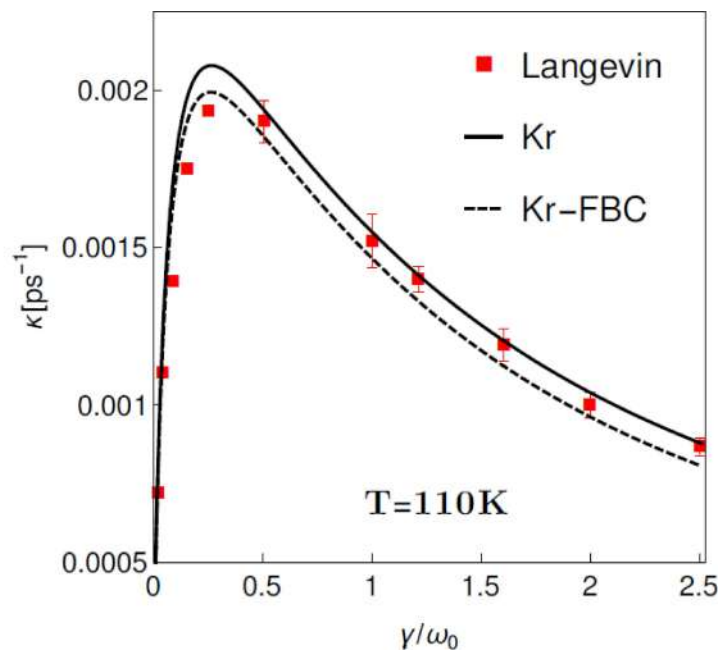
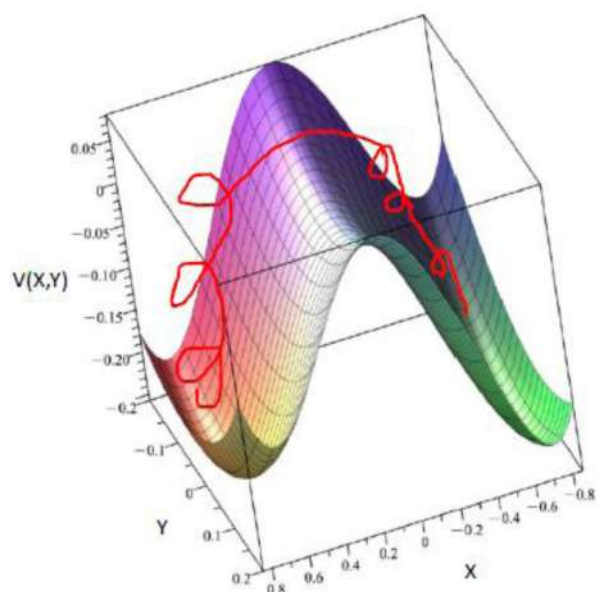


Recent Developments in Kramers' Theory of Reaction Rates

Special
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In this short review, we provide an update of recent developments in Kramers' theory of reaction rates. After a brief introduction stressing the importance of this theory initially developed for chemical reactions, we briefly present the main theoretical formalism starting from the generalized Langevin equation and continue by showing the main points of the modern Pollak, Grabert and Hänggi theory. Kramers' theory is then sketched for quantum and classical surface diffusion. As an

illustration the surface diffusion of Na atoms on a Cu(110) surface is discussed showing escape rates, jump distributions and diffusion coefficients as a function of reduced friction. Finally, some very recent applications of turnover theory to different fields such as nanoparticle levitation, microcavity polariton dynamics and simulation of reaction in liquids are presented. We end with several open problems and future challenges faced up by Kramers turnover theory.

1. Introduction

Hendrik Anthony Kramers published in 1940 arguably his most famous article, entitled "Brownian Motion in a Field of Force and the Diffusion Model of Chemical Reactions".^[1] Although his contributions to science were numerous and include the so-called Kramers-Kronig relations,^[2] the WKB method^[3] and much more, it is his seminal contribution to rate theory that by far has the most citations (over 7000), as may be inferred from the Web of Science. The innovations in this paper are many. This was the first implementation of the Langevin equation to rate theory. Kramers derived here the phase space Fokker-Planck equation. But perhaps it is the question that he posed but left unanswered in his paper, which continues to intrigue the Chemistry and Physics communities.

Kramers analyzed a very simple one-dimensional model to obtain insight into how a surrounding affects the rate of a chemical reaction. In his model, the surrounding influences the reacting species through a frictional force. When it is strong, it hampers the movement of the particle and therefore slows down the reaction rate. Conversely, without interaction with the surroundings, the particle typically does not have sufficient energy to react. In the limit that the friction is weak, increasing the friction increases the exchange of energy with the medium and the rate increases. Considering the rate as a function of the friction coefficient, it initially increases and then decreases – this is the "Kramers turnover". Kramers derived an expression for the initial increase of the rate in the so-called energy diffusion-limited regime as well as the decrease when the friction is moderate to strong. This is known as the spatial diffusion-limited regime since friction literally makes it more difficult for the reacting species to move. However, he did not derive an

expression for the rate which would go smoothly from one regime to the other, this is the Kramers' turnover problem, which is the topic of reviews^[4,5] and to this very day inspires and underlies many avenues of research and is a central topic of this review.

The derivation of an expression that correctly describes the turnover problem was made in two steps. Mel'nikov and Meshkov^[6] derived an expression that covered the range from weak to moderate friction. Their theory will be denoted henceforth as MM. Pollak, Grabert and Hänggi,^[7] using the method of Mel'nikov and Meshkov derived an expression that covered the full range of friction and demonstrated that it is not limited only to Ohmic friction but could be used also to predict the rate when the dynamics is influenced by memory friction. Their theory will be referred to as PGH theory.

Yet these solutions were not complete in many senses. The solutions were correct in the limit that the reaction barrier energy (V^\ddagger) is large when measured in terms of the temperature of the surrounding ($k_B T \equiv \beta^{-1}$). But what happens, as is often the case when $\beta V^\ddagger \sim 1$? It was necessary to derive "finite barrier" corrections to the activated decay rate.^[8–10] Only rather recently has a solution for the full finite barrier correction problem, without ad-hoc assumptions, been presented.^[11]


But there were additional problems. In the PGH formalism, the motion of the particle occurs along what is known as the unstable normal mode, and when considering motion along a periodic potential as in surface diffusion, this effective potential is no longer periodic. In its original form, the PGH theory could not be applied to surface diffusion. This problem did not occur in the Mel'nikov-Meshkov approach^[12] which was therefore used to provide insight into surface diffusion and especially the theory of multiple hops in surface diffusion.^[13,14] It is only in recent years that this difficulty has been solved.^[15]


An important parameter that appears in the turnover theory is the (reduced in terms of k_{BT}) energy loss δ . This is the energy lost by the particle as it traverses the region outside of the barrier, typically the stable well region. In the underdamped limit, δ is small and the rate is proportional to it. In the overdamped limit, it is large, and the rate is independent of it. In the MM solution, the energy loss is typically proportional to the product of the friction coefficient and the reduced barrier height. As the friction increases, the energy loss increases without bound, leading to values that can be substantially greater than the barrier height and so it becomes unphysical. This typically occurs for values of the (reduced in terms of the barrier frequency) friction coefficient which are somewhat less than the reduced barrier height. The PGH theory, in its original

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 An invited contribution to a Special Collection dedicated to Pablo Villarreal Herrán on the occasion of his 70th birthday

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form, goes to a finite limit but has the unphysical property that the PGH energy loss is not necessarily a monotonic increasing function of the friction coefficient.

As described thus far, the turnover theory is a purely classical theory. But in many cases, quantum effects cannot and should not be ignored. The classical diffusion coefficient diverges in the limit that friction vanishes, the quantum is smaller.^[16,17] Quantum tunneling cannot be ignored and so should be incorporated into the theory. In fact, both quantization of the harmonic bath underlying Kramers' model is possible and tunneling effects may be introduced by using parabolic barrier transmission and reflection coefficients.^[18] But, of course, these are not valid at low temperatures, below the so-called crossover temperature between tunneling-dominated reaction and thermal activation.^[19] The quantum turnover problem is thus not yet fully solved.

Another aspect of the turnover theory that continues to present a challenge is its extension to multi-dimensional systems. Some attempts have been made in this direction,^[20,21] but the question remains open to this very day. Is it important? Perhaps yes, as most reactions do not occur, or cannot be realistically described, in terms of motion along only a one-dimensional coordinate.

Thus far we have discussed only theory. Is the turnover theory of any experimental relevance? Especially in recent years, the answer to this question has become positive. The turnover has been observed experimentally using levitated nanoparticles.^[22] It is at the center of attempts at understanding reactions in microcavities^[23–25] and there have been numerous reports on its observation in reactions in liquids.^[26–30] It has also been used to gain insight into measured hopping distributions in studies of surface diffusion.^[31–34]

This long introduction should hopefully draw the reader deeper into the turnover problem. For this purpose, in Section 2 we provide a short review of the theory in its latest version. We then continue to discuss its application to surface phenomena in Section 3. Various additional experimental and theoretical applications are reviewed in Section 4 and we end with a Discussion of the future of the theory, to cite Kramers: "To do original physics and to get some results is as if one is kissed by an angel".^[35]

2. General Theory

2.1. The Generalized Langevin Equation and the Normal Mode Transformation

Underlying Kramers' 1940 paper is the Generalized Langevin Equation (GLE), in which the motion of a one-dimensional particle with mass M and coordinate q is governed by the dynamical classical equation of motion.

$$M\ddot{q} + \frac{dV(q)}{dq} + M \int_0^t dt' \gamma(t-t') \dot{q}(t') = F(t). \quad (2.1)$$

Dots denoted time derivatives, $\gamma(t)$ is termed the friction function, $F(t)$ is a Gaussian random force with zero mean whose correlation function is proportional to the friction function

$$\langle F(t)F(t') \rangle = Mk_B T \gamma(t-t'). \quad (2.2)$$

$V(q)$ is the potential function. In the case of escape of a particle from a well, as considered by Kramers, it has a well at q_0 with harmonic frequency ω_0 and a barrier at $q = 0$ with barrier frequency ω^\ddagger . The barrier separates the well from a continuum or perhaps a different adjacent stable well. Since the vicinity of the barrier plays a major role in rate theory, it is worthwhile to write down the potential as

$$V(q) = -\frac{1}{2}M\omega^{\ddagger 2}q^2 + V_1(q) \quad (2.3)$$

where $V_1(q)$ is termed the nonlinear part of the potential function. Although this form is quite general, it does not include all cases, for example a cusped barrier or a barrier whose form around the barrier top is $-q^{2n}$ with $n > 1$. There are ways of treating such difficulties, as described in Refs. [36,37].

It is well understood that the generalized Langevin equation may be derived as the continuum limit of a particle coupled bilinearly to a harmonic bath.^[38] This Hamiltonian has the form

$$H = \frac{p_q^2}{2M} - \frac{1}{2}M\omega^{\ddagger 2}q^2 + V_1(q) + \frac{1}{2} \sum_{j=1}^N \left[\frac{p_{x_j}^2}{m_j} + m_j \left(\omega_j x_j - \frac{c_j}{m_j \omega_j} q \right)^2 \right]. \quad (2.4)$$



EP was born in Israel in 1950, joined the Chemical Physics Department of the Weizmann Institute in 1979 and has been there ever since. His scientific work has focused mainly on rate theory, classical, semiclassical and quantum molecular dynamics. He is a Fellow of the American Physical Society, the American Association for the Advancement of Science, the Royal Chemical Society and has lately been elected as an Honorary Fellow of the Chinese Chemical Society.



SMA was born in Gandía (Valencia, Spain) in 1957, joined the Consejo Superior de Investigaciones Científicas in 1986 and he is director of the Instituto de Física Fundamental and Centro de Física Miguel Antonio Catalán. His scientific work is focussed mainly on atom-surface scattering (diffraction and surface resonances, electron-phonon coupling, surface diffusion), Bohmian mechanics and open quantum systems.

p_{x_j} , x_j , ω_j and m_j are respectively the momentum, coordinate, frequency, and mass associated with the j -th oscillator. c_j is the coefficient that couples the j -th bath oscillator to the system. The relationship of the Hamiltonian form to the generalized Langevin equation is found by noting that for this discretized form, one may derive an equation equivalent to the GLE. In this discretized equation the friction function takes the form

$$\gamma(t) = \sum_j \frac{c_j^2}{Mm_j\omega_j^2} \cos(\omega_j t) \quad (2.5)$$

and the random force is

$$F(t) = \sum_j c_j \left[\left(x_j(0) - \frac{c_j q(0)}{m_j \omega_j^2} \right) \cos(\omega_j t) + \frac{p_j(0)}{m_j \omega_j} \sin(\omega_j t) \right] \quad (2.6)$$

where $t = 0$ denotes the initial time. One immediately sees that due to the quadratic structure of the bath, any average over the bath variables with the thermal distribution $\exp(-\beta H)$ is a Gaussian average such that the random force is a Gaussian random force. The continuum limit is readily obtained by defining a spectral density of the bath modes

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) \quad (2.7)$$

such that the friction is given in terms of the spectral density as

$$\gamma(t) = \frac{2}{\pi M} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \cos(\omega t). \quad (2.8)$$

If one sets the nonlinear part of the potential equal to zero, one is left with a Hamiltonian with a quadratic form, in which the system mode has an imaginary frequency and all bath modes have a real frequency. This quadratic form may be diagonalized and one can show that this diagonalization will lead to one mode – the unstable mode – with an imaginary frequency and all other modes are stable.^[39] The resulting diagonalized Hamiltonian takes the form

$$H = \frac{p_\rho^2}{2} - \frac{1}{2} \lambda^{\pm 2} \rho^2 + V_1(q) + \frac{1}{2} \sum_{j=1}^N (p_{y_j}^2 + \lambda_j^2 y_j^2) \quad (2.9)$$

where the unstable normal mode is characterized by the (mass weighted) coordinate ρ and momentum p_ρ and barrier frequency λ^\pm . The stable bath mass weighted normal mode coordinates and momenta are denoted as y_j and p_{y_j} respectively and have stable frequencies λ_j .

Since the diagonalization is analytic one finds an explicit expression for the unstable normal mode frequency

$$\lambda^{\pm 2} + \hat{\gamma}(\lambda^\pm) \lambda^\pm = \omega^{\pm 2} \quad (2.10)$$

where $\hat{\gamma}(s)$ denotes the Laplace transform (with frequency s) of the time-dependent friction. This is the celebrated Kramers-Grote-Hynes relation.^[40] The normal mode transformation matrix U has elements u_{jk} , $j, k = 0, 1, \dots$ where the index 0 is chosen to single out the unstable mode. One may then express the system coordinate q in terms of the normal modes as

$$\sqrt{M}q = u_{00}\rho + u_1\sigma \quad (2.11)$$

with

$$u_1\sigma = \sum_{j=1}^N u_{j0}y_j \quad (2.12)$$

and

$$u_1^2 = 1 - u_{00}^2 = \sum_{j=1}^N u_{j0}^2. \quad (2.13)$$

The magnitude of the matrix element expressing the projection of the system coordinate onto the unstable mode is also known in terms of Laplace transforms of the friction function:^[7]

$$u_{00}^2 = \left[1 + \frac{1}{2} \left(\frac{\hat{\gamma}(\lambda^+)}{\lambda^+} + \frac{\partial \hat{\gamma}(s)}{\partial s} \Big|_{s=\lambda^+} \right) \right]^{-1} \quad (2.14)$$

and one notices that when the friction is weak this element is close to unity so that u_1^2 defined in the previous equation is small. A central part of PGH theory, as compared to MM theory is to develop a perturbation theory in terms of the small parameter u_1 rather than the reduced friction coefficient.

Just as there is a friction function for the system motion as defined in Eq. 2.5, and a bath spectral density as defined in Eq. 2.7 one also defines a normal mode friction kernel^[41]

$$K(t) = \sum_{j=1}^N \frac{u_{j0}^2}{\lambda_j^2} \cos(\lambda_j t). \quad (2.15)$$

and a spectral density of the stable bath normal modes

$$I(\lambda) = \frac{\pi}{2} \sum_{j=1}^N \frac{u_{j0}^2}{\lambda_j} \delta(\lambda - \lambda_j). \quad (2.16)$$

It is a matter of some straightforward algebra to show that Laplace transform of the normal mode friction kernel may be expressed in terms of Laplace transforms of the friction as

$$\hat{K}(s) = \left(\frac{su_{00}^2}{\lambda^{\pm 2}(s^2 - \lambda^{\pm 2})} + \frac{s + \hat{\gamma}(s)}{\omega^{\pm 2}(\omega^{\pm 2} - s^2 - \hat{\gamma}(s)s)} \right). \quad (2.17)$$

and that the spectral density of the stable modes is expressed as

$$I(\lambda) = \lambda \text{Re}[\hat{K}(i\lambda)] = \frac{\lambda \text{Re}[\hat{\gamma}(i\lambda)]}{(\omega_+^2 + \lambda^2)^2 + \lambda^2 \hat{\gamma}(i\lambda) \hat{\gamma}(-i\lambda)}. \quad (2.18)$$

2.2. The Rate Expression

The turnover theory is summarized in a single expression for the rate which involves a product of three terms.

$$\Gamma = \Gamma_{TST} \kappa_{SD} Y. \quad (2.19)$$

The first term (Γ_{TST}) is the “standard” transition state theory expression for the rate (assuming that the well is to the left of the barrier, located at $q = 0$):

$$\Gamma_{TST} = \frac{\exp(-\beta V^\ddagger)}{(2\pi M \beta)^{1/2} \int_{-\infty}^{\infty} dq \exp(-\beta V(q)) \theta(-q)}. \quad (2.20)$$

The second term (κ_{SD}) is responsible for the effect of friction on the spatial motion of the reacting particle. It is also known as the Kramers-Grote-Hynes transmission factor^[40]

$$\kappa_{SD}^0 = \frac{\lambda^+}{\omega^+} \quad (2.21)$$

and is the ratio of the normal mode barrier frequency to the physical barrier frequency. As may be inferred from Eq. 2.10, it is unity in the weak damping limit and goes to zero inversely with the damping strength in the strong damping limit.

It is the third factor (Y), known as the depopulation factor, which lies at the heart of the turnover theory. It accounts for the exchange of energy between the system and the bath and in the classical limit under discussion at this point, depends on one property only – the average (reduced) energy $\delta = \beta(\Delta E)$ lost to the bath, as the system traverses from the barrier over the well and back to the barrier. The expression, derived originally by Mel'nikov and Meshkov is

$$Y = \exp\left(\frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \frac{\ln[1 - \tilde{P}(\tau - \frac{i}{2})]}{\tau^2 + \frac{1}{4}}\right) \quad (2.22)$$

where

$$\tilde{P}\left(\tau - \frac{i}{2}\right) = \exp\left[-\delta\left(\tau^2 + \frac{1}{4}\right)\right]. \quad (2.23)$$

In the underdamped limit, the energy loss $\delta \ll 1$ and $Y \simeq \delta$, in the strong damping limit, the energy loss becomes large and the depopulation factor goes to unity.

There is a central difference between the MM and PGH theories. In the former, the dynamics is considered for the

system coordinate and the small parameter which underlies the perturbation theory is the reduced friction coefficient. In the latter, the dynamics is considered in the normal mode coordinates and the reduced parameter is related to the projection of the system coordinate onto the unstable mode and vice versa, as also described below. Due to this difference, the spatial diffusion factor comes out naturally in the PGH formalism, while in MM theory it is inserted “by hand”. It is for this reason that PGH theory is considered a full solution of the turnover theory, while MM laid out the framework but gave only a partial solution.

2.3. Modern PGH Theory

The central quantity which needs to be estimated is the reduced energy loss δ . This is implemented by perturbation theory. In its modern version, the perturbation theory which underlies PGH theory is based on defining a “small coordinate shift”^[15,42]

$$u_1 \Delta \sigma = u_1 \sigma + \left(u_{00} - \frac{\lambda^+}{\omega^+}\right) \rho. \quad (2.24)$$

It is small since typically the difference $(u_{00} - \frac{\lambda^+}{\omega^+})$ is of the same order as u_1 and as such can serve as the basis for a perturbation theory. The normal mode Hamiltonian, Eq. [2.9] takes the form:

$$H = \frac{p_\rho^2}{2} + V\left[\frac{1}{\sqrt{M}}\left(\frac{\lambda^+}{\omega^+}\rho + u_1 \Delta \sigma\right)\right] + \omega^+ \lambda^+ \rho u_1 \Delta \sigma + \frac{1}{2} \omega^{+2} u_1^2 \Delta \sigma^2 + \frac{1}{2} \sum_{j=1}^N [p_{y_j}^2 + \lambda_j^2 y_j^2]. \quad (2.25)$$

Setting $u_1 \Delta \sigma = 0$ one obtains the zeroth order Hamiltonian which governs the unstable mode dynamics:

$$H_0 = \frac{p_\rho^2}{2} + V\left(\frac{1}{\sqrt{M}} \frac{\lambda^+}{\omega^+} \rho\right) + \frac{1}{2} \sum_{j=1}^N [p_{y_j}^2 + \lambda_j^2 y_j^2] \quad (2.26)$$

and one notes that for a parabolic barrier potential $V(q) = -M\omega^{+2}q^2/2$, the potential $V\left(\frac{1}{\sqrt{M}} \frac{\lambda^+}{\omega^+} \rho\right) = -\frac{1}{2} \lambda^{+2} \rho^2$, so that in this limit the Hamiltonian reduces to the normal mode form as given in Eq. 2.9 (with $V_1(q) = 0$). The important result is that the shape of the potential which appears in the zeroth order Hamiltonian governing the unperturbed unstable mode motion is the same as that of the original potential. If it is periodic in the system coordinate, it is also periodic in the unstable mode coordinate. It is this property which enabled the extension of PGH theory to the general class of systems in which a particle interacts with a periodic surface.

But there is another physical aspect. One notes that the potential for the unstable mode is typically “softer” as compared to the system coordinate, since $\frac{\lambda^+}{\omega^+} \leq 1$. Equivalently, the effective mass governing the unstable mode motion ($M\omega^{\pm 2}/\lambda^{\pm 2}$) is increased as compared to the system coordinate. For example, this leads to the observation that the effective lattice constant in a periodic potential becomes larger. This softening of the unstable mode dynamics explains many of the qualitative features of the effect of friction on the dynamics of a system.

With these preliminaries, it becomes a matter of some algebra to derive the necessary equation for the energy loss, as detailed in Ref. [42], and one finds

$$\delta = \frac{\beta}{2\pi M} \int_{-\infty}^{\infty} d\lambda l(\lambda) \left| \int_{-\infty}^{\infty} dt \exp(-i\lambda t) V_1 \left(\frac{\lambda^+ \rho_{t,0}}{\sqrt{M}\omega^+} \right) \right|^2 \quad (2.27)$$

where $\rho_{t,0}$ is the trajectory of the unperturbed unstable mode as it traverses from the barrier and back, according to Newton's equation

$$\ddot{\rho}_{t,0} = -\frac{\partial}{\partial \rho_{t,0}} V \left(\frac{1}{\sqrt{M}} \frac{\lambda^+}{\omega^+} \rho_{t,0} \right). \quad (2.28)$$

2.4. An Example: Escape from a Cubic Potential Well

To exemplify various aspects of the turnover theory, we briefly consider the results for the escape rate when the potential has the cubic form

$$V(q) = -\frac{M\omega^{\pm 2}}{2} q^2 \left(1 + \frac{q}{q_0} \right) \quad (2.29)$$

such that the barrier height is

$$V^{\pm} = \frac{2M\omega^{\pm 2} q_0^2}{27}. \quad (2.30)$$

We consider the case of Ohmic friction

$$\gamma(t) = 2\gamma\delta(t) \quad (2.31)$$

where $\delta(t)$ is the Dirac “delta” function and γ is the friction coefficient. For Ohmic friction the spectral density $J(\omega) = \gamma\omega$ but the spectral density of normal modes is quite different:

$$l(\lambda) = \frac{\lambda\gamma}{(\omega^{\pm 2} + \lambda^2)^2 + \lambda^2\gamma^2}. \quad (2.32)$$

The trajectory of the unstable mode initiated from the barrier top at $t \rightarrow -\infty$, returning to it as $t \rightarrow \infty$ is:

$$\rho_{t,0} = -\frac{\omega^+ \sqrt{M} q_0}{\lambda^+ \cosh^2 \left(\frac{\lambda^+}{2} t \right)}. \quad (2.33)$$

This may be compared to the zeroth order trajectory appearing in MM theory

$$q_{t,0} = -\frac{q_0}{\cosh^2 \left(\frac{\omega^+ t}{2} \right)}. \quad (2.34)$$

One notes that in PGH theory the path length is longer, of the order of $(\omega^+/\lambda^+)q_0$ as compared to q_0 and the time evolution is slower, exemplifying the “softening” of the motion.

The expression for the PGH energy loss is:

$$\delta_{PGH} = 108\pi\beta V^{\pm} \nu(\nu-1)M_4(\nu) \quad (2.35)$$

where the parameter ν is the ratio λ_1/λ^{\pm} of the two solutions of the Kramers-Grote-Hynes equation for Ohmic friction (Eq. 2.10)

$$\nu = \frac{\gamma + \sqrt{\gamma^2 + 4\omega^{\pm 2}}}{\sqrt{\gamma^2 + 4\omega^{\pm 2}} - \gamma}, \quad (2.36)$$

the function $M_4(\nu)$ is

$$M_4(\nu) = \frac{2}{5\pi} - \frac{\nu^2}{3\pi} + \frac{2}{\pi} \nu^3 (\nu^2 - 1) \psi'(\nu) - \frac{2}{\pi} \nu^2 (\nu^2 - 1) - \frac{1}{\pi} \nu (\nu^2 - 1) \quad (2.37)$$

and

$$\psi'(\nu) = \sum_{n=0}^{\infty} \frac{1}{(\nu+n)^2}. \quad (2.38)$$

The MM energy loss has the much simpler form

$$\delta_{MM} = \frac{36}{5} \beta V^{\pm} \frac{\gamma}{\omega^+}. \quad (2.39)$$

In the weak damping limit the MM and PGH energy losses are identical, in the strong damping limit

$$\lim_{\gamma \rightarrow \infty} \delta_{PGH} = \frac{432}{35} \beta V^{\pm}. \quad (2.40)$$

so that the PGH energy loss is finite. The ratio of the PGH energy loss to the MM energy loss is plotted in Figure 1 as a function of the reduced friction coefficient $x = \gamma/\omega^{\pm}$. One notices that in the low friction regime - $0 \leq x \leq 0.68985$ the ratio is slightly greater than unity, reaching a maximum of ~ 1.032 at $x \sim 0.330$. In this region, the PGH energy loss is slightly larger than the MM energy loss so that the PGH rate in this region may be slightly larger. Conversely, when the friction

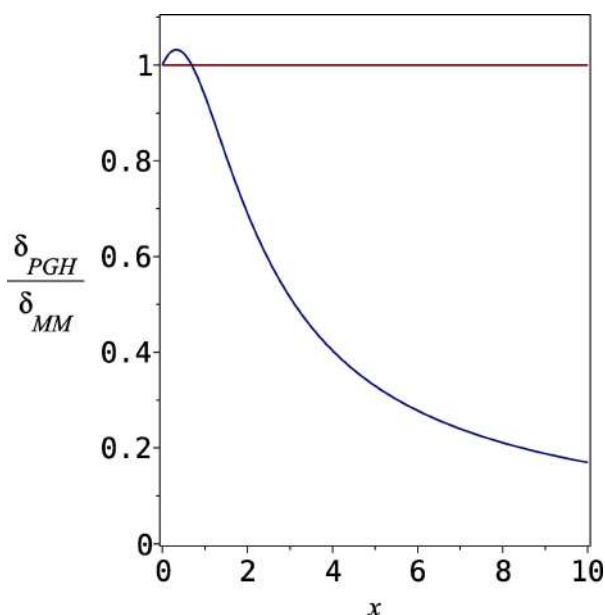


Figure 1. (color online) The ratio of the PGH to the MM energy loss for a cubic potential with Ohmic friction is plotted against the reduced friction coefficient $x = \gamma/\omega^\ddagger$. Note especially that the two estimates are rather close as long as the friction coefficient is not too much greater than unity.

becomes larger, the PGH energy loss becomes significantly smaller leading to a slightly smaller rate as compared with the MM rate.

2.5. Miscellaneous Topics

As mentioned, the turnover theory is in a sense an asymptotic theory, valid for large reduced barrier heights. However, finite barrier corrections to the theory have been derived, both in the spatial^[8] as well as in the energy diffusion limited regimes.^[11] These extend the range of the theory so that it gives reasonably good predictions for barriers as low as $\beta V^\ddagger = 2$. The finite barrier corrections have been tested numerically using classical mechanics. It remains to be seen whether the quantum version of the finite barrier corrections is accurate. For this purpose, numerical quantum simulations are needed.

A second aspect has to do with memory friction. PGH theory was tested against classical numerical simulations when the friction was exponential in time. The results especially in the limit of long memory friction point out the failure of MM theory as compared to PGH. However, the theory is not complete, one can show that there are long memory limits in which PGH also fails, these are described in Ref. [43]. The central problem is that in PGH theory a central assumption is that each sojourn of the particle as it goes from the barrier and back is independent of the previous one or the future one. In the limit of long memory, this assumption can break down and a more sophisticated treatment is called for.

The version presented here is the classical turnover theory. It may be extended to temperatures above the crossover

temperature between quantum tunneling and thermal activation ($\beta_c = \frac{2\pi}{\hbar\lambda}$) by introducing the quantum energy-dependent reflection and transmission coefficients for tunneling through a parabolic barrier (see Eq. 3.15 below) into the master equation governing the change of population as the particle traverses from the barrier to the well and back. Such a quantum theory has been tested against numerically exact computations in Ref. [44]. However, the quantum version of the turnover theory, especially in the context of surface diffusion has not been seriously tested against numerically exact quantum simulations. The upshot of all of this is that PGH theory has been improved significantly in recent years yet there are some remaining questions that are challenging.

3. Kramers' Theory for Surface Diffusion

3.1. General Framework

In 1954 van Hove^[45] showed that the scattering cross-section of probe particles such as low energy neutrons by a system of interacting particles can be expressed, within the Born approximation, in terms of the so-called generalized pair-distribution function $G(\mathbf{r}, t)$, depending on the space vector \mathbf{r} and time t . Given the pair distribution function, the scattering problem is reduced essentially to a problem of statistical mechanics where, in general, the nature of the scattered particles (neutron, light, atoms, etc.) and the interaction potential with the interacting system is no longer relevant.^[46] This G -function gives us the probability that given a particle at the origin and at time $t = 0$, any particle including the same one is to be found at the position \mathbf{r} at time t . In other words, the G -function also gives us the space-time correlation function between the presence of a particle at position \mathbf{r} and at time t and the presence of a second particle (the same one or a different one) at the origin and at time $t = 0$.

In the linear response theory, the scattering cross section $R(\mathbf{K}, \omega)$ is proportional to the so-called scattering law or dynamic structure factor (DSF) $S(\mathbf{K}, \omega)$ according to [45]

$$\frac{d^2 R(\mathbf{K}, \omega)}{d\Omega d\omega} = n_d F^2 S(\mathbf{K}, \omega) \quad (3.1)$$

where n_d is the diffusing particle concentration on the surface, F is the so-called atomic factor which depends on the interaction potential between the probe particles such as the He atoms and the adparticles or adsorbates and Ω is the final solid angle. The energy transfer in this scattering is written as ω . Moreover, in the surface literature, any variable parallel to the surface is written in capital letters; thus, the scattering momentum transfer along one of the symmetry directions of the surface is written as \mathbf{K} and the position on the surface of the adatoms as \mathbf{R} .

The corresponding inverse Fourier transform in time of S , which is also a response function and an observable, is known as the intermediate scattering function (ISF), $I(\mathbf{K}, t)$ (which

should not be confused with the spectral density of normal modes defined in Eq. 2.16)

$$S(\mathbf{K}, \omega) = \frac{1}{2\pi} \int dt e^{-i\omega t} I(\mathbf{K}, t), \quad (3.2)$$

and the double inverse Fourier transform (in momentum and energy) of $S(\mathbf{K}, \omega)$ gives us the $G(\mathbf{R}, t)$ -function. Thus, one can write

$$G(\mathbf{r}, t) = (2\pi)^{-3} N^{-1} \cdot \int d\mathbf{K} e^{-i\mathbf{K} \cdot \mathbf{r}} \sum_{l,j=1}^N \langle e^{-i\mathbf{K} \cdot \mathbf{R}_l(0)} \cdot e^{i\mathbf{K} \cdot \mathbf{R}_j(t)} \rangle, \quad (3.3)$$

where $\langle . \rangle$ stands for thermal (Boltzmann) averages or quantum expectation values depending on whether one is considering classical or quantum scattering. In contrast to neutron scattering where coherent and incoherent scattering can take place, this atom scattering is fully coherent. Within the classical approximation, $\mathbf{R}_l(0)$ and $\mathbf{R}_j(t)$ represent the initial location of particle l and the classical trajectory of particle j along the surface, respectively. In the quantum realm, these vector positions are replaced by the corresponding position operators.

Two well-established surface experimental techniques are used to measure the intermediate scattering function and the dynamical structure factor. These are the so-called quasi-elastic He atom scattering (QHAS)^[47,48] and neutron scattering (QENS)^[49] methods which overlap in spatial and time resolution.^[50,51] QENS is, in general, more convenient for processes occurring in bulk and QHAS is essentially sensible for surfaces. More recently, these two techniques have been complemented by using spin-echo (SE), HeSE^[50,51] and neutron spin-echo NSE techniques.^[49]

A proper theoretical framework to process the experimental results and extract relevant information about the physical systems of interest such as diffusion coefficients, jump distributions, escape rates, etc. is needed. A full description of the force fields (adsorbate-adsorbate and adsorbate-substrate interactions) involved is necessary in principle. The Langevin formalism or its generalization to include memory effects is widely applied starting from the system-bath Hamiltonian (Eq. 2.4) also known as the Zwanzig-Caldeira-Leggett Hamiltonian.^[38,52] Stochastic classical trajectories $\mathbf{R}(t)$ are then calculated for each adsorbate, except for very light adsorbates where surface tunneling can be present due to the corrugation of the surface and the classical approximation is no longer valid. If the surface coverage is small, the dynamics of only one adsorbate is studied by averaging over many trajectories and this is the case for which the Kramers turnover theoretical framework is relevant. Analytical expressions for I and S are readily obtained for flat and corrugated surfaces^[53] or with memory friction^[54] within the so-called Gaussian approximation. It is also possible to extend the theory to include the effect of (low) coverage through a model known as the interacting single adsorbate (ISA) model where

the added interaction among adsorbates is replaced by a shot noise simulating collisional friction.^[55,56]

Finally, it is worth mentioning that two extreme time regimes are well characterized for this open dynamics, the *ballistic regime*, at very short times, where the dynamics is friction and noise free and the *diffusive regime*, at very long times, where thermal equilibrium is finally reached with the surface. In the first regime, both response functions are Gaussian functions and, in the second regime, I is an exponential function and S is a Lorentzian function.

As already mentioned, when dealing with light adparticles, one cannot ignore quantum effects. Position operators do not commute at different times ($\hat{\mathbf{R}}_l(0)$ and $\hat{\mathbf{R}}_l(t)$) however an extension of the methodology used for classical diffusion can be still used to provide reasonable analytical expressions.^[57] A second approach is to consider stochastic quantum trajectories within the Bohmian framework.^[58] A widely used method for dealing with quantum open systems is the so-called *system-plus-environment* approach. The reduced density matrix in the coordinate representation describing the system of interest is obtained by tracing out the degrees of freedom of the environment. A master equation is then derived which contains both frictional and thermal effects, and is known as the Caldeira-Leggett (CL) master equation^[52] which is of Markovian type. The corresponding diagonal matrix elements give the quantum probabilities and the off-diagonal elements, the so-called coherences. Time evolution of coherences gives us an indication of how the decoherence process is gradually established leading to certain timescales of the system under study and exponential suppression of spatial interference terms. The CL formalism is used to describe the motion of a quantum Brownian particle linearly coupled to an Ohmic environment in the weak-coupling and high-temperature limits.^[59,60]

3.2. Intermediate Scattering Function and Dephasing Rates

The HeSE surface scattering technique provides a direct measurement of dynamical correlations on an atomic scale in both position and time. The ISF is an observable and in the diffusive regime it is an exponentially decaying function of time

$$I(\mathbf{K}, t) \propto e^{-\alpha(\mathbf{K})t}. \quad (3.4)$$

The exponential decay is ruled by what is known as the dephasing rate, α . This rate depends explicitly on the momentum transfer and, in general, the initial conditions of the particles and the surface temperature. From this observable, a detailed microscopic picture of motion on the surface can be extracted once a theoretical model or theory is chosen for such a goal. Several alternatives are available in the literature.

The QHAS surface technique has also been successfully applied to study the diffusion of single atoms and molecules on metal surfaces where the observable is the dynamic structure factor which has a Lorentzian shape (the so-called quasi-elastic peak or Q-peak)

$$S(\mathbf{K}, \omega) \propto \frac{\alpha(\mathbf{K})}{\omega^2 + \alpha(\mathbf{K})^2}. \quad (3.5)$$

With this line shape, the diffusion coefficient D can be extracted from the full width at half maximum (FWHM) Γ_{FWHM} of the quasielastic peak with respect to ω (around $\omega = 0$) at small \mathbf{K} values, which should be equal to $\Gamma_{FWHM} = 2D \mathbf{K}^2$ so that

$$S(\mathbf{K}, \omega) \propto \frac{D \mathbf{K}^2}{\omega^2 + D^2 \mathbf{K}^4}. \quad (3.6)$$

In general, the FWHM is a function of \mathbf{K} . This coefficient can also be extracted from the long time limit of the position variance:

$$D = \lim_{t \rightarrow \infty} \frac{1}{4t} \langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle. \quad (3.7)$$

Numerical simulations of the ISF are implemented using several techniques: the standard or generalized Langevin equation, the master equation of the reduced density matrix within the CL framework and the Ito differential equation also known as the stochastic wave function method. Once the ISF is calculated, the DSF is obtained by a simple Fourier transform.

3.2.1. The Chudley-Elliott Model

One of the most widely used models used to extract jump rates and jump distributions from the ISF or DSF is due to Chudley and Elliot.^[61] An activated atom surface diffusion is assumed and instantaneous jumps between different sites are considered. Under these assumptions, a master equation for the pair-distribution function in space and time and for a simple Bravais lattice reads as

$$\frac{\partial G(\mathbf{R}, t)}{\partial t} = \sum_{\mathbf{j}} \frac{1}{\tau_{\mathbf{j}}} [G(\mathbf{R} + \mathbf{j}, t) - G(\mathbf{R}, t)], \quad (3.8)$$

where $\tau_{\mathbf{j}}$ is the average time between successive jumps over the two-dimensional vector \mathbf{j} and the summation runs over all lattice vectors. If the time for a simple jump is very short compared with the time τ between successive jumps, the total jump rate can be written as $1/\tau = \sum_{\mathbf{j}} 1/\tau_{\mathbf{j}}$, with $\tau_{\mathbf{j}} = \tau_{-\mathbf{j}}$. Due to the linearity property of the Fourier transform, Eq. 3.8 is written as

$$\frac{\partial I(\mathbf{K}, t)}{\partial t} = -2I(\mathbf{K}, t) \sum_{\mathbf{j}} \frac{1}{\tau_{\mathbf{j}}} \sin^2 \left(\frac{\mathbf{j} \cdot \mathbf{K}}{2} \right), \quad (3.9)$$

whose solution is

$$I(\mathbf{K}, t) = I(\mathbf{K}, 0) e^{-\alpha(\mathbf{K})|t|}, \quad (3.10)$$

with the dephasing rate given by

$$\alpha(\mathbf{K}) = 2 \sum_{\mathbf{j}} \frac{1}{\tau_{\mathbf{j}}} \sin^2 \left(\frac{\mathbf{j} \cdot \mathbf{K}}{2} \right). \quad (3.11)$$

The FWHM of the S -function is given by

$$\Gamma_{FWHM}(\mathbf{K}) = 2\kappa \sum_{\mathbf{j}} P_{\mathbf{j}} [1 - \cos(\mathbf{j} \cdot \mathbf{K})]. \quad (3.12)$$

Here, $\kappa = 1/\tau$ and $P_{\mathbf{j}}$ is the relative probability for a jump with a displacement vector \mathbf{j} . This instantaneous jump model is a good approximation for barriers where $V^{\ddagger}/k_{\text{B}}T \geq 3$.

3.2.2. Quantum Kramers' Theory of Activated Surface Diffusion above Crossover Temperature

One of the main drawbacks of the Chudley-Elliott model is that in practice, the probabilities $P_{\mathbf{j}}$ are fitting parameters and not known a priori. It is here that Kramers' theory provides a prediction for all jump probabilities, based on knowledge of a single parameter, namely the reduced energy loss as the system moves from one barrier to the next. The turnover theory as applied to surface diffusion is based on a master equation for the populations in the wells, governed by an energy exchange kernel. In its original formulation, the theory considered that a transition would be possible only if the energy of the particle is greater than the barrier height. In later developments, this demand was relaxed and a transmission and reflection probability was introduced mainly in the form of a parabolic barrier probability.^[18] This simplification enables inclusion of tunneling and above barrier reflection in the analytic solution of the turnover problem. In addition, it is not necessary to consider a classical bath, but rather harmonic quantum bath. As a result, the Kramers-Grote-Hynes spatial diffusion prefactor is replaced by the Wolynes prefactor.^[62,63] The PGH quantum theory for surface diffusion in its modern form is given in Ref. [64]. All this results in a semiclassical-like theory since the zeroth-order motion of the unstable mode is still treated as classical.

The starting point for the evaluation of escape rates, jump distributions and diffusion coefficients is the stationary flux of particles at reduced energy $\varepsilon = E/(k_{\text{B}}T)$ exiting each well at either the barrier to the left of the well or to its right. When considering quantum surface diffusion along one dimension one may write down a steady state equation that describes the relationship between the number of particles per unit energy and per unit time hitting the right (left) $f_{\mathbf{j}}^+$ ($f_{\mathbf{j}}^-$) barrier of the \mathbf{j} th well with positive (negative) velocity

$$f_{\mathbf{j}}^+(\varepsilon) = \int_{-\infty}^{\infty} d\varepsilon' P(\varepsilon|\varepsilon') [f_{\mathbf{j}}^-(\varepsilon') R(\varepsilon') + f_{\mathbf{j}-1}^+(\varepsilon') T(\varepsilon')]. \quad (3.13)$$

Here, $P(\varepsilon|\varepsilon')$ is the conditional probability that a particle initiated at a given barrier with energy ε' will arrive at the

adjacent barrier with energy ε . The kernel has a Gaussian form^[12]

$$P(\varepsilon|\varepsilon') = \frac{1}{\sqrt{4\pi\delta}} \exp\left[-\frac{(\varepsilon - \varepsilon' + \delta)^2}{4\delta}\right], \quad (3.14)$$

with δ being the reduced average energy loss to the bath as the particle traverses from one barrier to the next. Its double-sided Laplace transform is given in Eq. 2.23. The resulting theory is analytic if one approximates the reflection and transmission coefficients using the parabolic barrier expressions

$$R(\varepsilon) = \frac{1}{1 + \exp(a\varepsilon)}, T(\varepsilon) = \frac{\exp(a\varepsilon)}{1 + \exp(a\varepsilon)}, a = \frac{2\pi}{\hbar\beta\lambda^\ddagger}. \quad (3.15)$$

It is convenient to define a friction-independent “quantity parameter”

$$b = \frac{2\pi}{\hbar\beta\omega^\ddagger} = a \frac{\lambda^\ddagger}{\omega^\ddagger}, \quad (3.16)$$

The relevant classical results are obtained from the quantum ones by taking the limit $\hbar \rightarrow 0$, or equivalently $a, b \rightarrow \infty$.

The boundary conditions on the fluxes are that initially, the particle is located in the $j = 0$ well with a thermal distribution so that

$$f_j^\pm(\varepsilon)_{\varepsilon \rightarrow -\infty} = \delta_{j0} \frac{C}{2\pi\hbar\beta} \exp(-\varepsilon). \quad (3.17)$$

In the spatial diffusion-limited regime, only nearest neighbor hops are allowed. The coefficient C is chosen so that in this limit, the rate of escape from the initial well is just twice the spatial diffusion rate (Γ_{sd}) for escape over one of the two adjacent barriers and

$$C = \Gamma_{sd} \sin\left(\frac{\pi}{a}\right) \frac{2\pi}{\lambda^\ddagger}. \quad (3.18)$$

The spatial diffusion escape rate is then

$$\Gamma_{sd} = \Gamma_{TST} \frac{\lambda^\ddagger}{\omega^\ddagger} \kappa_{FB} \Xi, \quad (3.19)$$

where κ_{FB} is the finite barrier correction to the rate in the spatial diffusion-limited regime,^[65] in its classical limit.^[8] Γ_{TST} is the escape rate estimate without taking frictional effects into account, that is

$$\Gamma_{TST} = \frac{2 \exp(-\beta V^\ddagger)}{(2\pi M\beta)^{1/2} \int_{-\infty}^{\infty} dq \exp(-\beta V(q)) \theta\left(q + \frac{l}{2}\right) \theta\left(\frac{l}{2} - q\right)}. \quad (3.20)$$

The factor of two in the numerator comes from the fact that the particle can escape from the well in either direction. Ξ – the Wolynes factor – is the ratio of the quantum partition function

at the barrier to that of the well expressed in terms of the so-called Matsubara frequencies

$$\tilde{\omega}_n = 2\pi n / (\beta\hbar) = nb\omega^\ddagger \quad (3.21)$$

as^[62]

$$\Xi = \prod_{n=1}^{\infty} \frac{\omega_a^2 + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)}{-\omega^\ddagger{}^2 + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)}. \quad (3.22)$$

In the classical limit $b \rightarrow \infty$, all the Matsubara frequencies go to infinity and $\Xi \rightarrow 1$.

Since we chose the $j = 0$ well to be populated while all other wells are not, we have the symmetry property

$$f_j^\pm(\varepsilon) = f_{-j}^\mp(\varepsilon). \quad (3.23)$$

Furthermore, the trapping rate in the j -th well is

$$\Gamma_j = \int_{-\infty}^{\infty} d\varepsilon T(\varepsilon) \left[f_{j-1}^+(\varepsilon) + f_{j+1}^-(\varepsilon) - f_j^-(\varepsilon) - f_j^+(\varepsilon) \right]. \quad (3.24)$$

From the double-sided Laplace transform of the Gaussian kernel ($P_0(\varepsilon|\varepsilon') = P_0(\varepsilon - \varepsilon')$)

$$\tilde{P}_0(is) = \exp[\delta(s^2 + s)] \quad (3.25)$$

and the function

$$G(is, k) = \frac{1 - \tilde{P}_0^2(is)}{1 + \tilde{P}_0^2(is) - 2\tilde{P}_0(is)\cos(k)}, \quad (3.26)$$

the hopping rates are analytically expressed as^[64]

$$\Gamma_j = -\frac{\Gamma_{sd}}{\pi} \int_0^{2\pi} dk \cos(jk) \sin^2\left(\frac{k}{2}\right) \cdot \exp\left(\frac{\sin\frac{\pi}{a}}{a} \int_{-\infty}^{\infty} d\tau \frac{\ln G(\tau - \frac{i}{2}, k)}{[\cosh(2\frac{\pi\tau}{a}) - \cos\frac{\pi}{a}]}\right). \quad (3.27)$$

The diffusion coefficient is expressed in terms of the rates as

$$D = \frac{1}{2} l^2 \sum_{j=-\infty}^{\infty} j^2 \Gamma_j = \frac{1}{2} \Gamma \langle l^2 \rangle, \quad (3.28)$$

where the escape rate $\Gamma = -\Gamma_0$ and $\langle l^2 \rangle$ is the mean squared hopping length, where the averaging is over the probability Γ_j/Γ for a hop of length l . Carrying out the summation analytically one finds a relatively simple expression for the diffusion coefficient

$$D = \frac{1}{2} \Gamma_{sd} l^2 \cdot \exp\left(\frac{1}{a} \int_{-\infty}^{\infty} d\tau \ln \left[\frac{1 + \tilde{P}_0(\tau - \frac{i}{2})}{1 - \tilde{P}_0(\tau - \frac{i}{2})} \right] F(a)\right) \quad (3.29)$$

$$\lim_{\gamma \rightarrow \infty} \delta = \frac{16}{3} \beta V_0^\ddagger. \quad (3.37)$$

with

$$F(a) = \frac{\sin \frac{\pi}{a}}{\left[\cosh\left(2 \frac{\pi \tau}{a}\right) - \cos \frac{\pi}{a} \right]}. \quad (3.30)$$

This expression includes the contributions of tunneling through the barrier and above barrier reflection as expressed by means of the quantality parameter a . It does not include finite barrier corrections which have been discussed in Ref. [64]. A well studied example is based on the cosine periodic potential

$$V(q) = -\frac{V_0^\ddagger}{2} \left[\cos\left(\frac{2\pi q}{l}\right) + 1 \right] \quad (3.31)$$

such that V_0^\ddagger is the barrier height for escape, the barrier frequency squared is

$$\omega^{+\ddagger} = \frac{2\pi^2 V_0^\ddagger}{M l^2}. \quad (3.32)$$

The energy loss is obtained from Eq. 2.26 which is based on the classical trajectory of the particle initiated at the barrier energy as it goes from one barrier to the next. For the cosine potential of Eq. 3.31 this trajectory as would be used in MM theory is

$$\tan\left(\frac{\pi q_t}{2l}\right) = \exp(\omega^{+\ddagger} t), \quad (3.33)$$

while for PGH theory and the effective Hamiltonian governing the unstable mode motion, it is

$$\tan\left(\frac{\pi \rho_t}{2l_\rho}\right) = \exp(\lambda^{+\ddagger} t), \quad (3.34)$$

and one notes the use of the renormalized lattice length l_ρ . For the improved PGH theory, one finds that the energy loss is^[15]

$$\delta = 2\beta V_0^\ddagger (\nu - 1) \left[2\nu + (1 - \nu^2) \sum_{k=0}^{\infty} \frac{1}{\left(\frac{\nu+1}{2} + k\right)^2} \right], \quad (3.35)$$

where the parameter ν has been defined in Eq. 2.36. This function is a monotonically increasing function of the friction coefficient. In the small friction limit, it is identical to the MM estimate

$$\lim_{\gamma \rightarrow 0} \delta = 4\beta V_0^\ddagger \frac{\gamma}{\omega_+^\ddagger} = \delta_{MM}, \quad (3.36)$$

and in the large friction limit

This is not identical to the MM result which diverges, however, we do note that it is larger than the barrier energy and so it too is not physical. This poses the challenge of finding a way of obtaining an estimate which is never greater than the barrier height.^[64]

PGH theory contains a few parameters, some of them structural such as the barrier height and frequencies, and the other ones are dynamical – the friction coefficient and the energy loss. One way of obtaining these parameters is through fitting experimental data, but note the limited number of parameters as compared for example with the Chudley-Elliott model.

The quantum version of the theory leads to insight into the effects of quantum mechanics on surface dynamics. One of the most striking effects is the reduction of the diffusion constant due to quantality in the low friction regime. This leads to an inverse isotope effect, the heavier the mass of the diffusing particle, the faster is the diffusion.^[16] This effect occurs only in the energy diffusion-limited regime. “Normal” isotope effects, where the diffusion of H is faster than that of D have been reported.^[66] An interesting question in this regard is, can one study experimentally the diffusion on a surface where the friction is sufficiently low so as to induce the inverse mass effect?

As already mentioned, the turnover theory is based on a mixed classical quantum mechanical description of the dynamics. The motion of the unstable mode as the particle traverses the well is treated classically. Although our experience indicates that this is a good approximation in the quantum limit, numerically exact quantum simulations are needed based on, for example, the stochastic wave function method.^[67] One hopes that the present theory will serve as a benchmark for such simulations which could also be used to explore quantum effects on the diffusion dynamics at temperatures below the crossover temperature between quantum deep tunneling and thermal activation. Furthermore, turnover theory is based on incoherent tunneling through the barriers. As the friction and bath temperature become sufficiently low one may expect that coherence effects in the form of the band structure of the quantum levels of the periodic potential will further affect the quantum hopping distribution and escape rate. They are not interesting in the context of the parameter range studied here, where the temperature is sufficiently high so that deep tunneling effects may be ignored. However, these too could and should be studied using numerically exact simulations since the low temperatures needed are accessible experimentally.

3.2.3. Kramers' Theory of Activated Surface Diffusion in the Classical Limit

From the previous quantum analysis particularized to a cosine potential, the corresponding classical analysis is quite straightforward. Thus, from l , the lattice constant of the surface, and the barrier height $V_0^\ddagger = 2V_0$, the energy loss within MM theory

is written as in Eq. 3.36 where for the cosine potential the harmonic well and barrier frequencies are identical and given as $\omega^\ddagger = \omega_0 = 2\pi\sqrt{V_0/mP^2}$.

Using again a discrete Fourier transformation in j and a Laplace transform in energy and the change of variable $\tau = \tan x/2$, the partial rate in the classical limit is^[12,16]

$$\Gamma_j = -\frac{\Gamma_{SD}}{\pi} \int_0^{2\pi} dk \sin^2\left(\frac{k}{2}\right) \cos(jk) \times \exp\left\{\frac{2}{\pi} \int_0^{\pi/2} dx \ln\left[\frac{1 - P^2(x)}{1 + P^2(x) - 2P(x)\cos(k)}\right]\right\}, \quad (3.38)$$

where Γ_{SD} is the classical spatial diffusion escape rate assuming that the well is harmonic^[1]

$$\Gamma_{SD} = \frac{\lambda^\ddagger \omega_0}{\omega^\ddagger \pi} e^{-(V^\ddagger/k_B T)}. \quad (3.39)$$

With the change of variable $\tau = \tan(x/2)$ (see Eq. 2.23) the function $P(x)$ is particularized as

$$P(x) = \exp\left[-\frac{\delta}{4\cos^2(x)}\right]. \quad (3.40)$$

The diffusion coefficient is then expressed in closed form as

$$D = D_{SD} Y^{-1} \exp\left\{\frac{2}{\pi} \int_0^{\pi/2} dx \ln[1 + P(x)]\right\}, \quad (3.41)$$

with $D_{SD} \equiv \Gamma_{SD}^2/2$ denoting the diffusion coefficient in the (single hopping) spatial diffusion regime, and Y is the depopulation factor for motion in the metastable well given in Eq. 2.22.

Following the same procedure as previously used in the Chudley-Elliott master equation model (see Eq. 3.8) except that the parameters $\frac{1}{\tau_j}$ are replaced by the hopping rates Γ_j given in Eq. 3.38, using the discrete Fourier transform

$$\hat{\Gamma}(k) = \sum_{j=-\infty}^{\infty} e^{ikj} \Gamma_j, \quad (3.42)$$

assuming that in the diffusive regime the dynamical structure factor is Lorentzian, one finds an explicit expression for the FWHM of the DSF^[14,68]

$$\Gamma_{FWHM}(k) = 2\hat{\Gamma}(k) = 4\Gamma_{sd} \sin^2\left(\frac{k}{2}\right) \cdot \exp\left\{\frac{2}{\pi} \int_0^{\pi/2} dx \ln\left[\frac{1 - P^2(x)}{1 + P^2(x) - 2P(x)\cos(k)}\right]\right\}. \quad (3.43)$$

Thus, when comparing the turnover theory with the experiment, information about the energy loss, barrier height, friction coefficient, barrier frequency, and spatial diffusion rate can be extracted. As pointed out above, this theory is a one-parameter theory – the energy loss δ rather than the multiparameter fitting of hopping rates, needed for the “standard” implementation of the Chudley-Elliott model. In principle, the turnover

theory as such is valid only when the reduced barrier height $V^\ddagger/(k_B T)$ is much larger than unity. When it is small, typically smaller than 5 one may extend the theory using finite barrier corrections for the spatial diffusion coefficient as well as the depopulation factor. Details of the derivation can be found in Refs. [11, 69, 70].

As an example of the application of the turnover theory, we bring results for the diffusion of Na atoms on a Cu(001) surface by assuming a one-dimensional cosine function for the corrugation. In this case, the classical theory is sufficient due to the large mass of the atoms involved. The lattice constant is $l = 2.56 \text{ \AA}$ and the barrier height $V^\ddagger = 82.8 \text{ meV}$. In Figure 2, escape rates (in ps^{-1}) are plotted as functions of the reduced friction coefficient (γ/ω_0) at two surface temperatures, 110 K and 200 K.

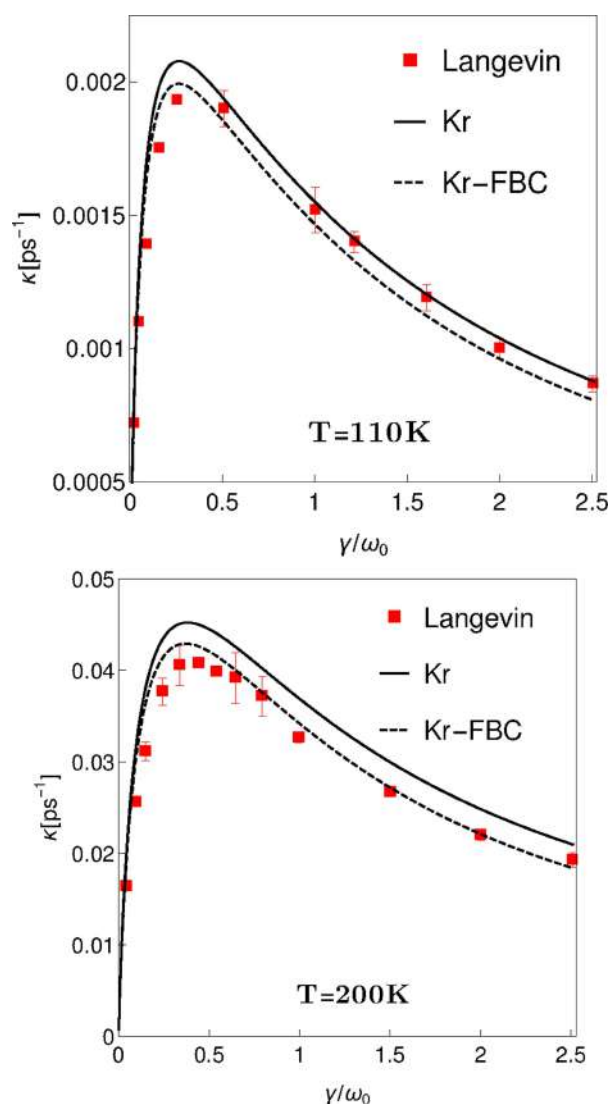


Figure 2. Escape rates κ (in ps^{-1}) are plotted as a function of the scaled friction γ/ω_0 for the symmetric one-dimensional cosine potential simulating the motion of Na atoms on a Cu(001) lattice. The energy barrier $V^\ddagger = 82.8 \text{ meV}$ at surface temperature $T = 110 \text{ K}$ and $T = 200 \text{ K}$. In both panels, Langevin numerical simulations are shown as red circles with error bars, as well as Kramer's theory without (black solid curve) and with the finite barrier correction term (black dashed curve).

$T = 110, 200$ K.^[68,71] In these two cases the reduced activation barrier (assuming 82.8 meV) $V^\ddagger/(k_B T) = 8.7, 4.8$ respectively, large enough to consider the escape as activated and Kramers' theory should be a good approximation. As can be seen in this figure, the decay rate κ obtained by Langevin simulations is well approximated by Kramers' theory. The agreement becomes quantitative over the whole friction range when including the finite barrier correction (FBC).

For the same system, jump distributions are plotted in Figure 3 and the same two surface temperatures $T = 110$ K and 200 K. In both plots the reduced friction coefficient is 0.15 .^[68] Blue bars are Langevin simulation results and white bars are from Kramers' turnover theory. In this figure, it is clearly seen

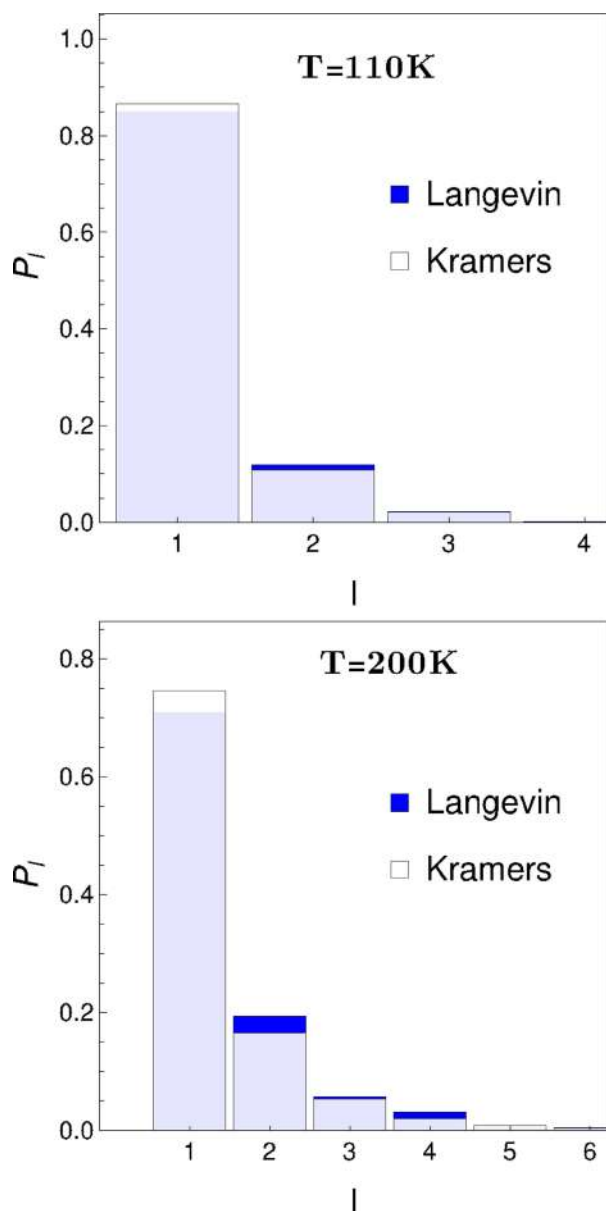


Figure 3. Jump length probability distributions are shown for the diffusion of Na on a Cu surface. All parameters are as in Figure 2. The upper panel is at $T = 110$ K and the lower at 200 K. Blue bars are Langevin results adapted from Ref. [68] and white bars are obtained using Kramers turnover theory.

that the probability of long jumps becomes more important as the temperature increases. The comparison between simulation and theory is quantitative.

As has been shown elsewhere,^[34] when the (reduced) energy loss for motion from one barrier to the next is unity or greater, one may expect the hopping distribution to become exponential:

$$P_{j,1}(j \geq 2) \sim \frac{2(j-1)^{-3/2}}{\sqrt{\pi\beta\delta}} \exp[-(j-1)\beta\delta/4] \quad (3.44)$$

At a surface temperature of 200 K, hopping probabilities up to $j = 4$ are still observed, as expected from this expression.

The dependence of the diffusion coefficient on the reduced friction for the diffusion of Na on the Cu(001) surface, using the same parameters as above is plotted in Figure 4, at the two surface temperatures $110, 200$ K. Solid black curves as given in Eq. 3.41 with finite barrier corrections. Red squares are Langevin diffusion coefficients obtained from the Einstein relation, Eq. 3.7. As before, the agreement between both sets of results is good.

This example, modeled for the diffusion of Na on a Cu(001) surface exemplifies the utility and viability of the turnover theory for analyzing theoretical (for example, from Langevin simulations) and experimental results on surface diffusion. We stress that the theory is reliable provided that one includes finite barrier corrections when the reduced barrier height is lower than ~ 5 but will fail when lower than ~ 2 . Another drawback of the theory in its present form is that it is limited to low surface coverages, that is when adsorbate-adsorbate interactions can be neglected. However, it may be extended to moderate coverage when combined with the ISA model mentioned earlier. Finally, more work is needed to extend the turnover theory when the diffusive dynamics is not one-dimensional.

4. Applications of Turnover Theory

4.1. Nanoparticle Levitation

Experimentally creating the conditions needed for unequivocal observation of Kramers' turnover is not a trivial challenge. One of the clearest experimental observations in recent years has been the study of levitated nanoparticles trapped in an optical potential by Rondin et al.^[72] Conceptually, the experiment is straightforward. A 68 nm silica particle is trapped in an optical double well potential. The chamber is in principle a vacuum chamber, so that one may allow the addition of an inert buffer gas to enter it with a known pressure. The "instantaneous" location of the particle is monitored interferometrically with a weak laser beam (532 nm). In the absence of the buffer gas, the particle, trapped in one of the wells would stay there "forever". Allowing a low pressure gas to enter will lead to exchange of energy between the nanoparticle and the small gas molecules. The dynamics is well modeled in terms of a Langevin equation, whose friction coefficient is proportional to the buffer gas pressure.

The results of the measurement are a clear turnover of the dwell time in the well as a function of the pressure, decreasing

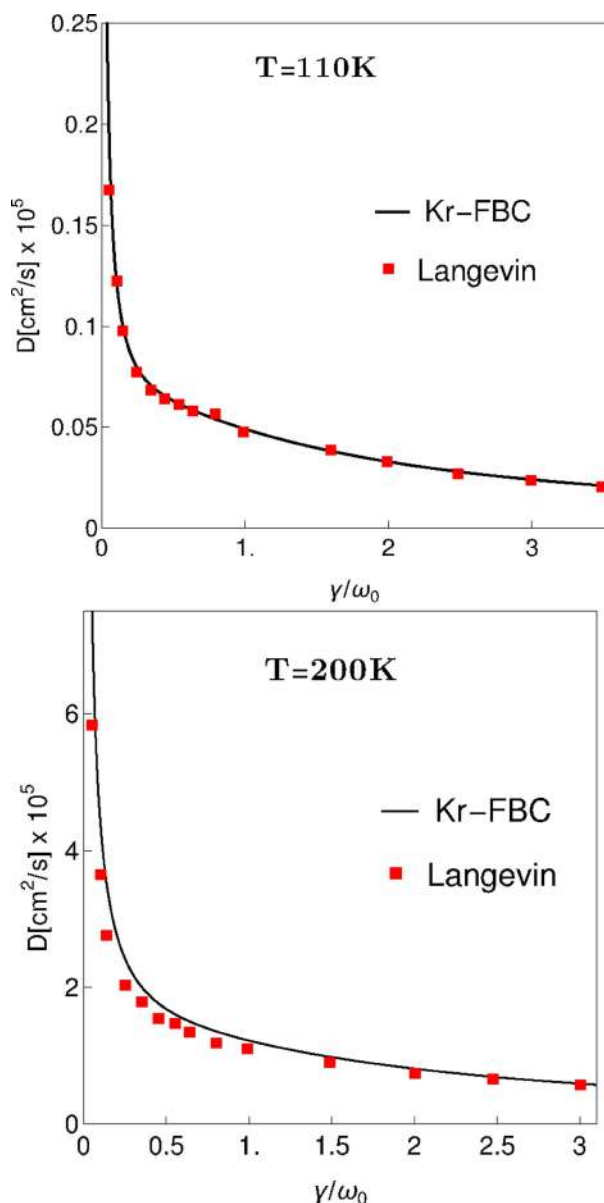


Figure 4. Diffusion coefficients in (cm^2/s) are plotted as a function of the reduced friction for the diffusion of Na on the Cu(001) surface at two surface temperatures 110 and 200 K. Solid black curves are from Kramers' turnover theory.

at low pressure and then increasing when the pressure is sufficiently strong. Moreover, within the experimental uncertainties the authors find quantitative agreement between the experiment and MM theory, where it should be stressed, that in principle, all the parameters needed for the application of the theory are obtained from the experiment. On the other hand, in this case, the Hamiltonian representation of the Langevin equation as in Eq. 2.4 is not physical but only a mathematical construct. The "instantaneous" collisions between the gas particles and the nanoparticles lead within a binary collision theory to a Langevin equation, however, the physics is not that of coupling to a harmonic bath.^[73]

This class of experiments has been then further explored to include non-equilibrium effects on the rates, such as the application of an external force on the nanoparticle, which is achieved by charging it and placing it in an electrostatic potential.^[74] It has also been used to explore transition path dynamics,^[75] a topic of intense interest when considering protein folding. Another twist on this class of experiments is to immerse the nanoparticle in a fluid and study the effects of Newtonian and non-Newtonian fluids on the transition dynamics as expected from the turnover theory.^[76]

4.2. Microcavity Polariton Dynamics

Experimental investigations of chemical reactivity in microcavities have challenged theory in many ways. A fundamental observation is that the electromagnetic field of an optical cavity can profoundly influence the dynamics of molecules in what is known as the strong coupling limit. Especially intriguing is the orders of magnitude effect on activated reactions in liquid. As reported in Refs. [76,77] tuning the cavity electromagnetic frequency such that it is in resonance with a vibrational frequency of a reacting molecule, may change the reactivity significantly, even by an order of magnitude. The experimental observations continue to challenge theory. However, Kramers' turnover theory turns out to be a fundament of many theoretical attempts to understand the polariton-induced dynamics.

Yang and Cao^[78] used the Hamiltonian formulation of the GLE as in Eq. 2.4, adding to it coupling to the cavity field and proceeded to study the effects of this coupling on the rate in the spatial diffusion limited regime, that is by using the Wolyne prefactor as in Eq. 3.22. Lindoy et al.^[79,80] further extended this approach so that it covers the whole friction range, demonstrating with the turnover theory that the weak friction case causes sharper and larger changes in the rate than in the spatial diffusion-limited regime. They also conclude that quantum effects cannot be ignored. Similar results, based on the turnover theory were found in Ref. [81].

These works were limited to a single system, one of the characteristics of the polariton dynamics is that it seems that a large number of systems are coupled coherently to enhance the effect. Du et al.^[82] made an attempt to use PGH theory to study the collective phenomenon but in their model, collectivity reduced the magnitude of the effect rather than enhance it. The last word on this exciting topic is not yet in, but it would seem that Kramers' turnover theory and its formalism may play a central role in finally obtaining a "good" theory for microcavity enhanced reaction dynamics.

4.3. Simulations of Reactions in Liquids

The first theoretical observation of Kramers' turnover in simulations of reactions in liquids was reported in 2008 by Mueller et al.^[83,84] for the Li-NC \leftrightarrow LiCN isomerization reaction in a bath of Ar atoms as a function of the density of the Ar atoms. Comparison of the simulation results with PGH theory was

favorable. This model system continues to be a rich testing ground for PGH theory even when the barrier is low, as discussed in Ref. [85]. The turnover was also observed in simulations of model isomerization reactions in Lennard-Jones solvents in Ref. [86]. Shigemitsu and Ohga^[87] used PGH theory to analyze molecular dynamics simulations of the isomerization of azobenzene, however, their central conclusion was that in reality, the reaction occurs in the spatial diffusion-limited regime so that the turnover theory as such is not really that important.

More recently, Hori et al.^[88] considered frictional effects on the folding rates of various RNA molecules (eg human telomerase hairpin) as a function of solvent viscosity. They observed a Kramers turnover, however, they used a more primitive turnover theory expression which extrapolates between the low and high friction limits in their analysis. A similar study was reported a bit earlier by Dupuis et al.,^[89] however, here only the spatial diffusion-limited regime was considered. Kramers' turnover theory has been also used to unravel the mechanisms underlying the dihedral dynamics of butane in water, which turns out to be rather insensitive to the viscosity of the water surroundings.^[90] All these various applications seem to indicate that Kramers' turnover theory will continue to show up in the various simulations of molecular dynamics influenced by an environment. What is though missing most in the chemistry context is experimental observation for reactions in liquids. Since the turnover appears through the prefactor it is masked by the Arrhenius exponent, and one needs rather accurate measurements to resolve it.

5. Discussion

In many ways, the turnover theory in its present form has solved the original Kramers turnover problem. The turnover theory is derived, and corrections terms to improve it in the limit of low barriers have been presented and successfully tested. However, like any theory, this is not the end of the story, challenges remain. The quantum version of the theory in which the bath is treated quantum mechanically and tunneling is possible is still limited in various aspects. The most obvious one is that in its present form, the theory is valid only above the crossover temperature between tunneling and thermal activation. It should be possible to extend it to lower temperatures, following the same perturbation theory used by Hänggi and Hontscha for the spatial diffusion-limited regime.^[91] In the deep tunneling regime, we know from the numerical simulations of Ref. [44] that the turnover disappears as the particle may escape from the well without any interaction with the surroundings through quantum tunneling. A theory that covers the turnover theory for the whole range of temperatures remains an open challenge.

It is relatively straightforward to verify the classical turnover theory by comparing it with classical numerical computations. However, quantum benchmarks are rather limited to date. The escape rates have been tested by Topaler and Makri^[44] however especially the turnover theory for diffusion remains to be compared with numerically exact quantum computations. Of special interest in this context is the observation that for light

atom surface diffusion, one should expect to find in the weak damping regime a shortening of the hopping length due to quantum above barrier reflection.^[16] This phenomenon leads to an inverse isotope effect which has yet to be observed experimentally.

Another topic of interest is the effect of external forces on the rates. The turnover theory at this point has not been extended to include external non-equilibrium effects. On a more formal footing, the turnover theory as such is based on a quadratic expansion of the force field about the potential top. A different question is what happens when the potential is cusped or quartic or any other form which is not parabolic? In the spatial diffusion-limited regime, this question has been answered to some extent^[36,37] but only in the classical limit. The theory has not been tested against quantum benchmarks.

A turnover should also be observed when considering the effect of friction on non-adiabatic transitions. Some progress has been made in the spatial diffusion-limited regime.^[92–95] However, the turnover theory as formulated at present is limited to adiabatic, single-surface dynamics. Both theoretical extensions of the turnover theory, as well as numerically exact quantum simulations, would be needed to verify the effect.

The turnover theory as such presents some fundamental progress in rate theory. However, the bottom line is how "important" it really is. We have reviewed some recent experimental verifications and applications of the theory, however, the real challenge is to demonstrate the applicability of the theory and the insight it gives toward understanding chemical dynamics, whether in the form of bimolecular or unimolecular reactions or within the context of surface phenomena. In theory, it is always possible to change the friction coefficient, in nature, this is a much more challenging task and perhaps is the reason why it is difficult to apply the theory to experiments.

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Conflict of Interests

The authors declare no conflict of interest.

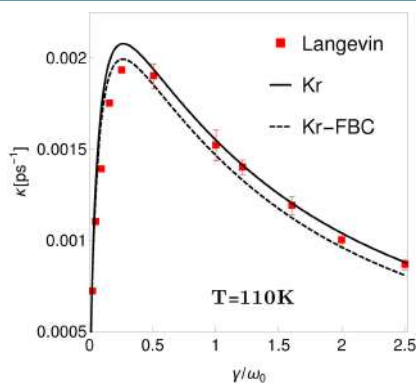
Keywords: Kramers turnover theory · surface diffusion · quantum tunneling and reflection · transition state theory

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PERSPECTIVE

Illustration of Kramers' turnover theory for surface diffusion. Escape rate is plotted as a function of the scaled friction for a cosine potential simulating the one-dimensional motion of Na atoms on a Cu(001) lattice at surface temperature $T = 110$ K.



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Recent Developments in Kramers' Theory of Reaction Rates

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