Velocity dependence of friction and Kramers relaxation rates

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Abstract

We study the influence of the velocity dependence of friction on the escape of a Brownian particle from the deep potential well ($E_b \gg k_B T$, $E_b$ is the barrier height, $k_B$ is the Boltzmann constant, $T$ is the bath temperature). The bath-induced relaxation is treated within the Rayleigh model (a heavy particle of mass $M$ in the bath of light particles of mass $m \ll M$) up to the terms of the order of $O(\lambda^4)$, $\lambda^2 = m/M \ll 1$. The term $\sim 1$ is equivalent to the Fokker-Planck dissipative operator, and the term $\sim \lambda^2$ is responsible for the velocity dependence of friction. As expected, the correction to the Kramers escape rate in the overdamped limit is proportional to $\lambda^2$ and is small. The corresponding correction in the underdamped limit is proportional to $\lambda^2 E_b/(k_B T)$ and is not necessarily small. We thus suggest that the effects due to the velocity-dependent friction may be of considerable importance in determining the rate of escape of an under- and moderately damped Brownian particle from a deep potential well, while they are of minor importance for an overdamped particle.
I. INTRODUCTION

Many chemical reactions in a condensed phase can be modeled as an escape of a Brownian particle from a potential well. The conventional means for describing this kind of problems are the Fokker-Planck equations (FPEs), or master equations, or the (generalized) Langevin equations for the reaction coordinate and the conjugated momentum of the particle in the external potential. Since the seminal work of Kramers, his approach has further been refined, and the influences of different dissipation (collision) mechanisms, non-Poissonian collision statistics, non-Markovian effects, and position-dependent friction on the reaction rates have been investigated (see also reviews).

In the present paper, we study the effects due to the velocity dependence of friction. Our motivation is as follows. There have been collected evidences in the literature that relaxations of linear and angular velocities and kinetic energies in liquids under (highly) non-equilibrium conditions are reproduced neither by conventional FPEs with constant frictions nor by master equations with constant collision frequencies, so that one has to take into account (linear and/or angular) velocity dependence of friction. Indeed, if we consider relaxation under equilibrium conditions, then all the relevant energies are of the order of \( k_B T \) (\( k_B \) being the Boltzmann constant and \( T \) being the temperature of the bath). Putting aside non-Markovian effects, we can then always introduce a certain effective velocity-independent friction. This means that the effects due to the velocity dependence of friction are normally small and can safely be neglected. If we consider relaxation under non-equilibrium conditions, when initial energies of the particles are much higher than the typical bath energies \( \sim k_B T \), then the velocity dependence of friction cannot be ignored, in general.

It is not unreasonable to expect that similar effects may become relevant in the evaluation of the activated escape rates for underdamped or moderately damped Brownian particles. If an underdamped particle is trapped in a deep potential well \( (E_b \gg k_B T) \), see Fig. 1) then friction is the rate determining parameter: fluctuations must supply the particle with the energy \( \sim E_b \gg k_B T \) in order to surmount the barrier. Thus, we have to adequately describe the Brownian particle relaxation not only within the thermal energy interval \( \sim k_B T \) but also for much higher energies \( \sim E_b \). In such a case the constant friction approximation might be an oversimplification, so that the velocity dependence of friction may become crucial.
the contrary, the effect of the velocity-dependent friction on the overdamped Brownian particle is expected to be minor, since dissipation manifests itself through the diffusion coefficient which equals to the integral relaxation time of the equilibrium velocity correlation function, which is determined by the typical energies $\sim k_B T$. The present paper is aimed at proving and elucidating the above qualitative expectations.

II. ESCAPE RATES IN RAYLEIGH MODEL

All the models studied so far within the framework of the theory of activated rate processes treat dissipation either via the FPE with velocity-independent friction or via master equations with velocity-independent collision frequency. In order to take into account velocity-sensitive dissipation, we must start either from the FPE with velocity-dependent friction or from master equations with velocity-dependent collision rates. To avoid introducing phenomenological dissipation models, we use the Rayleigh model of the nonlinear Brownian motion, which describes a one-dimensional (1D) relaxation of a heavy particle of mass $M$ in the bath of light particles of mass $m \ll M$. Within this model, collisional relaxation of the heavy particle is described by the master equation with the velocity-dependent collision frequency. The model possesses a small parameter $\lambda^2 = m/M \ll 1$. Then, according to van Kampen, we can run a systematic expansion of this master equation, which allows us to construct the dissipation operator to any desirable order in $\lambda$. Up to the terms of the order of $O(\lambda^4)$, our starting equation reads

$$
\partial_t \rho(x, v, t) = \left\{ -v \partial_x + M^{-1} U'(x) \partial_v + \xi(L_1 + \lambda^2 L_2) \right\} \rho(x, v, t). \tag{1}
$$

Here $\rho(x, v, t)$ is the probability density function in the position ($x$) – velocity ($v$) phase space, $U(x)$ is an external potential which is schematically depicted in Fig. 1,

$$
\xi = \frac{8\eta}{\sqrt{2\pi}} \lambda^2 \sigma^{-1/2} \tag{2}
$$

is the friction, $\eta$ is the number of the bath particles per unit length,

$$
\sigma = \beta M, \quad \beta = \frac{1}{k_B T}. \tag{3}
$$

The dissipation operator in Eq. (1) consists of two parts.

$$
L_1 = \partial_v v + \frac{1}{\sigma} \partial^2 \tag{4}
$$

The present paper is aimed at proving and elucidating the above qualitative expectations.
is the standard Fokker-Planck operator, while the next-order correction to it is explicitly written as

\[
L_2 = -\partial_v v + \frac{\sigma}{6} \partial_v v^3 - \frac{2}{\sigma} \partial_v^2 v^2 + \frac{3}{2} \partial_v^2 v^2 + \frac{8}{3\sigma} \partial_v^3 v + \frac{4}{3\sigma^2} \partial_v^4.
\]  

(5)

After doing some algebra, we can rewrite Eq. (1) in the following compact form:

\[
\partial_t \rho(x, v, t) = \left\{ -v \partial_x + M^{-1} U'(x) \partial_v + \xi \partial_v \rho_B(v) \hat{S}(v) \partial_v \rho_B^{-1}(v) \right\} \rho(x, v, t).
\]  

(6)

Here

\[
\hat{S}(v) = 1 + \lambda^2 \delta + \lambda^2 p(\partial_v + (q - \sigma)v)(\partial_v - qv)
\]  

(7)

is the core of the dissipation operator, and

\[
\rho_B(v) = \sqrt{\sigma/(2\pi)} \exp\{-\sigma v^2/2\}
\]  

(8)

is the equilibrium Boltzmann distribution, and

\[
p = \frac{4}{3\sigma^2}, \quad q = \frac{2 \pm \sqrt{2}}{4}, \quad \delta = \pm \frac{\sqrt{2}}{3\sigma}.
\]  

(9)

The standard Kramers FPE is recovered in the limit \(\lambda^2 \to 0\), \(\hat{S}(v) \to 1\). Eq. (6) can be solved numerically for any values of parameters (9). To get a better understanding of the effect of velocity-dependent friction on the escape rates, we analyze the problem analytically.

Applying the projector operator technique, we can reduce 2D Eq. (6) to the corresponding 1D equations in the limit of the high (\(\xi \gg \Omega\)) and weak (\(\xi \ll \Omega\)) friction, \(\Omega\) being a characteristic well frequency. In the former case, the Brownian particle’s velocity is a fast variable. We can thus introduce the projection operators

\[
P = \rho_B(v) \int dv, \quad Q = 1 - P,
\]

and arrive at the Smoluchowski diffusion equation for the position-dependent probability density:

\[
\partial_t \rho(x, t) = D \partial_x \{ \beta U'(x) + \partial_x \} \rho(x, t).
\]  

(10)

Here the diffusion coefficient, \(D\), equals to the integral relaxation time of the equilibrium velocity correlation function in the overdamped limit, \(\int_0^\infty dt \langle vv(t) \rangle\). Within the present model this correlation function has been evaluated by Hynes,\(^{33}\) so that

\[
D = \frac{1}{\xi \beta} \left\{ 1 + \frac{\lambda^2}{18} \right\} + O(\lambda^4)
\]  

(11)
and the Kramers rate (in the limit of low temperature and/or high barrier height, $\beta E_b \gg 1$) reads

$$k = D \frac{\omega_0 \omega_b}{2\pi} \exp\{-\beta E_b\} + O(\lambda^4).$$  \tag{12}

The frequencies $\omega_0$ and $\omega_b$ determine the shape of the potential linearized in the vicinity of the bottom of the well and at the barrier,

$$U(x) \approx \omega_0(x - x_0)^2/2 \quad \text{and} \quad U(x) \approx E_b - \omega_b(x - x_b)^2/2,$$  \tag{13}

respectively, see Fig. 1. As expected, the velocity-dependent friction increases the diffusion coefficient,\textsuperscript{21,33} but the effect is of the order of $\lambda^2$ and is therefore small.

The underdamped limit ($\xi \ll \Omega$) is much more interesting. We can either switch to the action ($I$) – angle ($\phi$) variables and introduce the projectors

$$P = \frac{1}{2\pi} \int_0^{2\pi} d\phi, \quad Q = 1 - P,$$

or change to the energy variable, $E$. In any case, we can start from Eq. (6) and arrive at the energy FPE

$$\partial_t \rho(E, t) = \xi \partial_E \hat{D}(E) \rho_{eq}(E) \partial_E \rho_{eq}^{-1}(E) \rho(E, t).$$  \tag{14}

The core of the energy FPE operator (6) is explicitly written as

$$\hat{D}(E) = D_0(E) + D_1(E) \partial_E + D_2(E) \partial_E^2;$$  \tag{15}

$$D_0(E) = \frac{2}{\beta} \{b_1(E) + \lambda^2(\beta b_3(E)/3 - b_1(E))\},$$  \tag{16}

$$D_1(E) = \frac{8\lambda^2}{3\beta} \{3b_1(E)/\beta - 2b_3(E)\},$$  \tag{17}

$$D_2(E) = \frac{16\lambda^2}{3\beta^2} b_3(E).$$  \tag{18}

The equilibrium distribution reads

$$\rho_{eq}(E) = Z_{eq}^{-1} a_{-1}(E) \exp\{-\beta E\}, \quad Z_E = \int dE a_{-1}(E) \exp\{-\beta E\},$$  \tag{19}

and we have introduced the quantities

$$a_n(E) = \int dx (E - U(x))^{n/2}, \quad b_n(E) = a_n(E)/a_{-1}(E)$$  \tag{20}
(integration is presumed over all \( x \) for which \( E > U(x) \)). The standard Kramers energy-diffusion FPE\textsuperscript{11,12,34} is recovered in the limit \( \lambda^2 \to 0 \). Eq. (14) can be used to run perturbative series in \( \lambda^2 \) to calculate the mean first passage time, \( \tau(E) \), the inverse of which yields the relaxation rate, \( k \) (see Appendix). If we again assume that \( \beta E_b \gg 1 \), we get then

\[
k = k_{Kr} \left[ 1 + \frac{\lambda^2 \beta a_3(E_b)}{3a_1(E_b)} \right] + O(\lambda^4).
\]

This is the main result of the present paper. If we neglect the \( \sim \lambda^2 \) correction, then we recover the Kramers expression for the rate in the underdamped limit\textsuperscript{11,12,34}

\[
k_{Kr} = 2 \xi \beta \exp\{-\beta E_b\} \frac{a_1(E_b)}{a_{-1}(0)}.
\]

On the other hand, the expression in the square brackets in Eq. (21) can easily be evaluated. For the harmonic oscillator (13), for example, it equals \( 1 + \lambda^2 \beta E_b/4 \). For the Morse oscillator it yields \( 1 + \lambda^2 \beta E_b/6 \). Therefore, the actual small parameter of the problem in the underdamped limit is \( \lambda^2 \beta E_b \) rather than \( \lambda^2 \). Since Eq. (21) has been derived in the limit \( \beta E_b \gg 1 \), the product \( \lambda^2 \beta E_b \) can be \( \sim 1 \) or higher even for \( \lambda^2 \ll 1 \). In this case, evidently, the perturbative expansion of the dissipative operator in \( \lambda^2 \) may break down, and the description within the Rayleigh master equation\textsuperscript{27,29} might be necessary.

We did not consider the influence of non-Markovian effects on the escape rates. These effects normally reduce molecular friction and therefore decrease the escape rates in the underdamped limit. Their influence is just the opposite to that of the velocity-dependent friction. However, as has been pointed out in\textsuperscript{11,12} the non-Markovian effects are of minor importance in the case of a deep well, \( \beta E_b \gg 1 \). It is in this latter case we predict the velocity dependence of friction can give rise to a dramatic increase of the escape rate, \( \sim \lambda^2(E_b \beta)^1 \), despite its influence on the velocity relaxation under equilibrium conditions is small, \( \sim \lambda^2(E_b \beta)^0 \ll 1 \).

### III. CONCLUSIONS

The main result of our paper can be formulated as follows: the effects due to the velocity-dependent friction\textsuperscript{20} may be of considerable importance in determining the rate of escape of an under- and moderately damped Brownian particle from a deep potential well. Similar effects due to the (possible) energy dependence of vibrational relaxation rates might also be
significant in describing unimolecular reactions under non-equilibrium conditions, like those investigated in\cite{36,37}.

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**APPENDIX A: CALCULATION OF THE FIRST PASSAGE TIME IN THE UNDERDAMPED LIMIT**

The first passage time in the underdamped limit, $\tau(E)$, can be evaluated through the equation\cite{34}

$$-1 = \rho_{eq}^{-1}(E)\partial_E \hat{D}(E)\rho_{eq}(E)\partial_E \tau(E)$$ (A1)

obeying the boundary conditions $\tau'(0) = 0$, $\tau(E_b) = 0$. The adjoined energy FPE operator, $\rho_{eq}^{-1}(E)\partial_E \hat{D}(E)\rho_{eq}(E)\partial_E$, is explicitly defined via Eqs. (15)-(20)\cite{35}. In order to solve Eq. (A1) perturbatively, note that $D_0(E)$ possesses contributions both $\sim 1$ and $\sim \lambda^2$, while $D_1(E)$ and $D_2(E)$ are both $\sim \lambda^2$. Thus we get

$$\tau(E) = \int_{E_b}^{E} dE' \rho_{eq}^{-1}(E') \left\{ 1 - \hat{Y}(E') \right\} \int_{0}^{E'} dE'' \rho_{eq}(E'') + O(\lambda^4), \quad \text{(A2)}$$

$$\hat{Y}(E) = \rho_{eq}(E) \left\{ D_1(E)\partial_E + D_2(E)\partial_E^2 \right\} \frac{\rho_{eq}^{-1}(E)}{D_0(E)}.$$ (A3)

We further assume that the temperature is low, $\beta E_b \gg 1$. Then, taking into account the explicit form of $D_1(E)$ and $D_2(E)$, we see that the leading contributions stemming from $\hat{Y}(E)$, which are of the order of $\lambda^2(E_b\beta)^0$, cancel each other. Thus, $\hat{Y}(E)$ yields contributions $\sim \lambda^2(E_b\beta)^{-1}$, which can be neglected as compared with those $\sim \lambda^2(E_b\beta)^0$ and $\sim \lambda^2(E_b\beta)^1$. Then, omitting $\hat{Y}(E)$ in Eq. (A2) and evaluating integrals to the leading order, we arrive at the expression

$$\tau(E) = \frac{1}{\xi \beta^2} a_{-1}(E_b) \exp\left\{ \beta E_b \right\} \frac{a_{-1}(0)}{D_0(E_b)} + O(\lambda^4). \quad \text{(A4)}$$
Finally, retaining only the leading contribution $\sim \lambda^2 (E_b \beta)^1$ into $D_0(E_b)$ (16) and inverting Eq. (A4) one gets Eq. (21).

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FIG. 1: Sketch of the potential energy surface.