



**HAL**  
open science

# High-Frequency Resonance Absorption as Evidence for Oscillation in a Well Before Escape from a Metastable State in the Kramers Energy Controlled Diffusion Model

William Coffey, Yuri Kalmykov, Serguey Titov, Derrick Crothers

► **To cite this version:**

William Coffey, Yuri Kalmykov, Serguey Titov, Derrick Crothers. High-Frequency Resonance Absorption as Evidence for Oscillation in a Well Before Escape from a Metastable State in the Kramers Energy Controlled Diffusion Model. Kalmykov Y. Recent Advances in Broadband Dielectric Spectroscopy. NATO Science for Peace and Security Series B: Physics and Biophysics, Springer; Springer Netherlands, pp.151-162, 2012, NATO Science for Peace and Security Series B: Physics and Biophysics, 9789400750128. 10.1007/978-94-007-5012-8\_11 . hal-01898588

**HAL Id: hal-01898588**

**<https://hal.science/hal-01898588>**

Submitted on 9 Feb 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

# High-Frequency Resonance Absorption as Evidence for Oscillation in a Well Before Escape from a Metastable State in the Kramers Energy Controlled Diffusion Model

William T. Coffey, Yuri P. Kalmykov, Serguey V. Titov, and D.S.F. Crothers

**Abstract** A variety of disparate physical systems which are modeled in terms of their relaxation behavior by the Brownian motion in a potential and its extensions to anomalous diffusion exhibit slow overbarrier relaxation accompanied by relatively fast relaxation due to exponential decays in the potential wells and high frequency resonance absorption due to small oscillations about the minima of the wells. It is argued that the high frequency resonant process provides abundant evidence for the Kramers concept of oscillations in a potential well of particles with energy equal to the separatrix energy before escape as both are simply limiting cases of the same family of librational dynamical processes in a well.

---

W.T. Coffey (✉)

Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Ireland  
e-mail: wcoffey@mee.tcd.ie

Yu.P. Kalmykov

Laboratoire de Mathématiques et Physique, Université de Perpignan Via Domitia, 52, Avenue de Paul Alduy, 66860 Perpignan Cedex, France  
e-mail: kalmykov@univ-perp.fr

S.V. Titov

Kotelnikov Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Vvedenskii Square 1, Fryazino, Moscow Region 141190, Russian Federation  
e-mail: svt1212@fryazino.net

D.S.F. Crothers

Department of Applied Mathematics and Theoretical Physics, Queen's University Belfast, Belfast BT7 1NN, Northern Ireland  
e-mail: derrick.crothers@ntlworld.com

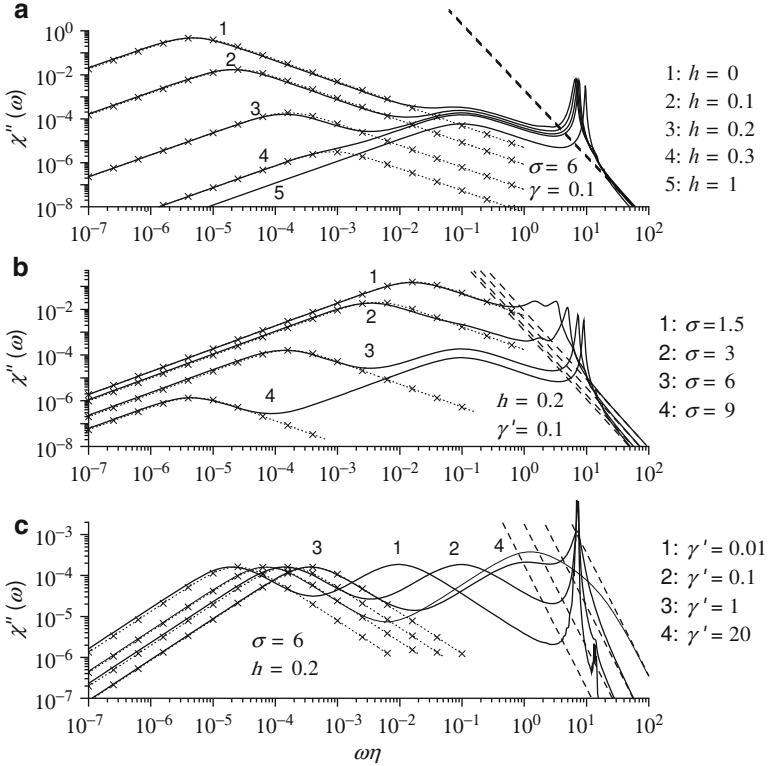
## 11.1 Introduction

The complex susceptibility associated with diverse relaxation phenomena which are usually modeled (see [1]) via the theory of the Brownian motion in a potential almost invariably exhibits a high frequency resonant absorption peak attributed to small inertial oscillations of the Brownian particles in the wells of the potential. The resonant phenomenon (which also appears in anomalous diffusion) occurs along with the low frequency (interwell) absorption due to escape of Brownian particles over the potential barriers (see [2]) and a second intermediate frequency (intra-well) one due to relatively fast exponential decays in the wells. Examples of the resonant absorption phenomenon occur in the complex susceptibilities associated with the position correlation function of the inertial translational Brownian motion in a 2–4 double well potential [1] (Duffing oscillator), the inertial rotational Brownian motion of a polar molecule in a double-well potential [1] and the Brownian motion of the magnetization of a single domain ferromagnetic nanoparticle in the simplest uniaxial potential of the magnetocrystalline anisotropy with an external field applied at an angle to the easy magnetization axis. In the case of polar molecules the peak in the complex susceptibility is generally in the THz region and is known as the Poley absorption [1]. In single domain particles the high frequency ferromagnetic resonance peak at GHz frequencies close to the Larmor precession frequency in the longitudinal complex susceptibility arises not from inertia but from the nonaxially symmetric nature of the potential [1] inducing coupling between the longitudinal and transverse modes of the magnetization. If the problem were axially symmetric the modes decouple and in the absence of the field essentially only the longitudinal mode characterized by the Kramers escape rate remains. In this context, the latter is called the Néel-Brown overbarrier relaxation mode [1] and yields the superparamagnetic relaxation time. By way of illustration of the various relaxation phenomena, the dielectric loss spectra for the inertial rotational Brownian motion of a fixed axis rotator in an asymmetric double-well potential [1] are shown in Fig. 11.1. The potential is of the form

$$\frac{V(\theta)}{kT} = -2\sigma(\cos \theta + h)^2, \quad (11.1)$$

where  $\sigma$  is the barrier height parameter,  $h$  is the external field or asymmetry parameter,  $\theta$  is the angular coordinate specifying the orientation of a dipole of moment of inertia  $I$ ,  $\eta = \sqrt{I/(2kT)}$ ,  $\gamma' = \gamma\eta$  is the normalized dissipation parameter,  $\gamma$  being the dissipation parameter as defined below.

Now the low frequency phenomena for anomalous diffusion have been discussed in detail elsewhere [1]. Thus it is the purpose of this chapter to indicate how the high frequency resonance phenomenon is intimately connected with the Kramers concept of oscillations of a particle in the wells of a potential before escaping which is used to calculate the very low damping (VLD) escape rate. In order to illustrate

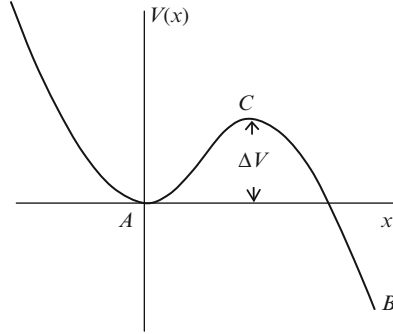


**Fig. 11.1** Dielectric loss spectra (*solid lines*) as functions of  $\sigma$ ,  $\gamma'$ , and  $h$ . The Debye spectra are shown by *dotted lines with crosses*. The high-frequency asymptotes are shown by *dashed lines*

this it will be necessary to summarize the main features of the calculation of the Kramers VLD rate. In so doing the opportunity will be taken to briefly describe how the Kramers result may be extended to all values of the dissipation of the particle to its surrounding heat bath because in general the calculations (see [3]) are not readily accessible and crucially depend on the Kramers oscillation concept.

## 11.2 Summary of the Contribution of Kramers to Escape Rate Theory

Our summary begins with Arrhenius who from a study of experimental data viewed a chemical reaction as very few particles from a huge assembly in a well ( $N \approx 10^{24}$ ) escaping over a potential barrier [4]. Particles just reaching the top can escape due to thermal agitation.



**Fig. 11.2** Single well potential function.  $A$  is the initial state,  $C$  is the transition state and  $B$  is the product state. Particles are initially trapped in the well near the point  $A$  by a high potential barrier at the point  $C$ . They are very rapidly thermalized in the well. Due to thermal agitation, however, a few may attain enough energy to escape over the barrier into region  $B$ , from which they never return (a sink of probability)

The Arrhenius equation for the escape rate,  $\Gamma$ , which can be found from transition state theory (TST) is [4, 5]

$$\Gamma = \Gamma_{TST} = f_A e^{-\Delta V/(kT)} = J/N = 1/\tau, \quad (11.2)$$

where

$$f_A = \frac{1}{2\pi} \sqrt{\frac{V''(x_A)}{m}}.$$

is the frequency of small oscillations of a particle about the bottom of the well, called the attempt frequency (which depends only on the shape of the potential),  $\Delta V$  is the barrier height,  $J$  is the current over the barrier and  $\tau$  is the greatest relaxation time. Thus we can find the lifetime  $\tau$  of a particle in the well (see Fig. 11.2).

However, TST assumes that thermal equilibrium prevails everywhere so that the Maxwell-Boltzmann distribution holds throughout the well even at  $C$ . This is not a valid assumption as particles leaving the well at  $C$  will disturb that distribution. Kramers [2] derived a formula for  $\Gamma$  accounting for the disturbance using the theory of Brownian motion in order to represent the heat bath [1]. In so doing he introduced a dissipation dependent prefactor,  $\mu$ , so that

$$\Gamma = \mu \Gamma_{TST} = \mu \frac{\omega_A}{2\pi} e^{-\Delta V/(kT)} \quad (11.3)$$

( $\omega_A = 2\pi f_A$ ). This removes the possibility that escape can occur in the absence of dissipation to the bath which is an unphysical result. Kramers was able to calculate the prefactor,  $\mu$ , in two specific regions of damping: intermediate to high damping (IHD) and very low damping (VLD) using two distinct methods of attack.

### 11.3 IHD or Spatially Controlled Diffusion Escape Rate

The TST case is called intermediate damping (ID) here and is the limiting case of IHD. Kramers treated the barrier as an inverted parabola. He was then able to solve the quasistationary Fokker-Planck equation (based on the Langevin equation) governing the reduced or single particle distribution function,  $\rho(x,p,t)$ , of the positions and momenta in phase space of a particle viz.

$$L_{FP}\rho = \frac{\partial \rho}{\partial t} = \frac{dV}{dx} \frac{\partial \rho}{\partial p} - \frac{p}{m} \frac{\partial \rho}{\partial x} + \gamma \frac{\partial}{\partial p} \left( \rho p + mkT \frac{\partial \rho}{\partial p} \right) = 0, \quad (11.4)$$

where  $\gamma$  is the friction coefficient per unit mass,  $x$  is the position and  $p$  is the momentum. The terms in  $\gamma$  represent the effect of the bath on the single particle distribution function. The conservative or Liouville terms essentially represent Hamilton's equations for the single (or tagged) particle, viz.,

$$\dot{p} = -\partial H / \partial x, \quad \dot{x} = \partial H / \partial p, \quad H = p^2 / (2m) + V(x).$$

The dissipative terms are contained in the (stochastic) Langevin equation

$$\dot{p} = -\frac{\partial V}{\partial x} - \gamma p + F(t),$$

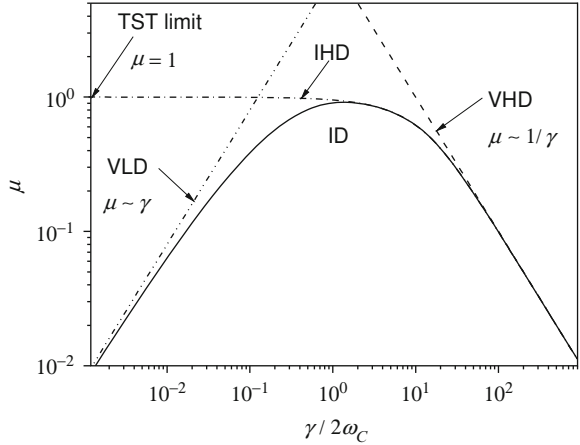
where the effect of the bath on the particle is represented by a systematic retarding force  $-\gamma p$  tending to kill the motion superimposed on which is a very rapidly fluctuating white noise force  $F(t)$  sustaining the motion. He then linearized the Langevin equation and so Eq. (11.4) about the barrier top allowing him to find the escape rate (as  $J/N$  where  $J$  is the current of particles over the barrier and  $N$ , the population, is the total number of particles in the well.) We may set  $\dot{\rho} = 0$  because the escape over the barrier is a very slow (quasistationary) process. In IHD the region of nonequilibrium is near the top of the barrier and lies well inside the range, where the barrier shape may be approximated by an inverted parabola. Thus

$$\Gamma_{IHD} = \left( \sqrt{1 + \frac{\gamma^2}{4\omega_C^2}} - \frac{\gamma}{2\omega_C} \right) \Gamma_{TST}, \quad (11.5)$$

where  $\omega_C$  is the natural angular frequency of oscillation of a particle if the potential is inverted, called the barrier frequency. Clearly if  $(\gamma/\omega_C \rightarrow 0)$  we have the ID case where  $\mu = 1$  corresponding to TST. If  $\gamma \gg \omega_C$ , we get the very high damping (VHD) result,

$$\Gamma_{VHD} = \frac{\omega_C}{\gamma} \Gamma_{TST}. \quad (11.6)$$

**Fig. 11.3** Prefactor  $\mu$  vs.  $\gamma/2\omega_C$ , showing the VLD, VHD and IHD regions and the TST limit

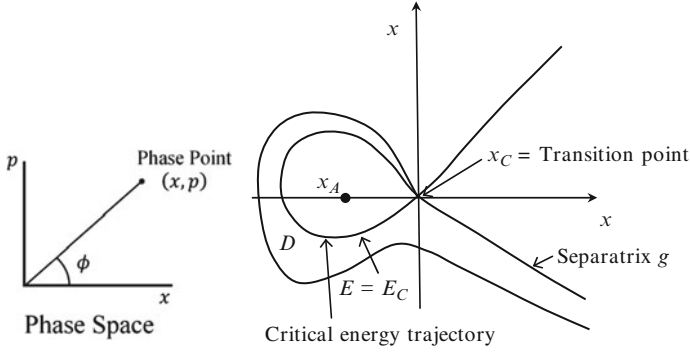


After the TST formula this is the best known of all the escape rate formulas mainly because it is easily obtained from the quasistationary solution of the Smoluchowski equation. This equation governs the evolution of the configuration space distribution function and approximately holds in the VHD or noninertial limit where the  $\dot{p}$  term in the Langevin equation is ignored as far as the dynamics is concerned (see Fig. 11.3).

Notice that the IHD prefactor is  $\mu = \lambda^+/\omega_C$  where  $\lambda^+$  is the positive eigenvalue of the linearized Langevin equation omitting  $F(t)$  (see [4]) (corresponding to the unstable barrier crossing mode) of an inverted damped oscillator so that, in the terminology of the damped oscillator, VHD and ID would represent the highly overdamped and critically damped oscillators respectively. The underdamped region would be characterised by  $\gamma^2/4\omega_C^2 < 1$ . Kramers treated the extremely underdamped case, when  $\gamma$  is almost vanishingly small, (now however using an energy controlled diffusion model) as follows.

## 11.4 VLD or Energy Controlled Diffusion Escape Rate

In VLD Kramers imagined (see [1, 3]) that the particles move in closed phase plane orbits (see [6]) which represented oscillatory motion in the well (called libration, [7, 8]) and that the particles librating with energy equal to the barrier energy are only slightly disturbed by the stochastic forces arising due to the heat bath i.e. the motion is almost deterministic. He took the top of the barrier as the zero of potential. Such librating particles can be kicked over the barrier by a small thermal fluctuation of amount  $kT$ . The resulting trajectory is then called the separatrix (because it divides the bounded motion in the well from the unbounded one outside) and it opens out the hitherto closed orbit (see Fig. 11.4).



**Fig. 11.4** The critical energy curve and the separatrix in phase space. Separation between  $E_C$  and separatrix trajectories is infinitesimal. The phase point,  $(x, p)$ , specifies the instantaneous state (phase) of the dynamical system

A separate treatment of VLD is required because in VLD the region of departure from equilibrium becomes much greater in spatial extent than that in which the potential may be represented as an inverted parabola. Therefore, one can no longer linearize the Fokker-Planck equation about the barrier top. Thus to tackle VLD Kramers transformed the quasistationary FPE into a new equation, using only the energy,  $E$ , and phase,  $\phi$ , as variables. The energy  $E$  diffuses very slowly (i.e., is almost conserved) while  $\phi$  (which would be the only variable in the completely conservative system) is very fast. Kramers can therefore average the transformed equation over  $\phi$  using the Liouville equation to eliminate the  $\phi$  dependence to get a one-dimensional energy diffusion equation leading to

$$\begin{aligned} \Gamma_{VLD} &= \frac{\gamma}{kT} S(E_C) \frac{\omega_A}{2\pi} e^{-\Delta V/(kT)} \\ &= \frac{\gamma}{kT} S(E_C) \Gamma_{TST} = \Delta \Gamma_{TST}, \end{aligned} \quad (11.7)$$

where

$$S(E_C) = \oint_{E=E_C} p dx$$

is the action per cycle of the motion in the well of a librating particle with energy equal to the critical barrier energy and the parameter (which represents the crowning achievement of the Kramers theory)

$$\Delta = \frac{\text{Energy loss per cycle of a librating particle with the barrier energy}}{\text{Thermal energy}} \quad (11.8)$$



determines the ranges of damping for which the IHD and VLD formulas can be used. If  $\Delta \gg 1$ , VHD; if  $\Delta \approx 1$ , ID; if  $\Delta \ll 1$ , VLD; if  $\Delta < 1$  we have the entire underdamped region. Kramers found that in VLD  $\Gamma \propto \gamma$  while in IHD  $\Gamma \propto 1/\gamma$ . He was not, however, able to solve the problem in the part of the underdamped region between ID and VLD, i.e.  $\Delta < 1$ . This became known as Kramers' turnover problem [1, 3, 4, 9] (c.f. Fig. 11.3).

Later we summarize how to solve the turnover problem using the methods given by Mel'nikov. However we first describe how the Kramers VLD calculation relates to the high frequency absorption.

## 11.5 Connection with the High Frequency Resonance Absorption

We now postulate that the high frequency resonance process observed in the susceptibility is already implicit in the Kramers energy controlled diffusion treatment of the very low damping escape rate from a metastable state. This is so because the calculation relies on the Newtonian concept of *undamped* oscillation of a particle in a well before escape. This may be explained in more detail as follows. In the Kramers model of energy controlled diffusion the *undamped* librational motion of a particle in the well before escape is governed by the Newtonian equation of motion with energy equal to the barrier energy. This equation is simply the Langevin equation underlying Eq. (11.4), where the systematic and rapidly fluctuating white noise random forces  $F(t)$  due to the bath are ignored. The librational motion at this critical energy which is defined by a *closed* trajectory in phase space with energy equal to the critical energy is then used to define the separatrix or *noise induced trajectory* on which a particle may escape the well. The separatrix trajectory which is now *open* is regarded as infinitesimally close to the (closed) critical energy trajectory  $C$  and for very low damping all particles having reached the separatrix are regarded as on their way out of the well. (This assumption has been discussed by Mel'nikov [6] who has rigorously justified it). Now the period  $T_C = \oint_{E_C} v^{-1} dx$  of the (large amplitude) Kramers oscillations with energy equal to the critical energy  $E_C$  always depends on their amplitude and may be evaluated [1] usually in terms of the Jacobian elliptic functions from the Newtonian equations (considering the one dimensional motion of a particle and an isolated well)

$$m\ddot{x} = -\frac{dV(x)}{dx}, \quad v = \dot{x} = \sqrt{\frac{2}{m} (E_C - V(x))} \quad (11.9)$$

where  $E_C$  denotes the closed orbit corresponding to the critical energy as traced out by the phase point  $(x, \dot{x})$ .

The prefactor of the very low damping Kramers rate is then solely determined by the action  $S(E_C)$  on the closed critical energy trajectory by using the energy

controlled diffusion equation (see below) representing a spread of energies about  $E_C$  and the flux over population, so that the escape rate is given by Eq. (11.7). However, there is nothing special about the closed critical energy trajectory *per se* save that it represents the librational motion with the *longest* period or largest closed orbit in phase space and so the lowest frequency of all the possible librational motions in the well with  $E \leq E_C$ . These must of necessity also include the almost harmonic, low energy but relatively high frequency motions near the bottom of the well which characterize the resonance absorption. Such a behavior is in complete contrast to the VLD escape rate which is essentially determined by the highest energy and lowest frequency out of all the possible undamped librational motions. It is obvious that the resonance absorption is dominated by the low energy undamped librational motion near the bottom of the well. This corresponds to a harmonic oscillator with natural angular frequency  $\omega_A$  given in terms of the period  $T_A = 2\pi/\omega_A$  of small oscillations about the bottom of the well.

This of course corresponds to the librational motion with the *smallest* periodic time and *highest* frequency which is simply the attempt frequency  $\omega_A/2\pi$  of transition state theory. Thus we may regard the times  $T_C$  and  $T_A$  as *upper* and *lower* bounds for the periodic time of the possible librational motions in the well. As far as the resonance absorption is concerned the contributions of the higher energy librational motions with  $E < E_C$  manifest themselves as an energy dependent frequency which may be calculated just as [8] the corrections to the periodic time of a simple pendulum resulting from the anharmonic nature of the librational motion which causes the periodic time to increase.

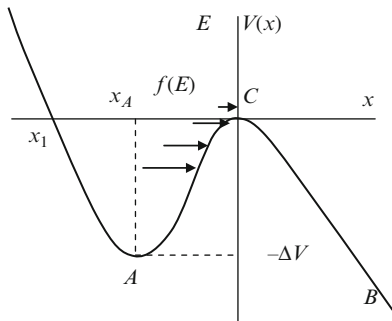
## 11.6 Mel'nikov's Solution of the Kramers Turnover Problem

The notion of oscillation in a well preceding escape is also crucial in Mel'nikov's solution of the Kramers turnover problem as we illustrate. Now when Kramers transformed the Fokker-Planck equation to  $E$  (slow) and  $\phi$  (fast) variables he ignored the coupling between dissipative and non-dissipative terms so that the Liouville equation may be used to eliminate the  $\phi$  dependence. Mel'nikov [6] solved this problem 50 years later. The calculations are, however, rather abstruse and are not readily accessible so we paraphrase them here. Mel'nikov first wrote the Fokker-Planck equation on trajectories near the critical energy as a diffusion equation in energy and action. This allowed him to take into account the coupling. He initially uses as variables the energy and the displacement so that unlike in VLD it is necessary to consider left and right going particles separately (see Fig. 11.5). Moreover near the separatrix the momentum satisfies

$$p(x, E) = \pm \sqrt{2m[E - V(x)]} \approx p(x, 0) = \pm \sqrt{-2mV(x)}, \quad (11.10)$$

because we have chosen the separatrix trajectory to effectively coincide with  $E = 0$  (see Fig. 11.4) and we suppose that the leading contributions to the escape stem

**Fig. 11.5** Escape from a single well



from diffusing particles very near the barrier in a narrow range of energy of order  $kT$ . Now we again define the action

$$S(E) = \oint_E p dx,$$

where  $E$  denotes a closed contour with energy  $E$ , pertaining to librational motion in the well via

$$\frac{dS}{dx} = \pm \sqrt{2m [E - V(x)]} \approx \pm \sqrt{-2mV(x)}, \quad (11.11)$$

recalling that inside the well  $V(x)$  is negative since the top of the well corresponds to the zero of potential. Hence we have the energy/action diffusion equation

$$\frac{\partial f_{R,L}}{\partial S} = \gamma \frac{\partial}{\partial E} \left( f_{R,L} + k_B T \frac{\partial f_{R,L}}{\partial E} \right), \quad (11.12)$$

describing diffusion and uniform drift in energy space in the separatrix region and so governing the noisy motion there. This equation can be reduced to an integral equation using the principle of superposition by first determining the Green function  $g(E, S | E', 0) \equiv g(E - E', S)$  (the transition probability in energy space)

$$\frac{\partial g}{\partial S} = \gamma \frac{\partial}{\partial E} \left( g + k_B T \frac{\partial g}{\partial E} \right). \quad (11.13)$$

This gives via Fourier transforms the characteristic function ( $\lambda$  is dimensionless)

$$\tilde{g}(\lambda, S) = \int_{-\infty}^{\infty} g(E - E', S) e^{i\lambda(E-E')/(k_B T)} dE = e^{-\gamma S \lambda (\lambda + i)/(k_B T)}, \quad (11.14)$$

showing that the energy distribution of the random variable  $E - E'$  i.e. the change in energy in one cycle near the top of the barrier in a narrow range  $kT$  is Gaussian with mean  $-\gamma S$  and variance  $2\gamma k T S$ , viz.

$$g(E - E', S) = (4\pi\gamma kTS)^{-1/2} e^{-(E-E'+\gamma S)^2/(4\gamma kTS)}. \quad (11.15)$$

This Gaussian is sharply peaked since the energy loss per cycle is supposed small. The energy distribution for an arbitrary initial distribution of energy  $f(E', 0)$  for a trajectory near the barrier is then, by the principle of superposition

$$f(E, S) = \int_{-\infty}^0 f(E', 0) g(E - E', S) dE', \quad (11.16)$$

which is a Wiener-Hopf equation (see [6]). We then find the escape rate by normalizing the flux over population so that [6, 9]

$$\tau^{-1} = J = \int_0^{\infty} f(E) dE.$$

This is accomplished by taking the Fourier transform of  $f(E)$ ,  $\varphi^{\pm}(\lambda)$ , in both halves ( $\pm$ ) of the complex ( $\lambda$ ) plane and then using the Wiener-Hopf method [1, 6] whence we can find  $\mu=A(\Delta)$  say in the underdamped region as it is equal to  $\varphi^+(0)$  where

$$\varphi^{\pm}(\lambda) = \frac{\pi}{\omega_A} e^{\frac{\Delta V}{kT}} \int_{-\infty}^{\infty} U(\pm E) f(E) e^{\frac{i\lambda E}{kT}} dE, \quad (11.17)$$

where  $U(x)$  is Heaviside's theta or step function. Thus for a single isolated well based on Mel'nikov's assumption that the prefactor of the overall escape is simply the product of the underdamped and IHD prefactors (which is reasonable in that they both tend to the TST limit from either side) we have

$$\Gamma = \left[ \left( 1 + \frac{\gamma^2}{4\omega_C^2} \right)^{1/2} - \frac{\gamma}{2\omega_C} \right] A(\Delta) \Gamma_{TST} = \mu \Gamma_{TST}, \quad (11.18)$$

where the depopulation factor

$$A(\Delta) = e^{\frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\ln\{1 - \exp[-\Delta(\lambda^2 + 1/4)]\}}{\lambda^2 + 1/4} d\lambda} \quad (11.19)$$

(so called because Kramers assumed zero particle density at the barrier in VLD) which is not so in general true for low damping [6]. For high damping  $\Delta \gg 1$  (details in [9]) and therefore  $A(\Delta) \rightarrow 1$ , giving us the original IHD result. Also for the VLD limit  $A(\Delta) \rightarrow \Delta$ , yielding the VLD result in Eq. (11.7).

The arguments leading to the general solution which we have summarized show very clearly how the Kramers concept of oscillations in the potential well plays

a vital role in that solution. The same concept is also implicit in the alternative method of attack on the problem due to Pollak et al. [10] which starts by envisaging the particle as bilinearly coupled to a bath of harmonic oscillators which mimic the stochastic forces acting on the particle. The hypothesis of oscillations in a potential well is also essential in the semiclassical quantum treatment of the calculations of the depopulation factor (see for detail [1, 3]).

Substantially the same conclusions regarding the oscillation concept apply to the anomalous diffusion governed by the Barkai-Silbey equation [11, 12], where the fractional derivative or memory term is supposed to act only on the dissipative part of the Fokker-Planck operator. This is so because in this equation like the normal diffusion the high frequency resonant process is dominated by the almost deterministic librational motion governed by a Newtonian equation. The same is not true however of alternative forms of anomalous diffusion equations [1], where the fractional derivative operates on both the Liouville and dissipative terms so that the underdamped motion in the well is no longer determined by the Newtonian dynamics. The nett result of this being to produce [1] a physically unacceptable divergence of the absorption coefficient at high frequencies.

## References

1. Coffey WT, Kalmykov YP (2012) *The Langevin equation*, 3rd edn. World Scientific, Singapore
2. Kramers HA (1940) Brownian motion in a field of force and the diffusion model of chemical reactions. *Physica (Amsterdam)* 7:284
3. Coffey WT, Kalmykov YuP, Titov SV, Dowling L (2012) Longest relaxation time of relaxation processes for classical and quantum Brownian motion in a potential: escape rate theory approach. *Adv Chem Phys (in press)*
4. Hänggi P, Talkner P, Borkovec M (1990) Reaction rate theory: 50 years after Kramers. *Rev Mod Phys* 62:251
5. Nitzan A (2006) *Chemical dynamics in condensed phases*. Oxford University Press, London
6. Mel'nikov VI (1991) The Kramers problem: 50 years of development. *Phys Rep* 209:2
7. Goldstein H (2001) *Classical mechanics*, 3rd edn. Addison Wesley, Reading
8. Landau LD, Lifshitz EM (1976) *Mechanics*, 3rd edn. Pergamon, London
9. Coffey WT, Garanin DA, McCarthy DJ (2001) Crossover formulas in the Kramers theory of thermally activated escape rates – application to spin systems. *Adv Chem Phys* 117:483
10. Pollak E, Grabert H, Hänggi P (1989) Theory of activated rate processes for arbitrary frequency dependent friction: solution of the turnover problem. *J Chem Phys* 91:4073
11. Barkai E, Silbey RS (2000) Fractional Kramers equation. *J Phys Chem B* 104:3866
12. Kalmykov YP, Coffey WT, Titov SV (2012) Spectral definition of the characteristic times for anomalous diffusion in a potential. In: Kalmykov YP (ed) *Recent advances in broadband dielectric spectroscopy*. Springer, Dordrecht, p 131