dependence with a good degree of accuracy. From Fig. 10, where the ratio $D(g)/D(0)$ is presented for different temperatures, one can see also that close to the critical point $g = 1/2$, when anharmonicity of transverse vibrations at the saddle point is large, the entropy factor strongly depends on T , especially at low temperatures.

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, where y_s is now a solution of the equation $\sin(y_s/2) = gy_s$. Near the saddle, the potential energy has the expansion (29) with frequencies $\omega_{sx} = [1 - (gy_s)^2]^{1/4}$ and $\omega_{sy} = (2g - \omega_{sx}^2)^{1/2}$. The saddle 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 a weak coupling between dimer atoms, $g < 1/\pi$, there are two saddle points between the adjacent minima $(0,0)$ and $(4\pi,0)$, with a local minimum of the potential energy between these saddle points. The coordinates of the saddle points are $(2\pi - x', \pi)$ and $(2\pi + x', \pi)$, where $x' = 2 \cos^{-1}(g\pi)$. These saddle points are characterized by the energy $\varepsilon_s(g) = \frac{1}{2}(\varepsilon + g\pi^2)$, so that $2 < \varepsilon_s < 2 + \pi/2$. Near the saddle, the potential energy has the expansion (29) with coefficients $\omega_{sx} = (g - G)^{1/2}$ and $\omega_{sy} = (g + G)^{1/2}$, where $G = [1 - (\pi^2 - 1)g^2]^{1/2}$.

The whole dependence $\varepsilon_s(g)$ is shown in Fig. 8(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 of Fig. 10 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, multidimensional effects may strongly affect dimer diffusivity.

IV. CONCLUSION

In the present paper we studied in detail the diffusion of a particle in two-dimensional space which is periodic along x and unbounded in the transverse direction. We calculated the entropy factor that emerges due to the transverse degree of freedom, both in the overdamped limit (analytically) and in the underdamped case (numerically), and compared it with the prediction of the transition-state theory. We showed that in the underdamped limit, the multidimensional effects lead to a reduction (compared with the one-dimensional motion) in jump lengths between subsequent trappings of the atom at the minima of the external periodic potential. The simulation predicts that jump lengths scale as $\langle \lambda \rangle / \langle \lambda_{1D} \rangle \propto \eta^{1/3}$. This leads to a decrease in diffusivity, which now scales as $D \propto \eta^{-1/3}$ instead of the 1D dependence $D_{1D} \propto \eta^{-1}$.

In the overdamped limit, the entropy factor (and, therefore, the prefactor in the Arrhenius formula for activated diffusion) does not depend on temperature as long as the transverse motion near the adiabatic trajectory can be described by the harmonic approximation. Simulation shows that this remains true, at least approximately, for low damping as well. Thus, in most cases the experimentally observed dependence of the prefactor on temperature must be attributed to collective effects due to interaction between diffusing particles or/and between the atom and (deformable) substrate. However, in the case of dimer diffusion at some value of the interaction between the atoms, when the saddle transverse frequency is equal to zero, the anharmonicity of the transverse potential begins to play the important role and the entropy factor strongly depends on T .

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