

## Theory of activated rate processes: A new derivation of Kramers' expression

Eli Pollak

Citation: *The Journal of Chemical Physics* **85**, 865 (1986); doi: 10.1063/1.451294

View online: <http://dx.doi.org/10.1063/1.451294>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/85/2?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[Theory of nonstationary activated rate processes: Nonexponential kinetics](#)

*J. Chem. Phys.* **109**, 5565 (1998); 10.1063/1.477174

[Variational transition state theory for curve crossing processes: A uniform rate expression](#)

*J. Chem. Phys.* **103**, 7912 (1995); 10.1063/1.470209

[Theory of activated rate processes in the weak and intermediate friction cases: New analytical results for one and many degrees of freedom](#)

*J. Chem. Phys.* **100**, 7331 (1994); 10.1063/1.466877

[Activated rate processes: Generalization of the Kramers–Grote–Hynes and Langer theories](#)

*J. Chem. Phys.* **97**, 2422 (1992); 10.1063/1.463081

[Theory of activated rate processes: Exact solution of the Kramers problem](#)

*J. Chem. Phys.* **85**, 1018 (1986); 10.1063/1.451844

---



# Theory of activated rate processes: A new derivation of Kramers' expression

Eli Pollak

Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel

(Received 24 October 1985; accepted 31 March 1986)

The generalized Langevin equation of motion for a particle trapped in a one-dimensional well with a barrier height  $V_0$  and coupled to a dissipative medium is modeled by a harmonic bath. Using the properties of the bath and a normal mode analysis we prove that the reactive frequency defined by Grote and Hynes for averaged motion across the barrier is actually a renormalized effective barrier frequency. We then show that the Kramers–Grote–Hynes expression for the rate of escape over the barrier is just the continuum limit of the usual gas phase harmonic transition state theory expression.

## I. INTRODUCTION

In his famous paper on the diffusion model of chemical reactions, Kramers<sup>1</sup> considered the following problem. Given a particle trapped in a one-dimensional potential well which is separated by a barrier of height  $V_0$  from say a different (deeper) well. Suppose, furthermore that the particle is immersed in a medium such that the medium exerts a frictional force on the particle but can at the same time activate the particle so that the particle can gain enough energy to escape from the well. The Kramers' problem is to find the rate of escape of the particle from the well through the barrier.

Kramers assumed that the motion of the particle may be described via a Langevin equation (LE):

$$M \frac{d^2 q}{dt^2} + \eta \frac{dq}{dt} + \frac{dV}{dq} = F_{\text{ext}}(t). \quad (1)$$

Here,  $M$  is the particle mass,  $q$  the coordinate,  $V(q)$  is the potential energy surface of the particle,  $\eta$  is the friction coefficient, while  $F_{\text{ext}}(t)$  is an external Gaussian random force. The random force is assumed to be zero centered  $\langle F_{\text{ext}}(t) \rangle = 0$  and is related to the friction coefficient via the fluctuation dissipation theorem

$$\langle F_{\text{ext}}(t) F_{\text{ext}}(\tau) \rangle = k_B T \eta \delta(t - \tau). \quad (2)$$

Here the average is over a thermal bath at temperature  $T$ .

If the friction coefficient  $\eta = 0$  then the (LE) reduces to a one-dimensional deterministic Newton equation. If one assumes a thermal distribution for the particle in the well, then transition state theory<sup>2</sup> would predict that the rate of escape from the well is

$$k_{\text{TST}} = \frac{\omega_0}{2\pi} \exp(-\beta V_0), \quad \beta \equiv \frac{1}{k_B T}, \quad (3)$$

where  $\omega_0$  is the harmonic frequency of motion around the bottom of the well [ $V(q=0)$ ]. In the limit of high friction, Kramers showed by solving the Smoluchowski diffusion equation that the solution for the rate of escape for the LE may be written as

$$k(\eta) = [(\alpha^2 + 1)^{1/2} - \alpha] k_{\text{TST}}; \quad \alpha = \frac{\eta}{2M\omega^*}. \quad (4)$$

Here  $\omega^*$  is the imaginary frequency at the barrier ( $q = q_*$ ) that is

$$\omega^* = \frac{1}{M} \cdot \frac{d^2 V}{dq_*^2}.$$

Kramers' result was generalized by Grote and Hynes.<sup>3</sup> These authors considered the rate of escape for a particle whose motion is governed by a generalized Langevin equation (GLE):

$$M\ddot{q} + \int_0^t d\tau \eta(\tau) \dot{q}(t - \tau) + \frac{dV}{dq} = F_{\text{ext}}(t). \quad (5)$$

Here  $\eta(t)$  is a time dependent friction related to the zero centered Gaussian random force  $F_{\text{ext}}(t)$  by the fluctuation dissipation relation

$$\beta \langle F_{\text{ext}}(0) F_{\text{ext}}(t) \rangle = \eta(t). \quad (6)$$

Grote and Hynes then considered the average motion of the particle in the vicinity of the barrier. They found that on the average the particle is slowed down by the friction. They define a reactive frequency  $\lambda_r$  and show that in the vicinity of the barrier the average motion of the particle goes as  $e^{\pm \lambda_r t}$  rather than  $e^{\pm \omega^* t}$  as would be in the frictionless case. Furthermore, Grote and Hynes found a simple relation between  $\lambda_r$  and the time dependent friction  $\eta(t)$ . Their major result however was a simple expression for the escape rate

$$k(\eta) = \frac{\lambda_r}{\omega^*} k_{\text{TST}}. \quad (7)$$

For a  $\delta$  function friction  $\eta(t) = \eta \delta(t)$ , this reduces to the Kramers expression [Eq. (4)]. Equation (7) has a neat physical interpretation. The bath modifies the rate of passage in the vicinity of the barrier. In fact if  $\eta(t) > 0$  for all  $t$  than  $\lambda_r < \omega^*$  so that the motion in the vicinity of the barrier is slowed down. The rate of escape is then decreased by the same ratio.

The analysis of Grote and Hynes is very suggestive. It would seem that on the average the particle is not moving on the bare barrier whose imaginary frequency is  $\omega^*$  but rather on an effective barrier whose imaginary frequency is  $\lambda_r$ . In Sec. II we will show that in fact the reactive frequency  $\lambda_r$  is exactly an imaginary frequency of a barrier that has been modified by the bath. To do this we model the GLE in terms of a system coupled linearly to a discrete set of harmonic oscillators.<sup>4</sup> For any finite number of bath oscillators one performs a normal mode analysis<sup>5,6</sup> in the vicinity of the

barrier and finds that there is a single imaginary mode whose imaginary frequency is  $\lambda_r$ . Thus one may go to the limit of a continuum of oscillators and find that  $\lambda_r$  is the imaginary normal mode frequency of the barrier even for a dissipative system. Of course as shown by Cortes West and Lindenberg<sup>4</sup> and others,<sup>7</sup> in the continuum limit the equation of motion of the system particle reduces to the GLE.

In Sec. III we repeat this exercise but now we consider the rate of escape for a system coupled linearly to a discrete set of harmonic oscillators. For a discrete set we may evaluate the rate via transition state theory. We prove that for any finite discrete set the TST rate is again exactly given by Eq. (7). By taking the continuum limit we regain the Kramers–Grote–Hynes result. This is the central result of this paper.

## II. THE REACTIVE FREQUENCY

### A. Preliminaries

Instead of deriving the GLE phenomenologically one may model the GLE via a harmonic bath.<sup>4</sup> The total Hamiltonian is of the form<sup>4,7</sup>

$$H = \frac{1}{2M} p_q^2 + V(q) + \sum_{j=1}^N \left( \frac{p_j^2}{2m_j} + \frac{m_j}{2} \left[ \omega_j x_j + \frac{C_j}{m_j \omega_j} q \right]^2 \right). \quad (8)$$

Here  $(p_j, x_j)$  are the momenta and coordinates of the  $j$ th bath oscillator whose mass and frequency are  $m_j, \omega_j$ , respectively.  $C_j$  couples the bath oscillator to the system. It is well known that the equations of motion for the system  $(p_q, q)$  may be written exactly in the form of a GLE under the following conditions.<sup>4</sup> The time dependent friction is identified as

$$\eta(t) = \sum_j \frac{C_j^2}{m_j \omega_j^2} \cos \omega_j t. \quad (9)$$

The external force is given in terms of the initial conditions of the bath variables  $(x_j^0, p_j^0)$  as

$$F_{\text{ext}}(t) = \sum_j C_j \left\{ \left[ x_j^0 + \frac{C_j}{m_j \omega_j^2} q(0) \right] \times \cos \omega_j t + \frac{p_j^0}{m_j \omega_j} \sin \omega_j t \right\}. \quad (10)$$

The Hamiltonian  $H$  may be decomposed as

$$H = H_{\text{sys}} + H_{\text{bath}}, \quad H_{\text{sys}} = \frac{1}{2M} p_q^2 + V(q). \quad (11)$$

If we assume that at time  $t = 0$  the bath is in thermal equilibrium such that the initial bath distribution in phase space is given as

$$P(\mathbf{x}^0, \mathbf{p}^0) = e^{-\beta H_{\text{bath}}} / \text{Tr}(e^{-\beta H_{\text{bath}}}), \quad (12)$$

then one can easily show that

$$\langle F_{\text{ext}}(t) \rangle = \text{Tr}[P(\mathbf{x}^0, \mathbf{p}^0) F_{\text{ext}}(t)] = 0 \quad (13)$$

and that

$$\langle F_{\text{ext}}(t) F_{\text{ext}}(0) \rangle = (1/\beta) \eta(t). \quad (14)$$

The trace operation is over the bath phase space variables  $(\mathbf{x}, \mathbf{p})$ . As stressed by Cortes *et al.*,<sup>4</sup> the GLE is derived exact-

ly from the Hamiltonian [Eq. (8)] by assuming that at time  $t = 0$  the bath is in thermal equilibrium in the presence of the system.

The spectral density of the bath  $J(\omega)$  is defined as<sup>7</sup>

$$J(\omega) \equiv \frac{\pi}{2} \sum_j \frac{C_j^2}{m_j \omega_j} \delta(\omega - \omega_j). \quad (15)$$

The time dependent friction [Eq. (9)] may be expressed in terms of the spectral density

$$\eta(t) = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega} \cos \omega t. \quad (16)$$

For future use we also define the Laplace transform of  $\eta(t)$ :

$$\hat{\eta}(\epsilon) = \int_0^{\infty} e^{-\epsilon t} \eta(t) dt = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega} \frac{\epsilon}{\epsilon^2 + \omega^2}. \quad (17)$$

The condition that

$$J(\omega) = \eta \omega \theta(\omega), \quad (18)$$

where  $\theta(\omega)$  is the Heaviside function, implies that for  $t > 0$   $\eta(t) = \eta \delta(t)$ , that is we regain the LE.

Note the methodology. We start with a discrete set of oscillators and derive a GLE with a specific time dependent friction and random force. However one then defines a spectral density which enables the passage to a continuum model and obtains an almost arbitrary time dependent friction [Eq. (16)] whose characteristics are determined by the spectral density.

### B. A normal mode analysis

Here, we study the properties of the Hamiltonian [Eq. (8)] in the vicinity of the barrier  $q \simeq q_*$ . The potential  $V(q)$  is approximately harmonic

$$V(q) \simeq V_0 - \frac{1}{2} M \omega_*^2 (q - q_*)^2. \quad (19)$$

This implies that by an orthogonal transformation the Hamiltonian may be written in a separable form as the sum of  $N + 1$  harmonic oscillators. This is achieved, in standard fashion,<sup>6</sup> by first transforming to mass weighted coordinates

$$q' = \sqrt{M} q, \quad x'_j = \sqrt{m_j} x_j \quad (20)$$

and then diagonalizing the  $(N + 1) \times (N + 1)$  force constant matrix  $\mathbf{K}$  defined by the second derivatives of the total potential energy surface evaluated at

$$q' = q'_*, \quad x'_j = - \frac{C_j}{\sqrt{m_j M}} \frac{1}{\omega_j^2} q'_*; \quad j = 1, N. \quad (21)$$

Let  $\lambda^2$  denote the eigenvalues, then the solution of the secular equation

$$\det(\mathbf{K} - \lambda^2 \mathbf{I}) = 0 \quad (22)$$

may be written as

$$\begin{aligned} & \left[ \prod_{i=1}^N (\omega_i^2 - \lambda^2) \right] [\omega_*^2 (\Gamma^2 - 1) - \lambda^2] \\ &= \sum_{i=1}^N \frac{C_i^2}{m_i M} \prod_{j \neq i, j=1, N} (\omega_j^2 - \lambda^2). \end{aligned} \quad (23)$$

Here

$$\Gamma^2 = \frac{1}{M\omega^{*2}} \sum_{j=1}^N \frac{C_j^2}{m_j\omega_j^2}. \quad (24)$$

Obviously, the coupling of the system to the bath modifies both the system and the bath frequencies. To find the new system eigenvalue which is presumably negative ( $-\lambda_0^{*2}$ ) we note that Eq. (23) may be rewritten as

$$\lambda_0^{*2} = \frac{2}{1 + (1/M) \sum_{i=1}^N (C_i^2/m_i\omega_i^2) [1/(\omega_i^2 + \lambda_0^{*2})]}. \quad (25)$$

By use of the spectral density [Eq. (15)] this may be written as

$$\lambda_0^{*2} = \frac{\omega^{*2}}{1 + (2/\pi)(1/M) \int_{-\infty}^{\infty} d\omega (J(\omega)/\omega) (\omega^2 + \lambda_0^{*2})^{-1}}. \quad (26)$$

Finally, one may use the Laplace transform of the time dependent friction [Eqs. (16) and (17)] to rewrite Eq. (26) as

$$\lambda_0^{*2} = \frac{\omega^{*2}}{\lambda_0^{*2} + (1/M)\hat{\eta}(\lambda_0^{*2})}. \quad (27)$$

Equation (27) is identical to Eq. (4.28) derived by Grote and Hynes<sup>3</sup> with the identification that their reactive frequency  $\lambda_r$  is identical to  $\lambda_0^{*2}$ . We have thus proved that the reactive frequency of Grote and Hynes may be interpreted, even in the continuum limit, as an effective barrier frequency. Instead of considering the motion in the  $q$  direction subject to friction and a random force we may think of the bath as providing a renormalized barrier whose height has not changed but whose direction in configuration space and whose imaginary frequency is determined by the coupling to the bath.

### III. THE RATE OF ESCAPE

According to classical transition state theory,<sup>2</sup> the rate of escape is given as the ratio of the partition function of all bath modes at the barrier to the partition function of the total system around the well. Since we assume that the bath is originally at thermal equilibrium [cf. Eq. (12)] it is easy to see that the harmonic transition state theory estimate for the rate of decay is simply

$$k(C_j; j=1, N) = \left[ \prod_{i=1}^N \left( \frac{\omega_i}{\lambda_i} \right) \right] \frac{\omega_0}{2\pi} e^{-\beta V_0}. \quad (28)$$

Here  $\lambda_i^2$   $i=1, N$  are the  $N$  positive eigenvalues of the force constant matrix  $\mathbf{K}$ . Note, that as might be expected from a transition state theory, the imaginary barrier frequency does not appear in Eq. (28). However it is easy to see from Eqs. (23) and (24) that

$$\begin{aligned} \det \mathbf{K} &= -\omega^{*2}(1 - \Gamma^2) \left[ \prod_{i=1}^N \omega_i^2 \right] \\ &= -\sum_{i=1}^N \frac{C_i^2}{m_i M} \left[ \sum_{j=1, N} \omega_j^2 \right] = -\omega^{*2} \left[ \prod_{i=1}^N \omega_i^2 \right]. \end{aligned} \quad (29)$$

On the other hand, by definition

$$\det(\mathbf{K}) = -\lambda_0^{*2} \left( \prod_{i=1}^N \lambda_i^2 \right). \quad (30)$$

From Eqs. (29) and (30) it follows that

$$\prod_{i=1}^N \left( \frac{\omega_i}{\lambda_i} \right) = \frac{\lambda_0^{*2}}{\omega^{*2}}. \quad (31)$$

This result together with Eq. (27) gives the Kramers-Grote-Hynes estimate for the decay rate [Eq. (7)].

### IV. DISCUSSION

The new derivation of the rate expression raises some interesting questions. For a finite set of bath oscillators one may find the reaction path leading from the well to the barrier. One may also describe the system via a reaction path Hamiltonian.<sup>8</sup> It should be of interest to study the continuum limit of the reaction path and the Hamiltonian associated with it. Conversely one may ask how many bath modes are actually needed before the dynamics of the system may be accurately described via a GLE. In similar vein, for a finite discrete bath one may look for the variational transition state. One may then try to find the continuum limit of variational transition state theory.

The present approach also has implications on a quantal solution of GLE's. For example, one can estimate the quantal tunneling rate through the barrier using a quantal transition state theory approach for the discrete set of oscillators and then take the continuum limit. Elsewhere<sup>9</sup> we show that such an approach describes correctly macroscopic quantal tunneling measured in Josephson junctions.<sup>7</sup>

### ACKNOWLEDGMENTS

This work has been supported by grants of the U.S.-Israel Binational Science Foundation and the Minerva Foundation.

<sup>1</sup>H. A. Kramers, *Physica* 7, 284 (1940).

<sup>2</sup>P. Pechukas, in *Dynamics of Molecular Collisions, Part B*, edited by W. H. Miller (Plenum, New York, 1976), Chap. 6.

<sup>3</sup>R. F. Grote and J. T. Hynes, *J. Chem. Phys.* 73, 2715 (1980).

<sup>4</sup>E. Cortes, B. J. West, and K. Lindenberg, *J. Chem. Phys.* 82, 2708 (1985), and references therein.

<sup>5</sup>G. van der Zwan and J. T. Hynes, *J. Chem. Phys.* 78, 4174 (1983); *Chem. Phys.* 90, 21 (1984).

<sup>6</sup>E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

<sup>7</sup>A. O. Caldeira and A. J. Leggett, *Ann. Phys.* 149, 374 (1983).

<sup>8</sup>W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.* 72, 99 (1980).

<sup>9</sup>E. Pollak, *Phys. Rev. A* 33, 4244 (1986).