Role of entropy barriers for diffusion in the periodic potential

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I. INTRODUCTION

A variety phenomena in physics and other fields can be modeled as Brownian motion in an external periodic potential. One of particular example, the surface diffusion of atoms or small clusters, is of great fundamental and technological interest. During crystal growth diffusion of atoms or small clusters, is of great fundamental and technological interest. During crystal growth a Fokker-Planck equation for the distribution function of a particle in the N-dimensional external potential 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 multi-dimensional effects lead to reduction (comparing with the one-dimensional motion) of jump lengths between subsequent trapping of the atom in bottoms of the external periodic potential. As application we consider the diffusion of a dimer adsorbed on the crystal surface.

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 multi-dimensional effects lead to reduction (comparing with the one-dimensional motion) of jump lengths between subsequent trapping of the atom in bottoms of the external periodic potential. As application we consider the diffusion of a dimer adsorbed on the crystal surface.

where

\[ D = D_f G(h), \]

with

\[ G(h) = \left( \frac{h}{2\pi} \right)^{1/2} e^{h} J_0^{-1}(h), \]

\[ J(h) = \int_0^\infty du \; e^{-3h/2} e^{-u} J_0^{-1}(u), \]

and \( J_0(u) \) is the complete elliptic integral of second kind. At low temperatures, \( k_B T \ll \varepsilon \), both expressions (1) and (2) take the Arrhenius form, \( D = D_0 \exp(-\varepsilon/k_B T) \) and \( D \approx \omega_0^2 a^2/2\pi \eta \) 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 \( D \approx \pi D_f/2 \) in the low-friction limit. In a general case the diffusion coefficient can be found numerically with practically any desired accuracy by the matrix continued-fraction-expansion method [7].

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 \( D = R A(\lambda^2) \), where \( R A \) is the rate of escape from a minimum of the external potential and \( \langle \lambda^2 \rangle \) is the mean-square jump length. For a 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) [8], 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 [9] (here \( \omega_s \) is the “saddle” frequency at the saddle point \( x = x_s \), near which the external potential has the form \( V(x) \approx \varepsilon - \varepsilon^2/m\omega_0^2(x-x_s)^2 \), for the sinusoidal potential \( \omega_0 = \omega_0 \)). The underdamped limit, \( \eta \ll \omega_0 \), is qualitatively different: in this case \( R \approx 2\pi \varepsilon/k_B T \propto \eta \) as was found firstly by Kramers [10], but the average jump length diverges as \( \lambda \propto \eta^{-1} \), thus this again leads to the dependence \( RA^2 \propto \eta^{-1} \), similarly to the overdamped case. The occurrence of large jumps, \( \lambda > a \), has been observed in a number of experiments on surface diffusion [11]. The interval from low to moderate friction is covered by the Mel’nikov-Meshkov formula [12]

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

where \( \Delta = 8h\eta/\omega_0 \). Thus, the whole interval of frictions may be described by the interpolation formula \( R \approx R_{\text{MM}} B(\eta) \), 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 \( D \approx R_{\text{TST}} A a^2 \), where the diffusion coefficient does not depend on the damping coefficient, operates in fact for a narrow interval of frictions close to the point \( \eta \sim \omega_0 \) only (which, fortunately, often corresponds to experimental situations).

Although the described above results 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. Multi-dimensional effects modify both the escape rate \( R \) and the jump length \( \lambda \). The escape rate can be presented as \( R = R_{\text{1D}} F \), where the coefficient \( F \) is known as the “entropy factor” [13]. The value of \( F \) can be found with the help of transition state theory [1] which yields \( F \approx (\Pi \omega_{0,i}) / (\Pi \omega_{s,i}) \), 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 given one along the diffusion path. In this approach \( F \) can be interpreted as \( F = \exp(\Delta S/kB) \), where \( \Delta S \) is the difference in entropy of the saddle and minimum-energy configurations. The entropy factor is often used to explain the “compensation effect” [1], when at experiment one observes that a decrease of the activation energy (calculated as a slope of the Arrhenius plot of \( \ln D \) versus \( T^{-1} \)) is compensated by 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 the multi-dimensional 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 the reduction of jump length, \( \lambda < \lambda_{\text{1D}} \). In particular, for the 2D-periodic substrate potential with the square symmetry it was found numerically [18] that \( D \propto \eta^{-0.75} \) which gives \( \lambda \propto \eta^{-0.5} \).

The multi-dimensional effects are also important in 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 dimer diffusion \( N = 2 \) at least. Diffusion of the dimer was studied numerically by Vollmer [19] with the help of 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 allowed 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 multi-dimensional effects in diffusion processes. We consider two typical examples: motion of a single atom in a “channel” which is periodic in one dimension and parabolic in others, and diffusion of a dimer (two-atomic 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 \( \eta \). The numerical results were obtained with the Verlet algorithm by calculating the trajectory \( x(t) \) and then splitting it into \( N_t \) pieces, each of the time duration \( \tau \). 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 \( V_N(x, y_1, \ldots, y_{N-1}) \) which is periodic in the \( x \) direction,

\[ V_N(x + a, \ldots) = V_N(x, \ldots), \]

and grows unboundedly in the other \( N - 1 \) dimensions,

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

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

With presence of a viscous friction, the particle motion should be diffusive at long-time scale. The diffusion coefficient \( D \) can be found with the Einstein relation \( D = T \mu \), where the mobility \( \mu \) 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

\[ V_f(x, y_1, \ldots, y_{N-1}) = V_N - fx, \]

and then take the limit \( f \rightarrow 0 \).

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

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

where \( W(x, y_1, \ldots, y_{N-1}; t) \) is the distribution function, \( \vec{J}(x, y_1, \ldots, y_{N-1}; t) \) is the density of 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. (6) takes the form

\[ T \frac{\partial W}{\partial x} + W \frac{\partial V_f}{\partial x} = -\eta J_x, \]

and then put \( t \rightarrow \infty \).
for the $x$ component, and a similar form for other degrees of freedom. The density $\bar{J}$ of the current should satisfy the equation
\[
\frac{\partial J_x}{\partial x} + \sum_{i=1}^{N} \frac{\partial J_{y_i}}{\partial y_i} = 0. \tag{9}
\]

To reduce notations, below we consider the case of $N = 2$ only; generalization to the $N > 2$ case is trivial. Let us introduce the one-dimensional density and current as
\[
\rho(x) = \int_{-\infty}^{+\infty} dy \ W(x, y), \tag{10}
\]
\[
J(x) = \int_{-\infty}^{+\infty} dy \ J_x(x, y). \tag{11}
\]
Owing to the condition (3), the current $j(x)$ does not depend on $x$,
\[
\frac{dj(x)}{dx} = -J_y(x, +\infty) + J_y(x, -\infty) = 0, \tag{12}
\]
where we have used Eq. (3). Thus, integrating both parts of Eq. (3) over $y$, we obtain the one-dimensional equation
\[
T \frac{d \rho(x)}{dx} + \rho(x) \frac{dV_F(x)}{dx} = -\eta j, \tag{13}
\]
where we introduced the potential $V_F(x)$ defined by the equation
\[
\frac{dV_F(x)}{dx} = [\rho(x)]^{-1} \int_{-\infty}^{+\infty} dy \ W(x, y) \frac{\partial V_F(x, y)}{\partial x}. \tag{14}
\]
Now, if $V_F(x)$ may be presented in the form
\[
V_F(x) = V_N(x; f) - f x, \tag{15}
\]
where $V_N(x; f)$ is a periodic function on $x$, Eq. (3) takes the form studied in [8], and the diffusion coefficient can be calculated as
\[
D = D_f (I_+ I_-)^{-1}, \quad I_{\pm}(T) = (2\pi)^{-1} \int_0^{2\pi} dx \ e^{\pm \eta V_{\text{eff}}(x)/T}, \tag{16}
\]
where $D_f = T/\eta$ and $V_{\text{eff}}(x) = \lim_{f \to 0} V_N(x; f)$. Thus, the diffusion coefficient $D$ is determined by the one-dimensional function $V_N(x; 0)$. In the limit $f \to 0$ we may substitute the equilibrium distribution function $W = W_{\text{eq}} \propto \exp(-V_N/T)$ into Eq. (14), thus obtaining
\[
\frac{dV_{\text{eff}}(x)}{dx} = \int_{-\infty}^{+\infty} dy \ e^{-V_N(x, y)/T} \frac{\partial V_N(x, y)}{\partial x} \int_{-\infty}^{+\infty} dy \ e^{-V_N(x, y)/T}. \tag{17}
\]
Emphasize that this is the key approximation which is rigorous in the overdamped limit only. For the underdamped case, $\eta \to 0$, 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 $f \to 0$ limit.

Let $V_N(x, y)$ has the form
\[
V_N(x, y) = V(x) + U(y) + v(x, y), \tag{18}
\]
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 following form,
\[
V_{\text{eff}}(x) = V(x) - T S(x, T), \tag{19}
\]
where the “entropy potential” $S(x, T)$ is defined by the expression
\[
S(x, T) = \ln \int_{-\infty}^{+\infty} dy \ \exp\{-[U(y) + v(x, y)]/T\}. \tag{20}
\]
Notice that $S(x)$ does not depend on $V(x)$.

### III. APPLICATIONS

#### A. Pure entropy barriers

Let $V(x) = 0$ in Eq. (18),
\[
U(y) = \frac{1}{2} m \omega_1^2 y^2, \tag{21}
\]
and
\[
v(x, y) = \frac{1}{4} m (\omega_2^2 - \omega_1^2) (1 - \cos x) y^2, \tag{22}
\]
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
\[
S(x) = -\frac{1}{2} \ln \left[ 1 + \frac{1}{2} \left( \frac{\omega_2}{\omega_1} \right)^2 - 1 \right] (1 - \cos x). \tag{23}
\]
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,
\[
F(z) = [I_+(z) I_-(z)]^{-1}, \tag{24}
\]
where
\[
I_{\pm}(z) = \pi^{-1} \int_0^{\pi} dx \left[ 1 + \frac{1}{2} (z^2 - 1)(1 - \cos x) \right]^{\pm 1/2}. \tag{25}
\]
Equations \(24, 25\) yield \(F(z) = (\pi/2)^2 K^{-1}(\sqrt{1 - z^2}) E^{-1}(\sqrt{1 - z^2})\), where \(K\) is the complete elliptic integral of 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 \(z \to 0\) 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 too strong, in particular, even for \(\omega_1/\omega_2 = 0.1\) the diffusion coefficient reduces comparing with the free-diffusion value by a factor of \(F(0.1) \approx 0.66\) only. Indeed, although the height \(\varepsilon_S\) tends to infinity at \(z \to 0\), the width of barriers becomes very narrow and thus cannot strongly modify the diffusion coefficient.

In the underdamped case, on the contrary, the role of entropy barriers is essential. The dependence of the diffusion coefficient on the damping constant \(\eta\) was obtained numerically and shown in Fig. 3. One can see that the function \(D(\eta)\) 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 lapse not shorter than \(2\eta^{-1}\)). The effect of entropy barriers 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 \(\varepsilon_S = S(\pi) \approx 2.3\), that would give the ratio \(D(\eta \to \infty)/D(\eta \to 0) \approx 2\varepsilon_S/k_B T \approx 4.6\) for the \(T = 1\) case, while the simulation leads to the ratio \(D(\eta \to \infty)/D(\eta \to 0) > 33\). From Fig. 3 one can see that \((\lambda/2\pi) \approx 10^2\) for the case of \(\eta = 10^{-5}\), while for the one-dimensional diffusion it should be \((\lambda/2\pi) \sim \eta^{-1} = \frac{\pi}{\eta} = \end{document}
10^9. Thus, multi-dimensional effects result in a strong reduction of jump’s length in the underdamped limit which leads to a decrease of the diffusion coefficient comparing with the 1D motion. Note also that the dependence on temperature (shown in inset of Fig. 3) is almost negligible as has to be expected for the entropy potential.

\[ D_{\text{Smoluchowski}} = D_f \frac{1}{T^2} (\varepsilon / 2T) \]

Because the entropy potential \( S(x) \) does not depend on the function \( V(x) \), it is still given by Eq. (23), and the integral (14) can be easily evaluated. The results for the overdamped limit are shown in Fig. 3, which can be compared with the simulation results for different frictions presented in Figures 4 and 5.

**FIG. 5.** Activated diffusion with the 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 the 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.

**FIG. 6.** \( D \) versus \( T \) for the activated motion with the barrier \( \varepsilon = 2 \) for three values of the transverse frequencies (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 the external damping: (a) \( \eta = 0.05 \), (b) \( \eta = 0.5 \), and (c) \( \eta = 5 \).

**B. Atom in a corrugated channel**

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

\[ V(x) = \frac{1}{2} \varepsilon (1 - \cos x), \]

where \( \varepsilon \) is the height of the external potential. At the minima of the potential (24) the transverse vibrations are characterized by the frequency \( \omega_1 \), while at the saddle points, by the frequency \( \omega_2 \). 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),

\[ P(\lambda / 2\pi) = \frac{1}{z} = \frac{\omega_2}{\omega_1} \]
From the $D(T)$ dependence of Figures 3 and 6 one can see that at high temperatures, when the motion is inactivated, the $\omega_1 = \omega_2$ case leads to the maximum of the diffusion coefficient similarly to the case with pure entropic barriers. With temperature decreasing, the energy barriers and the entropy barriers play “in phase” for the “narrow-barriers” case of $\omega_1 < \omega_2$, and “anti-phase” for the “wide-barriers” case of $\omega_1 > \omega_2$. At low temperatures $D > D_{1D}$ for the case of $\omega_1 > \omega_2$ at high and moderate frictions in agreement with predictions of the TST approach. The effect, however, is smaller than the TST predicts: in simulation we found that the diffusion coefficient changes only in three times when the ratio of frequencies is equal to ten. At very low frictions (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 frictions the simulation results of Fig. 3 can be fitted by a dependence $D(\eta) \propto \eta^{-1/3}$. Because the escape rate $R$ is still proportional to $\eta$ in the multi-dimensional 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 of pure entropic barriers presented in the previous 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 multi-dimensional effects lead to decreasing of diffusivity (comparing with the 1D case) due to reduction of 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 $x_2$ are the coordinates of two atoms coupled by the elastic spring with the constant $g$, and $a_0$ is the equilibrium distance ($0 \leq a_0 \leq \pi$). Then the Hamiltonian of the system takes the form

$$H = \frac{1}{2} m a \ddot{x}_1^2 + \frac{1}{2} m a \ddot{x}_2^2 + \frac{1}{2} \varepsilon_s (1 - \cos 2\pi x_1/a_0) + \frac{1}{2} \varepsilon_s (1 - \cos 2\pi x_2/a_0) + \frac{1}{2} g (x_2 - x_1 - a_0)^2.$$  (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

$$H = \frac{1}{2} m \left( \dot{x}^2 + \dot{y}^2 \right) + V_N(x, y),$$  (28)

which describes the motion of one particle of mass $m = m_a/2 = 1/2$ in the $x$-periodic potential of height $\varepsilon = 2\varepsilon_s = 4$ 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 $V_N(x, y) \approx \frac{1}{2} m (\omega_{sx}^2 x^2 + \omega_{sy}^2 y^2)$ with $\omega_{sx} = 1$ and $\omega_{sy} = (2g + 1)^{1/2}$. 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

$$V_N(x, y) \approx \varepsilon_s + \frac{1}{2} m \left[ -\omega_{sx}^2 (x - x_s)^2 + \omega_{sy}^2 (y - y_s)^2 \right]$$  (30)

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 approximately described as 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 previous 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 \( g \to 1/2 \) due to decreasing of the transverse curvature at the saddle point. The simulation results of Fig. 9 show that the harmonic approximation describes the \( D(g) \) dependence with a good 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.

![Figure 8](image1)

**FIG. 8.** (a) The activation energy \( \varepsilon_s \) and (b) the ratio of frequencies at the saddle and minimum points as functions of the elastic constant \( g \) for dimer’s diffusion.

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 transcendental equation \( \sin(y_s/2) = gy_s \). Near the saddle, the potential energy has the expansion [80] with the frequencies \( \omega_{sx} = \left[1 - (gy_s)^2\right]^{1/4} \) and \( \omega_{sy} = (2g - \omega_{sx}^2)^{1/2} \). The saddle is characterized by the energy \( \varepsilon_s(g) = \frac{1}{2} [1 + \cos(y_s/2)] + \frac{1}{2} g y_s^2 \), so that \( 2 + \pi/2 < \varepsilon_s < 4 \).

![Figure 9](image2)

**FIG. 9.** The dependence of the diffusion coefficient \( D \) (times \( \eta \)) 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 plussed diamonds show the simulation results for the “atom in channel” model with \( \eta = 5 \) and other parameters adjusted to the dimer case.

![Figure 10](image3)

**FIG. 10.** The ratio \( D(g)/D(0) \) as function of the elastic constant \( g \) for the dimer diffusion at \( \eta = 0.05 \) and different temperatures \( T = 3, 1.1/2, \) and 1/3.

Finally, for a weak coupling between dimer’s 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...
The activation energy monotonically increases from the potential energy has the expansion (30) with coefficients
so that $2 < \varepsilon_s < 2 + \pi/2$. Near the saddle, the potential energy has the expansion (30) with coefficients
$\omega_{sx} = (g-G)^{1/2}$ and $\omega_{sy} = (g+G)^{1/2}$, where $G = \left[1 - (\pi^2 - 1)g^2\right]^{1/2}$.

The whole dependence $\varepsilon_s(g)$ is shown in Fig. 8. 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 $g$ increasing. However, the simulation results of Fig. 11 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, $\eta \lesssim 0.5$, and the temperature is not too low, $T \gtrsim 1$ (recall $\varepsilon = 4$). Thus, multi-dimensional effects may strongly affect dimer’s diffusivity.

IV. CONCLUSION

In the present paper we studied in details 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 which emerges due to 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 multi-dimensional effects lead to reduction (comparing with the one-dimensional motion) of jump lengths between subsequent trapping of the atom in bottoms of the external periodic potential. The simulation predicts that jump lengths scale as $\langle \lambda \rangle / (\lambda_{1D}) \propto \eta^{1/3}$. This leads to a decrease of 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 may 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 has to 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 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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