# Escape from a cavity through a small window: Turnover of the rate as a function of friction constant

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To escape from a cavity through a small window the particle has to overcome a high entropy barrier to find the exit. As a consequence, its survival probability in the cavity decays as a single exponential and is characterized by the only parameter, the rate constant. We use simulations to study escape of Langevin particles from a cubic cavity through a small round window in the center of one of the cavity walls with the goal of analyzing the friction dependence of the escape rate. We find that the rate constant shows the turnover behavior as a function of the friction constant, $\zeta$: The rate constant grows at very small $\zeta$, reaches a maximum value which is given by the transition-state theory (TST), and then decreases approaching zero as $\zeta \to \infty$. Based on the results found in simulations and some general arguments we suggest a formula for the rate constant that predicts a turnover of the escape rate for ergodic cavities in which collisions of the particle with the cavity walls are defocusing. At intermediate-to-high friction the formula describes transition between two known results for the rate constant: the TST estimation and the high friction limiting behavior that characterizes escape of diffusing particles. In this range of friction the rate constants predicted by the formula are in good agreement with those found in simulations. At very low friction the rate constants found in simulations are noticeably smaller than those predicted by the formula. This happens because the simulations were run in the cubic cavity which is not ergodic.
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## I. INTRODUCTION

This paper deals with the escape of Langevin particles from a cavity through a small round window on the cavity wall. It is well known that the survival probability decays as a single exponential when the particle has to overcome a high energy barrier to escape from a potential well.[1–5] In 1991 Zhou and Zwanzig indicated that the survival probability also decays as a single exponential when the escape is controlled by an entropy barrier rather than the energy barrier.[6] This is just the case considered in the present paper. Indeed, when the window radius is much smaller than the cavity size, it takes the particle a lot of time to find the exit. For sufficiently small windows this time is much larger than the equilibration time in the cavity with no window. As a consequence, there is a gap in the eigenvalue spectrum of the evolution operator, and the survival probability decays as a single exponential.

The paper is focused on the rate constant defined as the inverse mean first passage time of the particle to the window. This problem has recently been studied for diffusing particles.[7] It has been shown that the rate constant $k$ is independent of the shape of the cavity and depends only on its volume $V$ as well as on the radius of the window $a$ and the particle diffusion constant $D$. The expression for $k$ found in Ref. 7 has the form

$$k = \frac{4Da}{V}. \tag{1.1}$$

Using the Einstein relation between $D$ and the friction constant $\zeta$, $D = k_B T/\zeta$, where $k_B$ and $T$ are the Boltzmann constant and the absolute temperature, one can write the rate constant in Eq. (1.1) as

$$k = \frac{4ak_B T}{V\zeta}. \tag{1.1a}$$

This expression diverges as $\zeta \to 0$. This is a consequence of the fact that it has a restricted range of applicability. It works only in the so-called high friction regime when the friction is high enough so that Langevin dynamics reduces to diffusion.

In the present paper we study the dependence of the rate constant on $\zeta$ over the entire range of friction when the particle motion varies from ballistic at $\zeta = 0$ to diffusive at sufficiently large values of $\zeta$. We will see that the rate constant

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has a turnover behavior as a function of the friction constant. The turnover differs from the known turnover in the Kramers theory of activated rate processes[1,5,8] and is similar to the turnover of the rate of activationless irreversible bimolecular reactions studied recently in Ref. 9. Another interesting feature of the rate constant is its dependence on the radius of the window. The transition-state theory[6] predicts the rate constant which is proportional to the area of the window and, hence, to $a^2$. At the same time, according to Eq. (1.1), for diffusing particles the rate constant is proportional to $a$. Thus, variation of the friction constant is accompanied by variation of the rate constant dependence on the radius of the window.

To find the rate constant one has to solve the Klein-Kramers equation in the phase space with mixed boundary conditions: absorbing on the window and reflecting on the rest of the cavity wall. This is an extremely complicated task. Instead we study the behavior of the rate constant by simulations. In the next section, based on the semiquantitative arguments partly discussed in Ref. 10, we suggest a formula that approximates the behavior of the rate constant over the entire range of friction. We compare the behavior predicted by the formulas with the results found in simulations in Sec. III. Section IV contains a brief summary and some concluding remarks.

## II. THEORETICAL PRELIMINARIES

Consider a particle of unit mass whose motion is governed by the Langevin equation

$$\dot{\mathbf{v}} = -\zeta \mathbf{v} + \mathbf{R}(t), \tag{2.1}$$

where $\mathbf{v}$ is the particle velocity and $\mathbf{R}(t)$ is the $\delta$-correlated Gaussian random force with zero mean, $\langle \mathbf{R}(t) \rangle = 0$, related to the friction constant $\zeta$ by the fluctuation-dissipation relation

$$\langle R_\mu(t) R_\nu(t') \rangle = 2 k_B T \zeta \delta_{\mu\nu} \delta(t-t'), \quad \mu, \nu = x, y, z. \tag{2.2}$$

The particle moves in a cavity and may escape through a small round window of radius $a$ on the cavity wall. It will be assumed that the particle escapes when its trajectory crosses the window area for the first time. Particle collisions with the cavity wall are assumed to be elastic. As the friction increases, the particle motion varies from ballistic in the absence of friction, i.e., at $\zeta=0$, to diffusive when the friction is high enough.

The simplest estimation of the rate constant is provided by the transition-state theory[6] (TST) that leads to

$$k_{\mathrm{TST}} = \frac{\pi a^2 \langle |\mathbf{v}| \rangle_{\mathrm{eq}}}{4V} = \frac{\sqrt{\pi k_B T} a^2}{\sqrt{2} V}, \tag{2.3}$$

where the notation $\langle F(\mathbf{v}) \rangle_{\mathrm{eq}}$ means the equilibrium average of the function $F(\mathbf{v})$ and we have used the relation $\langle |\mathbf{v}| \rangle_{\mathrm{eq}} = (8 k_B T/\pi)^{1/2}$. The TST provides an upper boundary for the rate constant. It fails both at high and low friction. As $\zeta \to \infty$ the rate constant vanishes [see Eq. (1.1a)] because the particle does not move and hence never escapes from the cavity. To estimate friction that leads to a noticeable deviation from $k_{\mathrm{TST}}$ one can compare the radius of the window and the velocity relaxation length, $l_v = \tau_v (k_B T)^{1/2}$, where $\tau_v = \zeta^{-1}$ is the velocity relaxation time. The slowdown occurs when $l_v$ becomes smaller than $a$, and the friction constant satisfies

$$\frac{a}{l_v} = \frac{a\zeta}{\sqrt{k_B T}} > 1. \tag{2.4}$$

To estimate the range of friction where the slowdown occurs at low friction we compare time $\tau_v$ with the TST estimation for the average lifetime in the cavity, $k_{\mathrm{TST}}^{-1}$. At sufficiently small values of $\zeta$ time $\tau_v$ becomes larger than $k_{\mathrm{TST}}^{-1}$, and escape leads to depletion of the velocity distribution at large $|\mathbf{v}|$. As a consequence, the process slows down and the rate constant decreases compared to $k_{\mathrm{TST}}$. The inequality determining the friction at which the slowdown becomes noticeable is given by

$$\frac{a}{l_v} = \frac{a\zeta}{\sqrt{k_B T}} < \frac{a^3}{V}. \tag{2.5}$$

The inequalities in Eqs. (2.4) and (2.5) show that the rate constant is close to $k_{\mathrm{TST}}$ when $\zeta$ satisfies

$$\frac{a^3}{V} < \frac{a\zeta}{\sqrt{k_B T}} < 1. \tag{2.6}$$

We will see that this estimation agrees well with our simulation results.

It is convenient to use $k_{\mathrm{TST}}$ as a scale for the rate constant and to write $k(\zeta)$ as

$$k(\zeta) = \kappa(\zeta) k_{\mathrm{TST}}, \tag{2.7}$$

where $\kappa(\zeta)$ is a function that varies between unity and zero. By analogy with the corresponding function in the theory of activated rate processes we will call $\kappa(\zeta)$ the "transmission factor." Qualitative pictures of the escape at low and high friction are quite different. To cover the entire range of friction we adopt the Visscher-Mel'nikov-Meshkov[8,11] (VMM) strategy: First we consider the two cases separately. Then we use the VMM interpolation formula to cover the entire range of friction.

### A. Intermediate-to-high friction

In this subsection we discuss the behavior of the transmission factor in the so-called intermediate-to-high (i-h) friction regime where $\kappa(\zeta)$ monotonically decreases from unity to zero as $\zeta$ increases from zero to infinity. One can use the rate constant in Eq. (1.1a) to find how the transmission factor approaches zero as $\zeta \to \infty$. This leads to

$$\kappa_h(\zeta) \approx \frac{4\sqrt{2 k_B T}}{\sqrt{\pi} a \zeta} = \frac{\omega_{\mathrm{eff}}}{\zeta}, \quad \zeta \to \infty, \tag{2.8}$$

where the subscript $h$ indicates that this expression is applicable in the high friction regime, and we have introduced the effective frequency $\omega_{\mathrm{eff}} = 4\sqrt{2 k_B T/\pi}/a$, which may be considered as an analog of the barrier frequency in the Kramers theory of activated rate processes.[1,5]

We cannot find $\kappa_{\text{i-h}}(\zeta)$ by solving the Klein-Kramers equation. One might guess that variation of $\kappa_{\text{i-h}}(\zeta)$ between

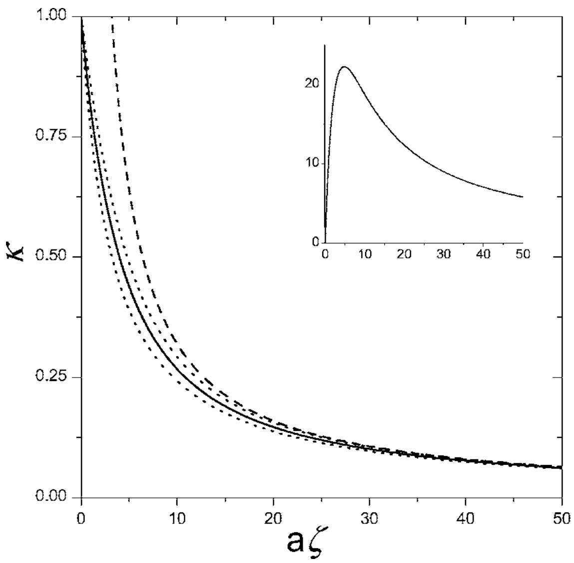


FIG. 1. Transmission factor at the intermediate-to-high friction. The solid curve shows $\kappa_{\text{i-h}}(\zeta)$ in Eq. (2.11) as a function of the dimensionless friction constant $a\zeta$. Transmission factors $\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)$ and $\kappa_{\text{i-h}}^{\text{CK}}(\zeta)$ given in Eqs. (2.9) and (2.10) are shown by the upper and lower dotted curves, respectively. The dashed curve represents the high friction asymptotic behavior of the transmission factor $\kappa_h(\zeta)$ given in Eq. (2.8). The inset shows the relative difference between the two transmission factors in percent, $g(\zeta)\times 100\%$, where $g(\zeta)=2[\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)-\kappa_{\text{i-h}}^{\text{CK}}(\zeta)]/[\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)+\kappa_{\text{i-h}}^{\text{CK}}(\zeta)]$, as a function of $a\zeta$.

unity at $\zeta=0$ and the large-$\zeta$ asymptotic behavior in Eq. (2.8) is reasonably well approximated by the Kramers (Kr) formula

$$\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)=\sqrt{1+\frac{\zeta^2}{4\omega_{\text{eff}}^2}}-\frac{\zeta}{2\omega_{\text{eff}}}. \tag{2.9}$$

Another potential candidate for the interpolation formula is the Collins-Kimball-type[12] (CK) formula

$$\kappa_{\text{i-h}}^{\text{CK}}(\zeta)=\frac{\kappa_h(\zeta)}{1+\kappa_h(\zeta)}=\frac{1}{1+\zeta/\omega_{\text{eff}}}. \tag{2.10}$$

Similar formula has been used in Ref. 9 to describe the decrease of the rate of an irreversible bimolecular reaction from its upper limit given by the TST to the high friction behavior obtained for diffusing molecules.

Functions $\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)$ and $\kappa_{\text{i-h}}^{\text{CK}}(\zeta)$ are shown in Fig. 1 for $k_BT=1$ where we also show their average denoted by $\kappa_{\text{i-h}}(\zeta)$,

$$\kappa_{\text{i-h}}(\zeta)=\frac{1}{2}[\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)+\kappa_{\text{i-h}}^{\text{CK}}(\zeta)]. \tag{2.11}$$

In addition, for the sake of comparison we show the dependence on $\zeta$ predicted by $\kappa_h(\zeta)$ in Eq. (2.8). One can see that this dependence provides a good approximation for the transmission factor when $\kappa(\zeta)<0.1$. To characterize how different the dependences predicted by the two candidates are, $\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)$ and $\kappa_{\text{i-h}}^{\text{CK}}(\zeta)$, we introduced function $g(\zeta)$ defined as $g(\zeta)=[\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)-\kappa_{\text{i-h}}^{\text{CK}}(\zeta)]/\kappa_{\text{i-h}}(\zeta)$. In Fig. 1 this function is shown in the inset. Function $g(\zeta)$ first grows with $\zeta$, reaches its maximum value which is close to 0.2, and then decreases slowly approaching zero as $\zeta\to\infty$. Its asymptotic behavior at large $\zeta$ is given by $g(\zeta)\approx 4\sqrt{2/\pi}/(a\zeta)$ $(k_BT=1)$. In simulations we found that the values of the transmission factor fall in between the two dependences. Therefore, we use $\kappa_{\text{i-h}}(\zeta)$ in Eq. (2.11) when discussing the simulation results.

According to Eqs. (2.8)–(2.11) the transmission factor is a function of the product $a\zeta$, which is equal to the ratio $a/l_v$ for $k_BT=1$. (Note that if $k_BT$ and the particle mass $m$ are not equal to unity the dimensionless ratio $a/l_v$ is equal to $a\zeta/\sqrt{mk_BT}$.) We checked this fact in simulations and found that for windows of different (but small) radii the results at the same values of $a\zeta$ are indistinguishable within the simulation error. This means that at given friction deviations from $k_{\text{TST}}$ are more strongly pronounced for larger windows.

### B. Low-to-intermediate friction

In this subsection we discuss the behavior of the transmission factor in the so-called low-to-intermediate friction regime where $\kappa(\zeta)$ monotonically increases with $\zeta$ from $\kappa(0)$ to unity, as $\zeta$ grows from zero to infinity. Our analysis below is close to that in Ref. 9 where the mathematically identical problem has been studied in a different context. Therefore we skip some steps which are discussed in detail in that paper.

At intermediate-to-high friction the escape rate and the survival probability are insensitive to the shape of the cavity. In the absence of friction the situation is quite different, and these functions depend on the cavity shape because the shape determines whether particle collisions with the walls are defocusing or not. When collisions are defocusing the particle motion in the cavity is ergodic.[13] In such a cavity the particle survival probability is given by the microcanonical transition-state theory (mTST) and has the form[6]

$$S_{\text{mTST}}(T|v)=\exp[-k_{\text{mTST}}(v)t], \tag{2.12}$$

where $v=|\mathbf{v}|$. The microcanonical rate constant $k_{\text{mTST}}(v)$ is given by

$$k_{\text{mTST}}(v)=\frac{\pi a^2 v}{4V}=\sqrt{\frac{\pi}{8}}k_{\text{TST}}\tilde{v},\quad \tilde{v}=\frac{v}{\sqrt{k_BT}}, \tag{2.13}$$

where we have introduced dimensionless velocity $\tilde{v}$.

Assuming that the probability density of the velocity distribution at $t=0$ is the equilibrium one, $f_{\text{eq}}(\tilde{v})$,

$$f_{\text{eq}}(\tilde{v})=\sqrt{\frac{2}{\pi}}\tilde{v}^2\exp\left(-\frac{\tilde{v}^2}{2}\right), \tag{2.14}$$

we can write the density at time $t$ as

$$f_{\zeta=0}(\tilde{v},t)=S_{\text{mTST}}(t|\tilde{v})f_{\text{eq}}(\tilde{v}). \tag{2.15}$$

Then the particle survival probability in the cavity is

$$S_{\zeta=0}=\int_0^\infty f_{\zeta=0}(\tilde{v},t)d\tilde{v}=\langle S_{\text{mTST}}(t|v)\rangle_{\text{eq}}$$
$$=(1+2\pi\tau^2)\exp(\pi\tau^2)\text{erfc}(\sqrt{\pi}\tau)-2\tau, \tag{2.16}$$

where $\tau=k_{\text{TST}}t/16$ is the dimensionless time. Note that in the absence of friction the survival probability is not single exponential in spite of the fact that the window is small. Eventually we can find the rate constant at zero friction,

$$[k(\zeta=0)]^{-1} = \int_0^\infty S_{\zeta=0}(t)dt = \langle k_{\text{mTST}}^{-1}(v)\rangle_{\text{eq}} = \frac{4}{\pi} k_{\text{TST}}^{-1}. \tag{2.17}$$

Thus, for ergodic cavities the transmission factor remains finite even at $\zeta=0$ and is given by

$$\kappa(\zeta=0) = \frac{\pi}{4}. \tag{2.18}$$

It does not depend on the shape of the cavity.

The situation is completely different in regular cavities which are not ergodic. In such cavities in the absence of friction the particle survival probability remains finite as $t \to \infty$. As a consequence, the average lifetime diverges, and both the rate constant and the transmission factor vanish as $\zeta \to 0$. In our simulations performed in a cubic cavity, at very low friction we found noticeably smaller values of the transmission factor than its limiting value for ergodic cavities given in Eq. (2.18).

In the rest of this section we discuss an approximate solution for $\kappa(\zeta)$ for ergodic cavities. This solution describes the monotonic increase of the transmission factor from $\pi/4$ to unity as $\zeta$ goes from zero to infinity. The qualitative picture of the escape at low-to-intermediate (l-i) friction is as follows. Particles with higher velocities escape faster than particles with lower velocities. This leads to a depletion of the velocity distribution at high velocities. Simultaneously, relaxation due to the presence of the friction and random forces tries to restore the Maxwell distribution. The density $f(\tilde{v},t)$ satisfies the evolution equation

$$\frac{\partial f}{\partial t} = \frac{\zeta}{\tilde{v}^2}\frac{\partial}{\partial \tilde{v}}\left\{\tilde{v}^2 \exp\left(-\frac{\tilde{v}^2}{2}\right)\frac{\partial}{\partial \tilde{v}}\left[\exp\left(\frac{\tilde{v}^2}{2}\right)f\right]\right\} - k_{\text{mTST}}(\tilde{v})f \tag{2.19}$$

that describes competition between the depletion and relaxation. This equation can be derived from the Klein-Kramers equation using the approximation which is quite natural in the low friction regime. Note that $f(\tilde{v},t)$ in Eq. (2.15) satisfies this equation at frozen relaxation, $\zeta=0$. Therefore, this equation leads to $\kappa_{\text{l-i}}(0)=\pi/4$. In the opposite limiting case of fast relaxation, $\zeta \to \infty$, the solution is given by the TST and has the form

$$f(\tilde{v},t) = \exp(-k_{\text{TST}}t) f_{\text{eq}}(\tilde{v}), \tag{2.20}$$

where we have used the relation $k_{\text{TST}}=\langle k_{\text{mTST}}(v)\rangle_{\text{eq}}$. This leads to $\kappa_{\text{l-i}}(\infty)=1$.

To describe variation of the transmission factor $\kappa_{\text{l-i}}$ from $\pi/4$ at $\zeta=0$ to unity as $\zeta \to \infty$ we use the formula[9]

$$\kappa_{\text{l-i}}(\zeta) = \frac{\pi/4 + \alpha\lambda^{2/3}}{1+\alpha\lambda^{2/3}}, \tag{2.21}$$

where $\lambda$ and $\alpha$ are given by

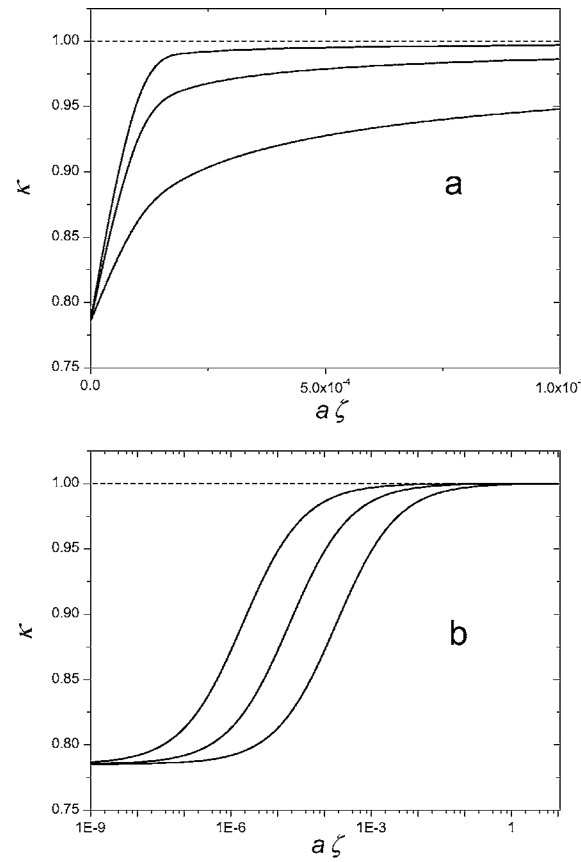


FIG. 2. Transmission factor $\kappa_{\text{l-i}}(\zeta)$ given in Eq. (2.21) is shown as a function of the dimensionless friction constant $a\zeta$ in linear (panel a) and logarithmic (panel b) scales. Different curves correspond to different values of the ratio $a^3/V=10^{-3},10^{-4},10^{-5}$ from bottom to top: the smaller the ratio, the larger the transmission factor at fixed $a\zeta$.

$$\lambda = \frac{\zeta}{k_{\text{TST}}} = \frac{\sqrt{2}V\zeta}{\sqrt{\pi k_B T}a^2}, \quad \alpha = \frac{3^{5/6}[\Gamma(2/3)]^2}{\pi^{1/3}(4-\pi)} \approx 3.643. \tag{2.22}$$

It has been shown[9] that the dependence predicted by Eq. (2.21) (i) agrees well with the corresponding dependence obtained from the numerical solution and (ii) correctly reproduces the initial increase of $\kappa_{\text{l-i}}$ at small $\lambda$, which can be derived analytically. The dependence of $\kappa_{\text{l-i}}(\zeta)$ is shown in Fig. 2 for several values of the ratio $a^3/V$. The figure shows that for sufficiently small values of the ratio $a^3/V$ transition of $\kappa_{\text{l-i}}(\zeta)$ from $\pi/4$ to unity occurs in a very narrow interval of the dimensionless friction constant $a\zeta$, where the deviation of $\kappa_{\text{i-h}}(\zeta)$ from unity can be neglected.

### C. Visscher-Mel'nikov-Meshkov interpolation formula

Having in hand the expressions for $\kappa_{\text{i-h}}(\zeta)$ and $\kappa_{\text{l-i}}(\zeta)$, Eqs. (2.11) and (2.21), we use the Visscher-Mel'nikov-Meshkov[8,11] interpolation formula to write an expression for the transmission factor that covers the entire range of friction,

$$\kappa(\zeta) = \kappa_{\text{l-i}}(\zeta)\kappa_{\text{i-h}}(\zeta). \tag{2.23}$$

This transmission factor shows a turnover behavior: It grows with $\zeta$ at small $\zeta$, reaches a maximum, and then tends to zero as $\zeta \to \infty$.

The expressions for the transmission coefficient discussed above are used in the next section when analyzing the transmission factors obtained in simulations. We will see that at not too low friction, where $\kappa(\zeta) \approx \kappa_{\text{i-h}}(\zeta)$, the values of the transmission factor found in simulations are in a good agreement with $\kappa_{\text{i-h}}(\zeta)$ predicted by Eq. (2.11). At very low friction the values of the transmission factor obtained numerically fall below the lower boundary $\kappa_{\text{l-i}}(0) = \pi/4$ predicted by Eq. (2.21) for ergodic cavities. This happens because the simulations were run in a cubic cavity which is not ergodic.

## III. SIMULATION RESULTS AND DISCUSSION

In this section we discuss the transmission factor obtained in the Langevin dynamics simulations at low and intermediate friction. The simulations were performed with a discretized version[14] of the Langevin equation (2.1) for particles that moved in a cubic cavity of unit size with a round window of radius $a$ in the center of one of the cavity walls. It was taken that a particle escaped from the cavity through the window when its trajectory crossed the window area for the first time. Most of the simulations were performed with $a = 0.05$, although some simulations were carried out with $a = 0.025$, $a = 0.1$, and $a = 0.2$. We chose $a = 0.05$ because earlier[7] we found excellent agreement between the theoretical predictions and numerical results for diffusing particles that escaped from the unit cubic cavity through the round window just of this size. The simulations were run with $N = 10\,000$ particles uniformly distributed in the cavity at $t = 0$. The particle initial velocities were randomly chosen from the three-dimensional Maxwell distribution. Collisions with the cavity walls were elastic and changed only the direction of the velocity, but not its magnitude. It was taken that $k_B T = 1$.

The output of the simulations was a set of lifetimes $t_i$, $i = 1, 2, \ldots, N$. This set was used to calculate the rate constant

$$k(\zeta) = \langle t \rangle^{-1} = \left( \frac{1}{N} \sum_{i=1}^{N} t_i \right)^{-1}. \tag{3.1}$$

The transmission factor was determined according to Eq. (2.7) with $k_{\text{TST}}$ given in Eq. (2.3). We estimated accuracy of our calculations of the average lifetime and found that the relative error did not exceed 5%. In addition, the set of lifetimes was used to find the particle survival probability $S(t|\zeta)$,

$$S(t|\zeta) = \frac{1}{N} \sum_{i=1}^{N} H(t_i - t), \tag{3.2}$$

where $H(z)$ is the Heaviside step function. This was done with the goal of checking whether the survival probability is single exponential,

$$S(t|\zeta) = \exp[-k(\zeta)t], \tag{3.3}$$

or not.

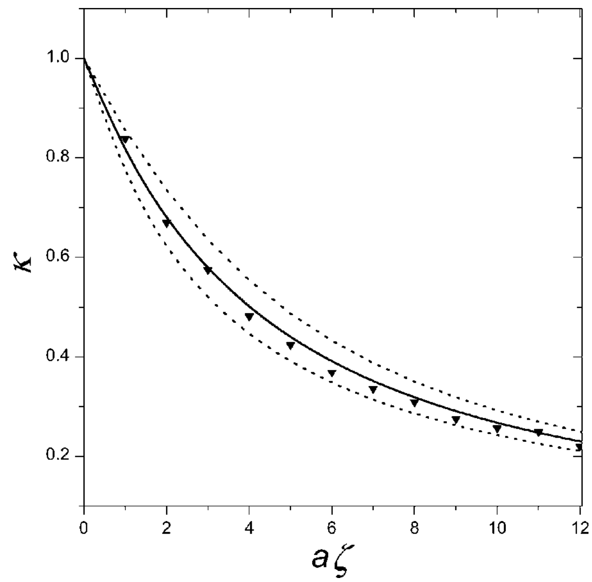


FIG. 3. Transmission factor $\kappa(\zeta)$ found in simulations at intermediate friction (black triangles) is compared with $\kappa_{\text{i-h}}(\zeta)$ given in Eq. (2.11), which is shown by the solid curve. The upper and lower dotted curves represent the dependences predicted by $\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)$ and $\kappa_{\text{i-h}}^{\text{CK}}(\zeta)$ given in Eqs. (2.9) and (2.10), respectively.

The values of the transmission factor found in simulations are shown in Figs. 3 and 4. In Fig. 3 we compare $\kappa(\zeta)$ found in simulations with $\kappa_{\text{i-h}}(\zeta)$ given in Eq. (2.11) (solid curve). One can see good agreement between simulated and predicted values of the transmission factor. The relative difference, defined as $|\kappa(\zeta) - \kappa_{\text{i-h}}(\zeta)|/\kappa(\zeta)$, is mainly less than 5% that does not exceed the relative error of our simulations. In Fig. 3 we also showed $\kappa_{\text{i-h}}^{\text{Kr}}(\zeta)$ and $\kappa_{\text{i-h}}^{\text{CK}}(\zeta)$ (upper and lower dotted curves, respectively). One can see that the numerical results fall in between the two curves. Thus, these two estimations provide upper and lower boundaries for the transmission factor.

The turnover behavior of the transmission factor is shown in Fig. 4, where the solid curve represents the dependence predicted for an ergodic cavity by $\kappa(\zeta)$ in Eq. (2.23) with $\kappa_{\text{l-i}}(\zeta)$ and $\kappa_{\text{i-h}}(\zeta)$ given in Eqs. (2.21) and (2.11). One can see that at very low friction the transmission factor found in simulations is smaller than $\kappa_{\text{l-i}}(\zeta)$ predicted by Eq. (2.21). We believe that this is due to the fact that our simulations were run in the cubic cavity which is definitely not ergodic. From Fig. 4 one can estimate the range of friction where $k_{\text{TST}}$ provides a good estimation for the rate constant as

$$10^{-4} < a\zeta < 1. \tag{3.4}$$

One can see that for the set of parameters used in the simulations, $k_B T = V = 1$ and $a = 0.05$, the estimation in Eq. (3.4) is in good agreement with that in Eq. (2.6).

The expressions in Eqs. (2.9)–(2.11) predict that at intermediate-to-high friction the transmission factor depends on $a$ and $\zeta$ only through their product, $a\zeta$. To check whether this is true or not we performed simulations with $a = 0.025$ for $a\zeta = 1, 2, \ldots, 8$ and compared the results with those obtained in simulations with $a = 0.05$ for the same values of $a\zeta$. We found excellent agreement between the transmission factors obtained in simulations with different values of $a$ for all

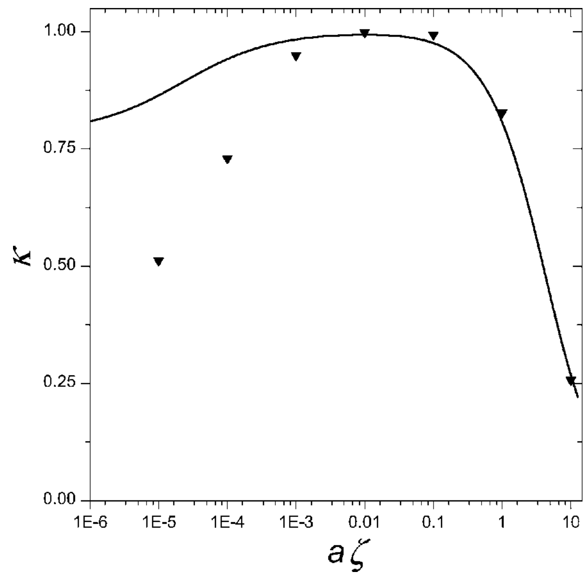


FIG. 4. Turnover behavior of the transmission factor found in simulations (black triangles) is compared with the turnover behavior predicted for ergodic cavities by $\kappa(\zeta)$ in Eq. (2.23) with $\kappa_{\text{l-i}}(\zeta)$ given in Eq. (2.21) and $\kappa_{\text{i-h}}(\zeta)$ given in Eq. (2.11) (solid curve).

values of $a\zeta$ from 1 to 8. The differences were within the range of the statistical error of our simulations, i.e., less than 5%. Thus, although the expressions in Eqs. (2.9)–(2.11) have not been derived, they correctly predict that at intermediate-to-high friction the transmission factor is a function of the product $a\zeta$.

In the high friction regime we found[7] that for particles diffusing in a unit cavity the rate constants predicted by Eq. (1.1) were in a reasonably good agreement with the rate constants obtained in simulations with $a=0.05$ and $a=0.1$, whereas for $a=0.2$ Eq. (1.1) underestimated the escape rate. The same is true at intermediate friction. One can see this from Fig. 5 where we compare $\kappa(\zeta)$ in Eq. (2.11) with the results for $\kappa$ obtained in simulations with $a=0.05$, 0.1, and

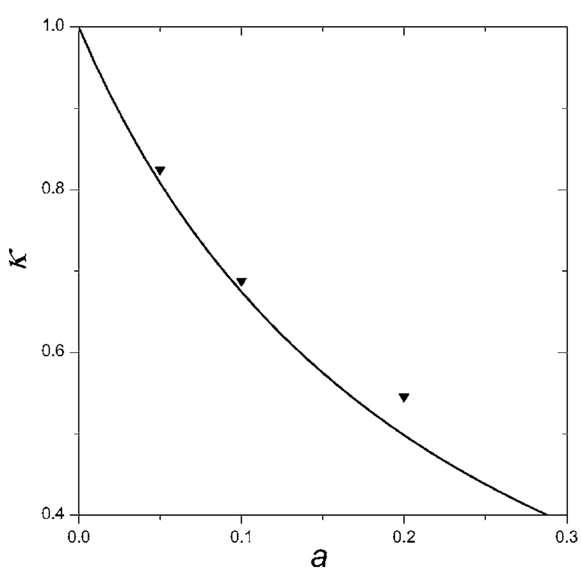


FIG. 5. Transmission factor as a function of $a$ at $\zeta=20$ predicted by Eq. (2.11) (solid curve) and found in simulations with $a=0.05$, 0.1, and 0.2 (black triangles).

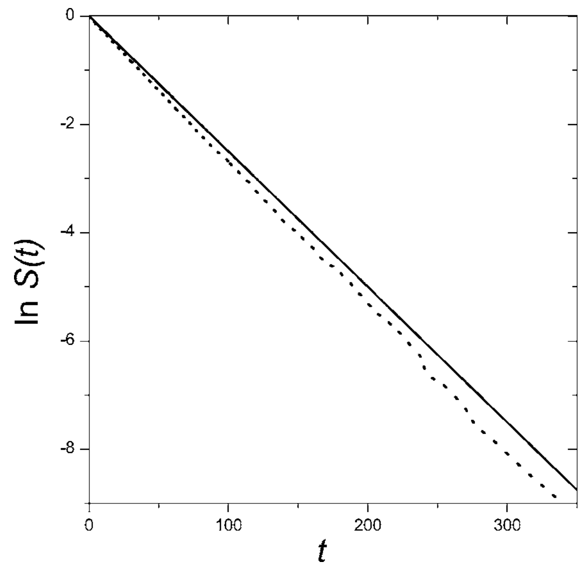


FIG. 6. The particle survival probability found in simulations at intermediate friction, $\zeta=20$, with $a=0.2$ (dotted curve) and the single-exponential approximation of $S(t)$ for the same values of $\zeta$ and $a$ (solid curve).

0.2 at $\zeta=20$ that correspond to $a\zeta=1$, 2, and 4. In Fig. 6 we present the survival probability obtained in simulations with $a=0.2$ at $\zeta=20$ and its single-exponential approximation, $S(t)=\exp(-kt)$, where $k$ is the rate constant given by Eq. (2.7). One can see that $S(t)$ found in simulations decays faster than its single-exponential counterpart.

The theory predicts single-exponential decay of the particle survival probability in the cavity with sufficiently small window. In Ref. 7 this prediction was checked and confirmed for particles diffusing in a unit cubic cavity with the window radius $a=0.05$, while for the cavity with the window of radius $a=0.2$ the decay was multiexponential. In our simulations we checked whether the decay of the survival probability is single exponential or not at intermediate friction. As for diffusing particles, we found that at $\zeta=20$ and $a=0.05$ ($a\zeta=1$) $S(t)$ obtained numerically was practically indistinguishable from the single-exponential approximation, $S(t)=\exp(-kt)$, where $k$ was the rate constant given by the inverse of the average lifetime found in simulations. However, the single-exponential approximation fails at the same $\zeta=20$ when $a=0.2$ ($a\zeta=4$). Noticeable deviations from the single-exponential behavior were found in $S(t)$ obtained in simulations, which is shown in Fig. 6.

## IV. CONCLUDING REMARKS

In summary, we run Langevin dynamics simulations to study the particle escape from a cubic cavity through a small round window in the center of one of the cavity walls with the goal of analyzing the escape rate at intermediate and low friction that complements our previous study[7] of the escape of diffusing particles, i.e., in the high friction regime. One of the main results of the present paper is the expression for the rate constant in Eq. (2.7) together with the expressions for $k_{\text{TST}}$ and $\kappa(\zeta)$ given in Eqs. (2.3) and (2.23). These formulas predict turnover behavior of the rate constant considered as a function of the friction constant $\zeta$ for ergodic cavities. At intermediate-to-high friction the formulas describe transition between the two known results: the TST estimation of the rate constant,[6] $k_{TST}$, and the high friction asymptotic behavior of the rate constant[7] given in Eq. (1.1a). The rate constants given by the formulas in this range of friction are in good agreement with those found in simulations. At intermediate-to-high friction the rate of escape is insensitive to the shape of the cavity. The shape manifests itself only at very low friction. In this range of friction the rate constants found in simulations are noticeably smaller than those predicted by the formula. This happens because the simulations were run in the cubic cavity which is not ergodic.

The escape rate derived in this paper can be used to generalize the model of dynamical disorder[15] suggested by Zwanzig in Ref. 16. In this model a point particle escapes from the cavity through a small round window, the radius of which fluctuates in time. It is assumed that variation of the radius $a(t)$ is controlled by the Brownian motion of the gate $(g)$ and can be described by the high friction version of the Langevin equation for harmonic oscillator of the form

$$\dot{a} = -\frac{D_g}{k_B T} K_g a + f_g(t), \quad (4.1)$$

where $D_g$ and $K_g$ are the diffusion constant of the gate and the force constant of the gate oscillator and $f_g(t)$ is the $\delta$-correlated Gaussian random force with zero mean, $\langle f_g(t)\rangle = 0$, related to the diffusion constant $D_g$ by the fluctuation-dissipation relation $\langle f_g(t) f_g(t')\rangle = 2D_g \delta(t-t')$. A hard reflecting barrier is imposed at $a=0$ so that only positive radii are involved.

Zwanzig assumed that the rate of escape from the cavity is given by the TST estimation of the rate constant in Eq. (2.3) with time-dependent radius of the window. This implies that the velocity relaxation length of the escaping particle, $l_v$, is much larger than the average radius of the window, $l_v \gg 1/\sqrt{K_g/(k_B T)}$. In other words, friction in the cavity should not be too high. When this requirement is not fulfilled, and the velocity relaxation length is comparable or even smaller than the average radius of the window, $1/\sqrt{K_g/(k_B T)}$, Zwanzig's analysis should be generalized. This can be done using the escape rate given in Eq. (2.7), which allows one to study the problem at arbitrary friction inside the cavity. In particular, when the friction is high enough, so that $l_v \ll 1/\sqrt{K_g/(k_B T)}$, we meet the case of diffusive rather than ballistic escape from the cavity. Here it is reasonable to use the rate constant in Eq. (1.1) which is a linear function of $a$, while $k_{TST}$ in Eq. (2.3) is proportional to $a^2$.

Another potential application of the results obtained in the present paper is a generalization of the theory of diffusion in periodic porous materials.[17] In Ref. 17 the theory is developed assuming diffusive motion of the particles in space with no constraints. The theory shows how the presence of periodic constraints slows down diffusion of the particles. Results obtained above can be used to extend the theory to the case when motion of the particles in space with no constraints is governed by the Langevin equation with arbitrary friction.

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