ON THE KRAMERS VERY LOW DAMPING ESCAPE RATE FOR POINT PARTICLES AND CLASSICAL SPINS

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I. INTRODUCTION

One of the seminal contributions of Kramers [1] to the theory of the escape of particles over potential barriers due to the shuttling action of the Brownian motion has undoubtedly been his calculation of the escape rate for very low dissipation (VLD) to the surrounding heat bath. The reason being that the VLD calculation, based on the large amplitude nonlinear oscillations with energy-dependent frequency of a lightly damped particle governed by Newton's equations in a potential well just before escape (at the barrier energy), leads directly to a parameter Δ namely the ratio of the mean energy loss per cycle of a particle librating at the barrier energy to the thermal energy. This parameter then determines the range of validity of various asymptotic escape rate formulas [2–4]. Moreover, his results, rooted in the fluctuation dissipation theorem, simultaneously explain why escape is impossible in the absence of coupling to the bath. The latter cannot be accounted for in the context of transition state theory (TST) [4] where Boltzmann equilibrium is assumed to obtain throughout the entire domain of the well. A third reason is that the principles underlying his VLD calculation provide a dynamical explanation of the high frequency resonance absorption observed [2, 5] in a host of disparate physical systems exhibiting overbarrier relaxation [5–9] as originating in the small oscillations about the minimum in a potential well. This is so because the *large* amplitude Kramers oscillations (at the barrier energy) before escape and the *small* oscillations in the well (with energy-independent frequency) giving rise to the high frequency resonance absorption must of their very nature be part of one and the same dynamical process. This fact was explicitly recognized long ago by Praestgaard and van Kampen [10] and has recently been revisited by Coffey *et al.* [5]. Yet another benefit of the Kramers calculation is that his VLD result provides the means whereby escape rate formulas may be extended to all values of the dissipation to the bath as described by Hänggi *et al.* [4], Mel'nikov [11], and Pollak *et al.* [12].

Despite its fundamental importance, the original derivation of the VLD rate by Kramers [1, 2] is to some extent imperfectly understood, indeed prompting

Hänggi *et al.* in their well-known review [4] to remark that Kramers achieved his result (based on an energy-controlled diffusion equation) by use of "some subtle, almost acrobatic mathematics." The later, more detailed discussion of the low damping rate by Praestgaard and van Kampen [10] yields an energy-controlled diffusion equation which is ostensibly different but which is in fact identical to that of Kramers as demonstrated in Section III. Moreover, various derivations of the energy-controlled diffusion equation based on transformation of the diffusion equation in a phase (representation) space of positions and momenta to energy/angle variables have appeared in several research monographs, notably those of Zwanzig [13], Nitzan [14], and Billing and Mikkelson [15]. Here, in contrast, we favor the derivation of the energy-controlled diffusion equation from the lightly damped Langevin equation which has been given by Stratonovich [16]. He, in the context of a general discussion of how one may derive probability density diffusion equations from fluctuation equations such as the Langevin equation, showed how that equation may be written in terms of the (slow) energy variable and the (fast) position variable. Both these variables, which are characteristic of the small dissipation to the bath, naturally give rise to the Kramers energy-controlled diffusion equation and thus the VLD rate. A merit of this *dynamical* approach, to paraphrase Nelson [17], which automatically involves a Langevin equation in two state variables with *multiplicative* noise [18], is that it also transparently yields [19] an energy-controlled diffusion equation for the classical giant spins characteristic of a single domain ferromagnetic particle. This equation arises in the theory of the magnetization reversal time of single domain ferromagnetic particles [19, 20] which is of immense technological importance in the magnetic recording industry [21] and latterly in spintronics [19]. The quasistationary solution of this equation, by following exactly the procedure of Kramers for point particles, then yields in novel fashion the VLD rate for spins and hence the magnetization reversal time as the inverse of the Kramers rate. Thus the more complicated [22, 23] method of uniform asymptotic expansion of the mean first-passage time (MFPT) given by Matkowsky *et al.* [24] as generalized to classical spins by Klik and Gunther [25, 26] is entirely avoided. Finally, in the spin context, one should note that the large amplitude Kramers oscillations represent *libration in the direction of precession* of the magnetization in a well of the magnetocrystalline-Zeeman energy potential before escape to another well where the precession is reversed.

It is the purpose of this chapter to demonstrate in didactic fashion how both the VLD escape rate for point particles with separable and additive Hamiltonians and the corresponding rate for giant classical spins where the Hamiltonian is nonseparable and nonadditive may be simply obtained by using the Stratonovich treatment based on the Langevin equation with multiplicative noise. In order to prepare the reader, we will at first present, following [5], a very brief introduction to the escape rate problem as envisaged by Kramers [1].

II. THE CONTRIBUTION OF KRAMERS TO ESCAPE RATE THEORY

We begin with the work of Arrhenius [4] 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 [5]. Particles just reaching the top can escape due to thermal agitation.

The Arrhenius equation for the escape rate Γ_{TST} which can be found from TST [4, 14] is represented by the flux-over-population, namely

$$\Gamma_{\mathrm{TST}} = \frac{\omega_A}{2\pi} e^{-\Delta V/(kT)} = \frac{J}{N} = \tau^{-1}, \tag{1}$$

where

$$\omega_A = \sqrt{\frac{V''(x_A)}{m}}, \tag{2}$$

is the angular 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), ΔV is the barrier height, kT is the thermal energy, J is the steady current of particles over the barrier, τ is the greatest relaxation time, and the primes denote the second derivative. Thus we can find the lifetime τ of a particle in the well (see Fig. 1) as the inverse of the escape rate.

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 [1] derived a formula for Γ accounting for the disturbance using the

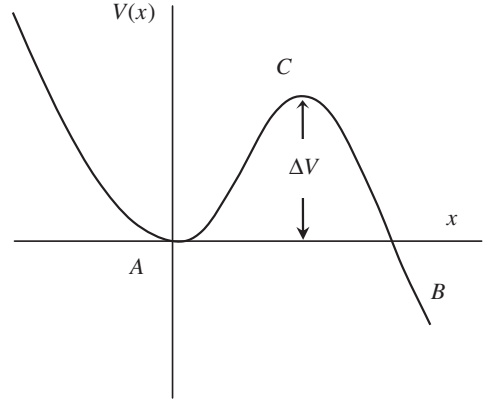

Figure 1. Single-well potential function $V(x)$. A is the initial state, C is the transition state, and B is the product state. Particles are initially trapped in the well near the point A by a high potential barrier at the point C. They are very rapidly thermalized in the well. Due to thermal agitation, however, a few may attain enough energy to escape over the barrier into region B, from which they never return (a sink of probability).

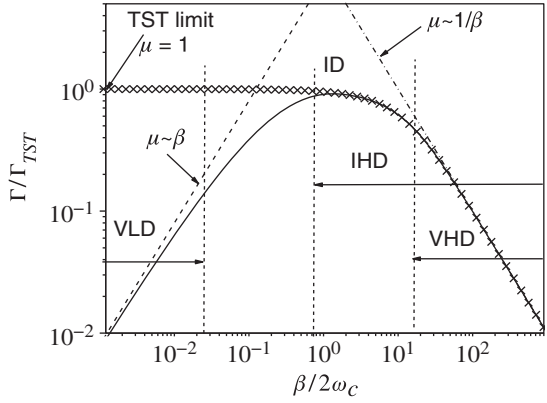

Figure 2. $\mu = \Gamma/\Gamma_{\rm TST}$ versus $\beta/2\omega_C$, showing the VLD, VHD, and IHD regions and the TST limit. Solid line: from exact numerical solution of Eq. (4). Crosses: IHD, Eq. (7). Dashed-dotted line: VHD, Eq. (8). Dashed line: VLD, Eq. (9).

theory of Brownian motion in order to represent the heat bath [2]. In doing so he introduced a dissipation-dependent prefactor μ so that

$$\Gamma = \mu\Gamma_{TST} = \mu\frac{\omega_A}{2\pi}e^{-\Delta V/(kT)}. \tag{3}$$

This prefactor removes the possibility that escape can occur in the absence of dissipation to the bath (see Fig. 2) which is an unphysical result. Kramers was able to calculate the prefactor μ in two specific regions of damping: intermediate-to-high damping (IHD) and very low damping (VLD) using two distinct methods of attack.

A. IHD or Spatially-Controlled Diffusion Escape Rate

The TST case is called intermediate damping (ID) here and is the limiting case of IHD, that is, when the friction coefficient per unit mass β vanishes (cf. Eq. 6 and Fig. 2). 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 evolution of the *reduced* or single particle distribution function, $W(x, p, t)$, of the positions and momenta in the phase space of a particle of mass m, namely,

$$\frac{\partial W}{\partial t} = L_{\rm FP}W = \frac{dV}{dx}\frac{\partial W}{\partial p} - \frac{p}{m}\frac{\partial W}{\partial x} + \beta\frac{\partial}{\partial p}\left(Wp + mkT\frac{\partial W}{\partial p}\right), \tag{4}$$

where x is the position and p is the momentum. The first two terms on the right-hand side of Eq. (4) comprise the Liouville term which describes, in the absence

of dissipation, the undamped streaming motion along the energy trajectories in phase space, corresponding to Hamilton's equations. The other terms represent the interchange of energy (dissipative coupling) to the heat bath. Everywhere we shall denote the space on which a probability density function is defined by simply specifying its arguments. The conservative or Liouville terms essentially represent Hamilton's equations for the single (or tagged) particle, namely,

$$\dot{p} = -\frac{\partial H}{\partial x}, \ \dot{x} = \frac{\partial H}{\partial p}, \tag{5}$$

where the Hamiltonian is

$$H = \frac{p^2}{2m} + V(x).$$

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

$$\dot{p} = -\frac{dV}{dx} - \beta p + F(t), \tag{6}$$

where the effect of the manifold degrees of freedom of the heat bath on the motion of the single particle is represented by a *systematic* retarding force $-\beta p$ tending to kill the motion superimposed on which is a very rapidly fluctuating *white noise* force $F(t)$ sustaining it. Kramers then linearized the Langevin equation (6) and thus Eq. (4) about the barrier top allowing him to find the escape rate using the flux-over-population method [4]. We may set $\dot{W} = 0$ because the escape over the barrier is a very slow (quasistationary) process. In IHD, the region of nonequilibrium is very near the top of the barrier and so lies well inside the range, where the barrier shape may be approximated by an inverted parabola. Thus

$$\Gamma_{\mathrm{IHD}} = \left(\sqrt{1 + \frac{\beta^2}{4\omega_C^2}} - \frac{\beta}{2\omega_C} \right) \Gamma_{\mathrm{TST}}, \tag{7}$$

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

$$\Gamma_{\mathrm{VHD}} = \frac{\omega_C}{\beta} \Gamma_{\mathrm{TST}}. \tag{8}$$

After the TST formula, Eq. (8) is the best known of all the Kramers escape rate formulas mainly because it is easily obtained from the quasistationary solution

of the Smoluchowski equation for the probability density function $W(x,t)$ in configuration space [2]

$$\frac{\partial W}{\partial t} = \frac{kT}{\zeta}\frac{\partial}{\partial x}\left[\frac{\partial W}{\partial x} + \frac{W}{kT}\frac{dV}{dx}\right].$$

This equation, in which $\zeta = m\beta$, 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. 2).

Notice that the IHD prefactor is $\mu = \lambda^+/\omega_C$ where λ^+ is the positive eigenvalue of the Langevin equation linearized about the barrier top, however, omitting $F(t)$ (see Ref. [2]). This corresponds 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 characterized by $\beta^2/4\omega_C^2 < 1$. Kramers treated the VLD case, when β is almost vanishingly small (now, however, using an energy-controlled diffusion model) as follows.

B. VLD or Energy-Controlled Diffusion Escape Rate

In VLD, Kramers imagined (see [1, 3]) that the particles move in closed phase plane orbits (see [11]) which represented large amplitude oscillatory motion in the well (called libration, [27–29]) 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, that is, the motion is almost deterministic. He took the top of the barrier as the zero of potential. Such high energy librating particles, which are essentially in a metastable state like that of an inverted pendulum, can be kicked over the barrier by a small thermal fluctuation of amount kT. The resulting phase space 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 phase plane orbit (see Fig. 3).

A separate treatment of VLD is required because in VLD, the region of departure from the Boltzmann equilibrium obtaining in the depths of the well becomes much greater in spatial extent than that in which the potential may sensibly be represented as an inverted parabola in configuration space. Therefore, one can no longer linearize the Fokker–Planck equation (4) in phase space (x,p) about the barrier top. Thus to tackle VLD, Kramers transformed the quasistationary Fokker–Planck equation into a new equation, using only the energy, $E(t)$, and phase, $\phi(t)$, as variables. The energy $E(t)$ diffuses very slowly over time (i.e., is almost conserved) while the phase $\phi(t)$ (which would be the only variable in the completely conservative system) is in contrast very fast. Kramers can therefore average the transformed equation over $\phi(t)$, using the Liouville equation

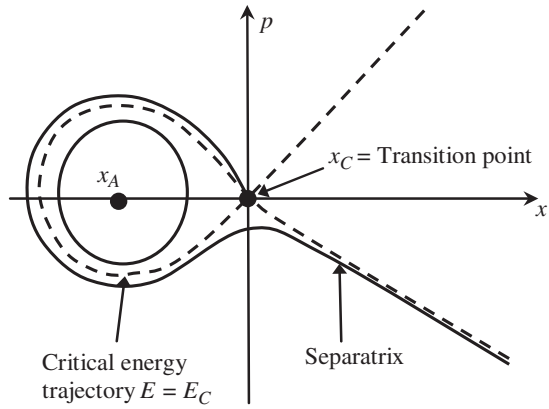

Figure 3. The critical energy curve (dashed line) and the separatrix in phase space. Separation between the closed E_C and separatrix trajectories is *infinitesimal*. The closed trajectory represents the bounded librational motion in the well. The phase point, (x,p), specifies the instantaneous state (phase) of the dynamical system.

to eliminate the $\phi(t)$ dependence, to get a one-dimensional diffusion equation for the distribution function of the energy ultimately leading to the VLD rate (cf. Fig. 2).

$$\Gamma_{\mathrm{VLD}} = \Delta \Gamma_{\mathrm{TST}} \tag{9}$$

Here,

$$\Delta = \frac{\overline{\overline{\delta E}}_{E_C}}{kT}, \tag{10}$$

where $\overline{\overline{\delta E}}_{E_C}$ is the mean energy loss per cycle of a particle librating in the well at the barrier energy given by

$$\overline{\overline{\delta E}}_{E_C} = \beta S_{E_C}. \tag{11}$$

The quantity

$$S_{E_C} = \oint_{R_{E_C}} p dx, \tag{12}$$

is the action in a cycle of the motion in the well of a librating particle with energy equal to the critical barrier energy E_C (R_{E_C} denotes the energy trajectory

of the undamped motion in phase space at E_C) and the double overbar represents the average over a period. The parameter Δ [4] (which represents the crowning achievement of the Kramers theory) 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 $\Gamma_{\mathrm{VLD}} \propto \beta$ while in IHD $\Gamma_{\mathrm{IHD}} \propto 1/\beta$. He was not, however, able to solve the problem in the part of the underdamped region lying between ID and VLD, that is, $\Delta < 1$, essentially due to the lack of a small parameter. This became known as Kramers' turnover problem [1, 3, 4] (cf. Fig. 2). The most recent detailed review of the turnover problem and its solution is available in this series [3]. For completeness, we summarize Mel'nikov's solution of the turnover problem in Section II.D. However, we first describe how the Kramers VLD calculation relates to the high frequency resonance absorption peak observed in systems which exhibit over-barrier relaxation.

C. Connection of the VLD Rate with the High Frequency Resonance Absorption

The background of how the VLD rate relates to high frequency resonance absorption, which was first mooted in Ref. [10], may be explained as follows. The spectra of the correlation functions and the corresponding complex susceptibilities associated with diverse relaxation phenomena, which are usually modeled (see [2]) via the theory of the Brownian motion in a potential, almost invariably exhibit a high frequency resonant absorption peak attributed to *small* inertial oscillations of the Brownian particles in the wells of the potential. The resonant phenomenon occurs along with the low frequency absorption due to escape of Brownian particles over the potential barriers (representing *interwell* relaxation) [2] and a second intermediate frequency (representing *intrawell* relaxation) one due to relatively fast exponential decays in the wells. Examples of the resonant absorption phenomenon occur [2] in the complex susceptibilities associated with the position correlation function of the inertial translational Brownian motion in a potential, the inertial rotational Brownian motion of a polar molecule in a potential, and the Brownian motion of the magnetization of a single domain ferromagnetic nanoparticle. For polar molecules, the librational peak in the complex dielectric susceptibility is generally in the THz region and is known [2] as the *Poley* absorption. However, in single-domain particles, the high frequency ferromagnetic resonance peak in the complex magnetic susceptibility at GHz frequencies close to the Larmor precession frequency arises not from inertial librations but from the precession of the magnetization in the wells of the magnetocrystalline-Zeeman potential. At low frequencies effectively only the overbarrier relaxation mode characterized by the escape rate for classical spins remains. In this context, the latter is called the Néel–Brown overbarrier relaxation mode [2] and the inverse escape rate, taking

account of the bi- or multi-stable nature of the potential, yields the superparamagnetic relaxation time or time of reversal of the direction of precession.

By way of illustration of the various relaxation phenomena for particles, we shall consider the *one-dimensional inertial translational diffusion* of a Brownian particle in a double-well potential

$$V(x) = \frac{a}{2}x^2 + \frac{b}{4}x^4, \tag{13}$$

where a ($a < 0$) and b are constants, and $-\infty < x < \infty$. This model is almost invariably used to model the noise-driven motion in bistable physical and chemical systems, e.g., simple isometrization processes, chemical reaction-rate theory, bistable nonlinear oscillators, second-order phase transitions, nuclear fission and fusion, and so on [2]. Here, the stochastic dynamics of the particle is governed by the Langevin equation (6). The position ACF $C(t) = \langle x(0)x(t)\rangle_0 / \langle x^2(0)\rangle_0$, its spectrum, and the characteristic times, may be calculated directly either from the Langevin equation (6) or from the Fokker–Planck equation (4) (details in Ref. [2]). In particular, the low-frequency part of the spectrum $\tilde{C}(\omega) = \int_0^\infty C(t)e^{-i\omega t}dt$ may be accurately approximated by a *single* Lorentzian [2], namely,

$$\frac{\tilde{C}(\omega)}{\tilde{C}(0)} \approx \frac{1}{1 + i\omega/\Gamma}, \tag{14}$$

(explicit equations for Γ are given in Ref. [2], v. also Eq. 95). The real part of $\tilde{C}(\omega)$ for various values of the dimensionless friction coefficient $\beta' = \beta\eta$ (where $\eta = [m\langle x^2\rangle_0/(2kT)]^{1/2}$ is a characteristic time and $\langle\ \rangle_0$ designates the statistical average over the equilibrium distribution function [2]) are shown in Fig. 4. One relaxation band dominates the low-frequency part of the spectra; this is a result of the slow overbarrier relaxation of the particles in the double-well potential. Clearly, the low-frequency part of the spectrum may be approximated by Eq. (14). The *half-width* $\Delta\omega_c$ of the low-frequency band strongly depends on ΔV as well as on the friction parameter β'. Regarding the dependence on the barrier height ΔV, we perceive that $\Delta\omega_c$ decreases exponentially as ΔV is increased, since the probability of escape of a particle from one well to another over the potential barrier (corresponding to interwell relaxation) exponentially decreases with increasing ΔV. For low damping, $\beta' < 0.1$, $\Delta\omega_c$ decreases with decreasing β' for given values of ΔV. The very high-frequency band visible in the figure is due to the fast inertial oscillations of the particles in the potential wells: this is a ubiquitous feature of inertial Brownian motion in a potential. Furthermore, for very small friction (large inertial effects), $\beta' \ll 1$, an additional peak appears in the high-frequency part of the spectra: this is a result of resonances at higher harmonic modes of the very

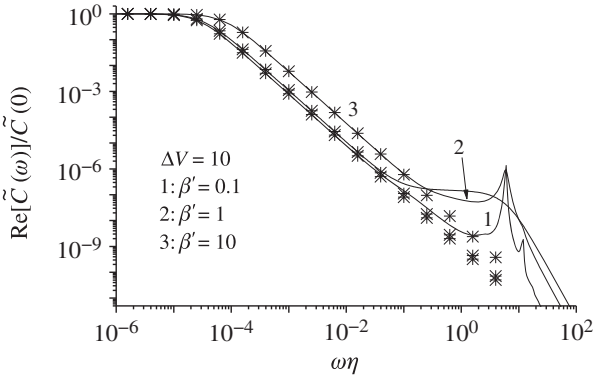

Figure 4. $\mathrm{Re}[\tilde{C}(\omega)/\tilde{C}(0)]$ of an assembly of particles in a double-well potential, Eq. (13), versus $\omega\eta$ for various values of the dimensionless damping parameter β'. Solid lines: exact matrix continued fraction solution [2]. Asterisks: Eq. (14) with Γ from Eq. (3) [2].

lightly damped motion in the wells of the (anharmonic) potential (v. Chapter 3 of Ref. [2]).

We now explain why the high frequency resonance process observed in the spectrum $\tilde{C}(\omega)$ 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 VLD Kramers calculation entirely relies on the Newtonian concept of undamped large amplitude oscillations of a particle in a well before escape, incidentally a concept which is also used [30] in discussing the inverted pendulum in which the bob has just enough energy to reach the upper vertical position. 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 effectively governed by the Newtonian equation of motion with energy equal to the barrier energy. This equation is simply the Langevin equation underlying Eq. (4), when 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 trajectory travelling on which a particle may escape the well (cf. Fig. 3). Moreover, comparing Fig. 5, it is unnecessary to treat the left and right going particles separately in VLD. The separatrix trajectory due to the thermal fluctuations which is now open is regarded as infinitesimally close to the (closed) critical energy trajectory 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 [11] who has rigorously justified it). Now the period $T_C = \oint_{E_C} \dot{x}^{-1} dx$ of the (large amplitude) oscillations with energy equal to the critical energy E_C always depends

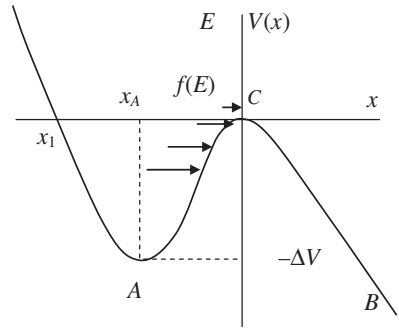

Figure 5. Escape from a single well.

on their amplitude and may be evaluated [27–29] from the Newtonian equations (considering the one dimensional motion of a particle and an isolated well)

$$m\ddot{x} = -\frac{dV}{dx},\ \dot{x} = \pm\sqrt{\frac{2}{m}[E_C - V(x)]}, \tag{15}$$

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

The prefactor of the VLD rate is then solely determined by the action S_{E_C} on the *closed* critical energy trajectory, that is, by the *deterministic dynamics*, as is immediately apparent from the quasistationary solution of the energy-controlled diffusion equation (see Section III.E). The effect of the noise, which is automatically contained in the energy-controlled diffusion equation is to give rise to a *spread* of energies about E_C. Subsequent use of the flux-over-population method shows that the escape rate is given by Eq. (9). However, as far as the deterministic Newtonian dynamics is concerned, 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 (cf. Fig. 3) also include the almost harmonic, low energy but relatively high frequency motions near the bottom of the well which characterize the resonance absorption. Such 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 ω_A given in terms of the period $T_A = 2\pi/\omega_A$ of small oscillations about the bottom of the well.

This behavior 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 TST. 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 [27–29] just as 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 ([28], Chapter 3, and also [30], [31]).

D. Connection of the VLD Rate with Mel'nikov's Solution of the Kramers Turnover Problem

The notion of large oscillations 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 Eq. (4) to E (slow) and ϕ (fast) variables he ignored the coupling between dissipative and nondissipative terms so that the Liouville equation may be used to eliminate the ϕ dependence. Mel'nikov [11] solved this problem 50 years later. The calculations [3, 11, 23] 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. Unlike in VLD, it is now necessary to consider left and right going particles separately (see Fig. 5). Moreover, near the separatrix the momentum satisfies (cf. Eq. 15)

$$p(x, E) = \pm\sqrt{2m[E - V(x)]} \approx p(x, 0) = \pm\sqrt{-2mV(x)}, \tag{16}$$

because we have chosen the separatrix trajectory to effectively coincide with $E = 0$ (see Fig. 5) and we suppose that the leading contributions to the escape stem only from diffusing particles very near the barrier in a narrow range of energy of order kT. Now we define the action as

$$S = S_E = \oint_{R_E} p\,dx, \tag{17}$$

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

$$\frac{dS}{dx} = \pm\sqrt{2m[E - V(x)]}, \tag{18}$$

recalling that inside the well $V(x)$ is negative since the top of the well corresponds to the zero of potential. Hence, [3] using the chain rule, we have the energy/action diffusion equation (R,L denoting the right and left going particles, respectively)

$$\frac{\partial f_{R,L}}{\partial S} = \beta \frac{\partial}{\partial E}\left(f_{R,L} + kT\frac{\partial f_{R,L}}{\partial E}\right), \tag{19}$$

describing diffusion and uniform drift in energy space in the separatrix region and so governing the noisy motion there. This equation can be reduced [3] to an integral equation using the principle of superposition by first determining the Green function $g(E,S|E',0) \equiv g(E-E',S)$, namely, the transition probability in energy space which is the fundamental solution of the energy-action diffusion equation

$$\frac{\partial g}{\partial S} = \beta \frac{\partial}{\partial E}\left(g + kT\frac{\partial g}{\partial E}\right). \tag{20}$$

This equation yields via Fourier transforms the characteristic function

$$\tilde{g}(\lambda, S) = \int_{-\infty}^{\infty} g(E-E',S)e^{i\lambda(E-E')/(kT)}dE = e^{-\beta S\lambda(\lambda+i)/(kT)}, \tag{21}$$

(λ is dimensionless) showing that the energy distribution of the random variable $E-E'$, that is, *the change in energy in one cycle near the top of the barrier in a narrow range kT*, is Gaussian with mean $-\beta S$ and variance $2\beta kTS$, namely,

$$g(E-E',S) = (4\pi\beta kTS)^{-1/2}e^{-(E-E'+\beta S)^2/(4\beta kTS)},\ -\infty < E-E' < \infty. \tag{22}$$

This Gaussian is sharply peaked, indeed resembling a delta function, since the variance is supposed very 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

$$f(E,S) = \int_{-\infty}^{\infty} f(E',0)g(E-E',S)dE', \tag{23}$$

which, by use of appropriate transformations and boundary conditions (details in Refs. 2 and 3), may be transformed into a Wiener–Hopf equation for the

distribution function $f(E)$ of particles with a possibility of escape (see [3, 11]). We then find the escape rate by normalizing the flux-over-population so that [2, 11]

$$\tau^{-1} = \int_0^\infty f(E)dE. \tag{24}$$

The calculation is accomplished by taking the Fourier transform of the distribution function $f(E)$ written as $\varphi^{\pm}(\lambda)$ in both halves $(\pm)$ of the complex (λ) plane and then using the Wiener–Hopf method [3, 11] to find $\mu = A(\Delta)$ in the entire underdamped region as it is equal to $\varphi^{+}(0)$, where

$$\varphi^{\pm}(\lambda) = \frac{\pi}{\omega_A} e^{-\frac{\Delta V}{kT}} \int_{-\infty}^{\infty} U(\pm E) f(E) e^{\frac{i\lambda E}{kT}} dE, \tag{25}$$

and $U(x)$ is Heaviside's theta or step function. Furthermore, for a single isolated well, based on Mel'nikov's assumption that the prefactor of the overall escape rate 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 the escape rate for all values of the damping

$$\Gamma = \left[\left(1 + \frac{\beta^2}{4\omega_C^2} \right)^{1/2} - \frac{\beta}{2\omega_C} \right] A(\Delta) \Gamma_{\mathrm{TST}}, \tag{26}$$

where the depopulation factor $A(\Delta)$ is

$$A(\Delta) = e^{\frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\ln\{1 - \exp[-\Delta(\lambda^2 + 1/4)]\}}{\lambda^2 + 1/4} d\lambda}, \tag{27}$$

(so called because Kramers assumed zero particle density at the barrier in VLD which is not in general true for low damping [11]). For high damping $\Delta \gg 1$ (details in Ref. [23]) and therefore $A(\Delta) \to 1$, giving us the original IHD result. Also for the VLD limit $A(\Delta) \to \Delta$, yielding the VLD result in Eq. (9). The arguments leading to the general solution which we have summarized show very clearly how the Kramers concept of large oscillations at the critical energy in the potential well before escape plays a vital role in that solution. The hypothesis of large oscillations in a potential well is also essential in the semiclassical quantum

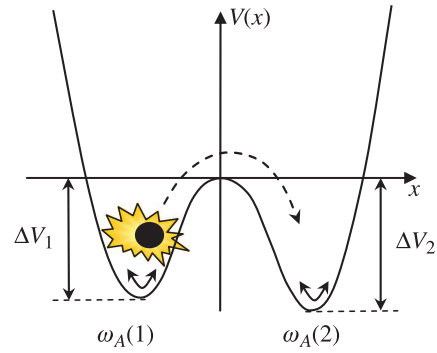

Figure 6. Double-well potential.

treatment of the calculations of the depopulation factor (see for detail [3, 11]). The same concept is also implicit in the alternative more general method of attack on the problem due to Grabert [32] and Pollak *et al.* [12] which starts by envisaging the particle as bilinearly coupled to a bath of harmonic oscillators which mimic the stochastic forces acting on it. Grabert [32] and Pollak *et al.* [12] presented a complete solution of the Kramers turnover problem and have shown that the Mel'nikov formula, Eq. (26), can be obtained without *ad hoc* interpolation between the weak and strong damping regimes. We remark that the theory of Pollak *et al.* [12] is also applicable to an arbitrary memory friction and not only in the "white noise" (memoryless) limit.

We saw earlier that along with the escape from a single well another important case is represented by a double-well potential (Fig. 6) such that when particles escape over the barrier they enter another well of finite depth. There is now a finite, non-negligible probability for the particle to return to the initial well in the underdamped case. Here, the particle (having escaped the first well) in the second well loses its energy so slowly that even after several oscillations there the white noise force may give it sufficient energy to send it back over the barrier [23] into the first well. This double-well situation was first analyzed by Mel'nikov and Meshkov [33] in 1986 and was reviewed in depth by Coffey *et al.* [23]. In this situation, the overall escape rate $\Gamma = \Gamma_1 + \Gamma_2$ is

$$\Gamma = \left[\left(1 + \frac{\beta^2}{4\omega_C^2}\right)^{1/2} - \frac{\beta}{2\omega_C}\right] \frac{A(\Delta_1)A(\Delta_2)}{A(\Delta_1 + \Delta_2)} \left[\frac{\omega_A(1)}{2\pi} e^{-\frac{\Delta V_1}{kT}} + \frac{\omega_A(2)}{2\pi} e^{-\frac{\Delta V_2}{kT}}\right], \tag{28}$$

where Γ_i is the escape rate from well i, Δ_i is the ratio of the energy loss per cycle of a particle librating in well i, moving with energy equal to the barrier energy, to the thermal energy.

III. ENERGY-CONTROLLED DIFFUSION EQUATION FOR PARTICLES WITH SEPARABLE AND ADDITIVE HAMILTONIANS

We now derive the VLD escape rate using the method of Stratonovich [16]. Before discussing energy-controlled diffusion of point particles with separable and additive Hamiltonians, it will be instructive to consider the motion of a lightly damped particle librating in the potential $V(x)$ in the absence of the stochastic noise term. In particular, we shall consider the mean energy loss per cycle of a particle librating with energy equal to the barrier energy E_C as an understanding of this is essential for the study of the VLD rate.

A. Mean Energy Loss per Cycle of a Lightly Damped Particle

We consider a very lightly damped particle executing large oscillations in a potential well with energy equal to the barrier or critical energy E_C in excess of which the particle may escape the well. The Newtonian equation of motion of the particle in a potential $V(x)$ is (the Langevin equation (6) omitting the noise term and $\zeta = m\beta$)

$$m\ddot{x} + \zeta\dot{x} + \frac{dV}{dx} = 0, \tag{29}$$

and we assume that the retarding force $-\zeta\dot{x}$ is very small compared to the inertial force so that the particle executes many large amplitude oscillations in the well before finally relaxing to the well bottom. To study the very lightly damped motion, we rewrite Eq. (29) in energy and configuration space (E,x) variables. We write the energy E as

$$E = \frac{1}{2}m\dot{x}^2 + V(x), \tag{30}$$

which we can rearrange as the evolution equation of the state variable x (for the purpose of our subsequent VLD calculations whether the positive or negative sign is used is immaterial as the signs will effectively always cancel each other out)

$$\dot{x} = \pm\sqrt{\frac{2}{m}[E - V(x)]}. \tag{31}$$

We assume that E varies slowly with time. Taking its derivative with respect to time yields the instantaneous power dissipated

$$\dot{E} = m\dot{x}\ddot{x} + \frac{dV}{dx}\dot{x} = \left(m\ddot{x} + \frac{dV}{dx}\right)\dot{x}. \tag{32}$$

Using Eq. (29) we have

$$\dot{E} = -\zeta \dot{x}^2. \tag{33}$$

Now from Eq. (31), we have for the evolution equation of the state variable E

$$\dot{E} = -2\beta[E - V(x)]. \tag{34}$$

Thus the nonstochastic lightly damped system is governed by the two Eqs. (31) and (34).

Since the time now represents that measured along a closed phase space trajectory with energy E we have the periodic time of the motion of a librating particle with energy E and the corresponding angular frequency ω_E in radians per second, namely,

$$T_E = \frac{2\pi}{\omega_E}. \tag{35}$$

The mean power loss in one cycle of the periodic motion in the well with energy equal to the barrier energy E_C is by definition using Eq. (33)

$$\bar{\bar{\dot{E}}}_{E_C} = \frac{1}{T_{E_C}} \int_0^{T_{E_C}} \dot{E} dt = -\frac{\zeta \omega_{E_C}}{2\pi} \int_0^{2\pi/\omega_{E_C}} \dot{x}^2 dt = -\frac{\zeta \omega_{E_C}}{2\pi} \oint_{R_{E_C}} \dot{x} dx, \tag{36}$$

where R_{E_C} denotes the energy trajectory of the *undamped motion* in phase space at the critical energy E_C and the double overbar represents the average over a period of this closed cycle. One should note that $\dot{x}$ may be understood in the conservative sense in Eq. (36) because we assume the VLD limit (i.e. all calculations are to first order in β). Using Eq. (12), we have the mean power dissipated

$$\bar{\bar{\dot{E}}}_{E_C} = -\frac{\beta \omega_{E_C}}{2\pi} S_{E_C}. \tag{37}$$

Equation (37) written in terms of the mean energy loss $\overline{\overline{\delta E}}_{E_C}$ over a cycle with energy equal to the barrier energy then becomes (cf. Eq. 11)

$$\overline{\overline{\delta E}}_{E_C} = -T_{E_C} \bar{\bar{\dot{E}}}_{E_C} = \beta S_{E_C}. \tag{38}$$

Thus all that is required to calculate the mean energy loss is a knowledge of the undamped deterministic dynamics. The introduction of a heat bath will now counteract, via thermal agitation, this energy loss due to the frictional forces imposed by the surroundings.

B. The Lightly Damped Langevin Equation

As we mentioned in the Introduction, our preferred method of treatment of the one-dimensional energy-controlled diffusion is that of Stratonovich [16]. His starting point is effectively the Langevin equation (all his calculations are, however, carried out in normalized variables)

$$m\ddot{x} + \zeta\dot{x} + \frac{dV}{dx} = F(t). \tag{39}$$

Here, the influence of the bath on the single degree of freedom system is represented by a systematic damping force $-\zeta\dot{x}$ slowing down the particle and a rapidly fluctuating random white noise force which sustains the Brownian motion and has properties

$$\overline{F(t)} = 0,\ \overline{F(t)F(t')} = 2D\delta(t - t'). \tag{40}$$

Now the spectral density $D = \zeta kT = \beta mkT$ and the overbars in the foregoing equations mean the statistical average over an ensemble of particles each of which starts with the same (sharp) initial conditions in phase space $(x, m\dot{x})$. Furthermore, the $F(t)$ obey Isserlis's (Wick's) theorem [2] concerning mean values of products of Gaussian white noise random variables

$$\overline{F(t_1)F(t_2)\cdots F(t_{2n})} = \sum \prod_{k_i<k_j} \overline{F\left(t_{k_i}\right)F\left(t_{k_j}\right)}, \tag{41}$$

where the sum is over all distinct products of expectation value pairs, each of which is formed by selecting n pairs of subscripts from $2n$ subscripts. For example, when $n = 2$, we have the decomposition into products of two-time averages

$$\overline{F_1F_2F_3F_4} = \overline{F_1F_2}\ \overline{F_3F_4} + \overline{F_1F_3}\ \overline{F_2F_4} + \overline{F_1F_4}\ \overline{F_2F_3}. \tag{42}$$

In general, there will be $(2n)!/(2^n\, n!)$ such distinct pairs. We also always have, for an odd number of observations (three-time averages and so on)

$$\overline{F(t_1)F(t_2)\cdots F(t_{2n+1})} = 0. \tag{43}$$

If ζ and $F(t)$ are small, Eq. (39) describes the behavior of a system performing nonlinear oscillations under the influence of *weak frictional* forces and *weak internal* fluctuations. In other words, the system is only *very lightly* coupled to the bath.

The energy of a particle moving in a potential $V(x)$ can be expressed via Eq. (30) using the same method as in the nonstochastic case. Thus, we have from Eqs. (32)

and (39), the stochastic evolution equations of the state variables x and E

$$\dot{x} = \sqrt{2[E - V(x)]/m} \tag{44}$$

$$\dot{E} = -\zeta \dot{x}^2 + F(t)\dot{x}, \tag{45}$$

which when combined yield an equation involving *multiplicative* noise terms, namely,

$$\dot{E} = -2\beta[E - V(x)] + \sqrt{2[E - V(x)]/m}F(t). \tag{46}$$

Thus the system is governed by the two stochastic Eqs. (44) and (46) in two state variables. The corresponding Fokker–Planck equation for the evolution of the probability density function underlying the two state variables x and E can now be written down.

C. The Fokker–Planck Equation

We first write the two Langevin equations (44) and (46) in state variable form for random variables $\xi_i(t)$ as (using Einstein's summation convention)

$$\dot{\xi}_i(t) = h_i[\{\boldsymbol{\xi}(t)\}, t] + g_{ij}[\{\boldsymbol{\xi}(t)\}, t]F_j(t). \tag{47}$$

Here, $\xi_1 = x$ and $\xi_2 = E$ with

$$h_1 = \sqrt{2[E - V(x)]/m},\ h_2 = -2\beta[E - V(x)] \tag{48}$$

and

$$g_{11} = g_{12} = g_{21} = 0,\ g_{22} = \sqrt{2[E - V(x)]/m}. \tag{49}$$

Next we can construct utilizing Isserlis's theorem, Eqs. (41) and (43), the Fokker–Planck equation as the first two terms in a Kramers–Moyal [18] expansion of the evolution of the representation space distribution W

$$\dot{W} = L_{\mathrm{FP}}W = -\sum_i \frac{\partial}{\partial \xi_i}\left[D_i^{(1)}W - \sum_j \frac{\partial}{\partial \xi_j}D_{i,j}^{(2)}W\right] \tag{50}$$

where the $D_i^{(1)}$ are the *drift* coefficients defined as

$$D_i^{(1)} = \lim_{\Delta t \to 0} \frac{\overline{[\xi_i(t + \Delta t) - x_i]}}{\Delta t} \tag{51}$$

and the $D^{(2)}_{i,j}(x,t)$ are the *diffusion* coefficients defined as

$$D^{(2)}_{i,j} = \lim_{\Delta t \to 0} \frac{\overline{[\xi_i(t+\Delta t) - x_i][\xi_j(t+\Delta t) - x_j]}}{2\Delta t}, \tag{52}$$

where the x_i are the state variables for initially sharp values at time t.

For purposes of exposition, we first find expressions for the drift and diffusion coefficients of the one-dimensional Langevin equation

$$\dot{\xi}(t) = h[\xi(t), t] + g[\xi(t), t]F(t). \tag{53}$$

In order to accomplish this, we must regard Eq. (53) as the integral equation [2, 18]

$$\xi(t+\Delta t) = \xi(t) + \int_t^{t+\Delta t} \dot{\xi}(t')dt', \tag{54}$$

so that, using Eq. (53),

$$\xi(t+\Delta t) - x = \int_t^{t+\Delta t} (h[\xi(t'), t'] + g[\xi(t'), t']F(t'))dt', \tag{55}$$

where x is the *sharp* value of ξ at an initial time t. Now expanding $h[\xi(t'), t']$ and $g[\xi(t'), t']$ as the first two terms in Taylor series expansions about the sharp initial value x, namely,

$$\begin{aligned} h[\xi(t'), t'] &= h(x, t') + (\xi(t') - x)\frac{\partial h(x, t')}{\partial x} + \cdots \\ g[\xi(t'), t'] &= g(x, t') + (\xi(t') - x)\frac{\partial g(x, t')}{\partial x} + \cdots \end{aligned} \tag{56}$$

and iterating for $(\xi(t') - x)$ using Eq. (55) we have a six-term expression for Eq. (55), namely, [18]

$$\begin{aligned} \xi(t+\Delta t) - x = &\int_t^{t+\Delta t} h(x, t')dt' + \int_t^{t+\Delta t}\int_t^{t'} h(x, t'')\frac{\partial h(x, t')}{\partial x}dt''dt' \\ &+ \int_t^{t+\Delta t}\int_t^{t'} g(x, t'')\frac{\partial h(x, t')}{\partial x}F(t'')dt''dt' + \int_t^{t+\Delta t} g(x, t')F(t')dt' \\ &+ \int_t^{t+\Delta t}\int_t^{t'} h(x, t'')\frac{\partial g(x, t')}{\partial x}F(t')dt''dt' \\ &+ \int_t^{t+\Delta t}\int_t^{t'} g(x, t'')\frac{\partial g(x, t')}{\partial x}F(t'')F(t')dt''dt' + \cdots \end{aligned} \tag{57}$$

On substituting this expression into the drift coefficient Eq. (51), the third, fourth, and fifth terms will vanish on averaging due to Eq. (40). Moreover, we can ignore the second term as it is of order $(\Delta t)^2$. Next, we can write the last term (involving a two-time product of noises) using Eq. (40) and the delta function property

$$\int_a^b \delta(b-x)y(x)dx = \frac{1}{2}y(b) \tag{58}$$

as [2, 18]

$$D^{(1)} = \lim_{\Delta t\to 0} \frac{\overline{\xi(t+\Delta t)-x}}{\Delta t} = h(x,t) + Dg(x,t)\frac{\partial g(x,t)}{\partial x}. \tag{59}$$

The last term represents our *noise-induced drift* while the first constitutes the *deterministic drift*. Finally all higher order terms in the expansion Eq. (57) will vanish in the limit of infinitesimally small Δt due to Isserlis's theorem as stated in the form of Eqs. (41) and (43) which renders them either as products of two-time averages or zero.

Similarly for the diffusion coefficient Eq. (52), we have

$$\begin{aligned}[\xi(t+\Delta t)-x]^2 = &\int_t^{t+\Delta t}\int_t^{t+\Delta t} h(x,t')h(x,t'')dt'dt'' \\ &+2\int_t^{t+\Delta t} h(x,t')dt' \int_t^{t+\Delta t} g(x,t')F(t')dt' \\ &+\int_t^{t+\Delta t}\int_t^{t+\Delta t} g(x,t')g(x,t'')F(t')F(t'')dt'dt'' + \cdots\end{aligned} \tag{60}$$

The first two terms of Eq. (60) will give contributions of the order $(\Delta t)^2$ and will vanish as prescribed by Eq. (52). Likewise, all higher order contributions will vanish due to Isserlis's theorem. Thus for our purposes

$$\begin{aligned}\overline{[\xi(t+\Delta t)-x]^2} &= 2D\int_t^{t+\Delta t}\int_t^{t+\Delta t} g(x,t')g(x,t'')\delta(t'-t'')dt'dt'' + O(\Delta t)^2 \\ &= 2Dg^2(x,t+\Theta_1\Delta t)\Delta t + O(\Delta t)^2\end{aligned} \tag{61}$$

$(0 \leq \Theta_1 \leq 1)$. Therefore, we have the diffusion coefficient [2, 18]

$$D^{(2)} = \lim_{\Delta t \to 0} \frac{\overline{[\xi(t + \Delta t) - x]^2}}{2\Delta t} = Dg^2(x, t). \tag{62}$$

In our two-dimensional equation for E and x, Eq. (59) generalizes to [2, 18]

$$D_i^{(1)} = h_i + D \sum_{k,j=1}^{2} g_{kj} \frac{\partial g_{ij}}{\partial \xi_k}. \tag{63}$$

Similarly, we can find the diffusion coefficients as [2, 18]

$$D_{i,j}^{(2)}(x, t) = D \sum_{k=1}^{2} g_{ik} g_{jk}. \tag{64}$$

Many explicit examples of the calculation of these coefficients are given in Refs. 2, 18, and 23. Since the Langevin equation for x, namely Eq. (44), does not explicitly involve a multiplicative noise we only have a deterministic (conservative) term in the corresponding drift coefficient so that

$$D_1^{(1)} = \sqrt{2[E - V(x)]/m}, \tag{65}$$

while the stochastic Langevin equation, Eq. (46), gives rise to the following deterministic and noise-induced terms

$$\begin{aligned} D_2^{(1)} &= -2\beta[E - V(x)] + \frac{2D}{m} \sqrt{E - V(x)} \frac{\partial}{\partial E} \sqrt{E - V(x)} \\ &= -2\beta[E - V(x)] + \beta kT. \end{aligned} \tag{66}$$

From inspection of Eq. (49), we can see that the only nonzero diffusion coefficient is

$$D_{2,2}^{(2)}(x, t) = 2\beta kT[E - V(x)]. \tag{67}$$

Thus we have the Fokker–Planck equation for the evolution of the joint probability density in (x, E) space, namely,

$$\dot{W} = -\frac{\partial}{\partial x}\left\{\sqrt{\frac{2}{m}[E - V(x)]}W\right\} + \beta kT\frac{\partial}{\partial E}\left\{2\frac{[E - V(x)]}{kT}W - W + 2\frac{\partial}{\partial E}[E - V(x)]W\right\}. \tag{68}$$

Thus it is clear how the lightly damped Langevin equations (44) and (46) give rise to a two-dimensional Fokker–Planck equation with x and E as variables. We must now reduce Eq. (68) to a one-dimensional equation in the energy.

D. Reducing the Fokker–Planck Equation to a One-Dimensional Equation in the Energy

In the very low damping case, E will be a *slow* variable and x will be a *fast* variable so that W will nearly equilibrate in x over long timescales. This allows us to integrate out the x dependence in Eq. (68) over the domain of the well R_E, where $V(x) \leq E$ and so reduce it to a one-dimensional equation in the energy. First, however, we will use the classical conditional probability for an underdamped oscillator and the two-dimensional joint probability density function to express $W(x, E, t)$ in a more convenient form. If β is small (low damping), E is sensibly preserved during a large number of oscillations in the well so that the time the particle spends in the interval between x and $x + \Delta x$ is inversely proportional to the velocity $\dot{x} = \sqrt{2[E - V(x)]/m}$. Hence, for a given energy, we have the conditional probability density function

$$W(x|E) = B\{2[E - V(x)]/m\}^{-1/2}, \tag{69}$$

where B is a constant. To determine B we have, since $W(x \mid E)$ is a probability density function,

$$\int_{R_E} W(x|E)dx = 1, \tag{70}$$

so that

$$B = \frac{1}{\int_{R_E}\{2[E - V(x)]/m\}^{-1/2}dx}. \tag{71}$$

To simplify, we introduce the action S_E, Eq. (17), on a trajectory of energy E in the well via the closed line integral

$$S_E = \oint_{R_E} \sqrt{2m[E - V(x)]}dx = 2\int_{R_E} \sqrt{2m[E - V(x)]}dx. \tag{72}$$

and its derivative with respect to E

$$\frac{\partial S_E}{\partial E} = 2\int_{R_E} \frac{dx}{\sqrt{2[E - V(x)]/m}}. \tag{73}$$

Thus from the definition of the action at energy E we have the constant

$$B = 2\frac{\partial E}{\partial S_E} = \frac{\omega_E}{\pi}. \tag{74}$$

By definition, the joint probability density function can then be written in the form

$$W(x, E, t) = W(E, t)W(x|E) = \frac{\omega_E W(E, t)}{\pi\sqrt{2[E - V(x)]/m}}. \tag{75}$$

Before we integrate over x, we consider the first term on the right-hand side of Eq. (68), namely,

$$\frac{\partial}{\partial x}\left[\sqrt{\frac{2}{m}[E - V(x)]}W(x, E, t)\right] = \frac{\partial}{\partial x}\left[W(E, t)\frac{\omega_E}{\pi}\right] = 0. \tag{76}$$

Thus we have the simplified form

$$\begin{aligned}\frac{d}{dt}\int_{R_E} W(x, E, t)dx = &-\frac{\partial}{\partial E}\left[\beta kT\int_{R_E} W(x, E, t)dx\right] \\ &+ 2\beta\frac{\partial}{\partial E}\left[1 + kT\frac{\partial}{\partial E}\right]\int_{R_E} [E - V(x)]W(x, E, t)dx.\end{aligned} \tag{77}$$

Next, we can integrate out the x dependence on the left-hand side and the first term on the right-hand side using Eq. (75)

$$\int_{R_E} W(x, E, t)dx = W(E, t)\int_{R_E} W(x|E)dx = W(E, t). \tag{78}$$

We can also integrate out the x dependence in the second term on the right-hand side using the action Eq. (72), we have

$$\begin{aligned}\int_{R_E} 2[E - V(x)]W(x, E, t)dx \\ &= W(E, t)\frac{\omega_E}{2\pi}\int_{R_E}\sqrt{2m[E - V(x)]}dx \\ &= \frac{\omega_E S_E}{2\pi}W(E, t). \end{aligned} \tag{79}$$

Hence, we have the one-dimensional Fokker–Planck equation for the probability density function $W(E, t)$ in energy space corresponding to the quasistationary (lightly damped) Langevin equation, Eq. (46)

$$\dot{W} = \beta\frac{\partial}{\partial E}\left(-kTW + \left[1 + kT\frac{\partial}{\partial E}\right]\left(W\frac{\omega_E S_E}{2\pi}\right)\right). \tag{80}$$

The last term on the right-hand side of Eq. (80) can be expanded and simplifies using Eq. (74) as follows:

$$\begin{aligned}\frac{\partial}{\partial E}\left(W\frac{\omega_E S_E}{2\pi}\right) &= W\frac{\omega_E}{2\pi}\frac{\partial S_E}{\partial E} + S_E\frac{\partial}{\partial E}\left(W\frac{\omega_E}{2\pi}\right) \\ &= W + \frac{S_E}{2\pi}\frac{\partial}{\partial E}(\omega_E W). \end{aligned} \tag{81}$$

Therefore, we have

$$\dot{W} = \beta\frac{\partial}{\partial E}\left(S_E\left[1 + kT\frac{\partial}{\partial E}\right]\left(W\frac{\omega_E}{2\pi}\right)\right). \tag{82}$$

This is the energy-controlled diffusion equation as originally derived by Kramers. Now since we are interested in energies in the neighborhood of the barrier energy E_C, one can anticipate how the Kramers parameter Δ, given by Eq. (10), enters into this equation, which will become more obvious when we find its quasistationary solution. An exactly similar equation was derived by Praestgaard and van Kampen [10]. On remembering that, averaging over a period,

$$\overline{\frac{p^2}{m}} = 2(E - \overline{V_E}) = \frac{\omega_E S_E}{2\pi}$$

and then substituting this into the Fokker–Planck Eq. (80), their equation reads

$$\dot{W} = \beta \frac{\partial}{\partial E}\left(\frac{\overline{\overline{p^2}}}{m} - kT\right) W + \beta kT \frac{\partial^2}{\partial E^2}\left(\frac{\overline{\overline{p^2}}}{m}\right) W. \tag{83}$$

Here the double-overbar denotes averaging involving the undamped motion, as in Eq. (36) over the fast (phase) variable, the phase is defined via the constant of integration in the differential equation $\dot{x} = \pm\sqrt{2[E - V(x)]/m}$, that is,

$$\int_{x(0)}^{x} (2[E - V(x')]/m)^{-1/2} dx' = t + w.$$

Moreover,

$$D^{(2)}(E) = \beta kT\overline{\overline{p^2}}/m = 2\beta kT(E - \overline{\overline{V}}) \tag{84}$$

may be interpreted as a diffusion coefficient in energy space.

E. Very Low Damping Escape Rate

Equation (82) represents a continuity equation in energy space, namely,

$$\frac{\partial W}{\partial t} = -\frac{\partial J}{\partial E}, \tag{85}$$

where $J(E)$ is the probability current. If we consider the quasistationary solution, where $\dot{W} = 0$ and $J(E) = J$ representing a steady injected current of particles to replenish those continually being lost at the barrier, we get

$$J = -\beta S_E \left[1 + kT\frac{\partial}{\partial E}\right]\left(W\frac{\omega_E}{2\pi}\right), \tag{86}$$

which we can arrange as a first-order linear differential equation for the quasistationary distribution $W(E)$, namely,

$$\frac{\partial}{\partial E}\left(W\frac{\omega_E}{2\pi}\right) + \frac{1}{2\pi kT}\omega_E W = -\frac{J}{\beta kT S_E}. \tag{87}$$

Following Kramers [1], we seek a particular solution of Eq. (87) under the assumption that $W(E_C) = 0$ at the barrier energy E_C, that is, all particles that reach the barrier go over. The particular solution due to the constant injected current is

$$W(E) = \frac{2\pi J e^{-E/kT}}{kT\beta\omega_E} \int_E^{E_C} \frac{e^{E'/kT}}{S_{E'}} dE'. \tag{88}$$

As detailed by Hänggi *et al.* [4], Eq. (88) for the density $W(E)$ has a logarithmic singularity at $S = 0$. However, for very high barrier heights, this singularity does not contribute to the population N in the well. Hence, to find the population, one may integrate the quasistationary distribution over the domain of the well energy so that

$$N = \int_{E_A}^{E_C} W(E)dE = \frac{2\pi J}{kT\beta} \int_{E_A}^{E_C} \frac{e^{-E/kT}}{\omega_E} \int_E^{E_C} \frac{e^{E'/kT}}{S_{E'}} dE' dE. \tag{89}$$

Thus, the characteristic escape (mean first-passage) time $\tau = 1/\Gamma$ from the well is via the flux-over-population method

$$\tau \sim \frac{N}{J} = \frac{2\pi}{kT\beta} \int_{E_A}^{E_C} \frac{e^{-E/kT}}{\omega_E} \int_E^{E_C} \frac{e^{E'/kT}}{S_{E'}} dE' dE. \tag{90}$$

On integrating by parts, we obtain the more convenient form

$$\tau \sim \frac{2\pi}{kT\beta} \int_{E_A}^{E_C} \frac{e^{E/kT}}{S_E} \int_{E_A}^{E} \frac{e^{-E'/kT}}{\omega_{E'}} dE' dE. \tag{91}$$

This is the time to reach the top of the barrier, provided that all particles there are absorbed, which is the boundary condition that W vanishes at $E = E_C$. Equation (91) can also be derived using the MFPT approach by solving the equation [4, 18, 23]

$$L_{\rm FP}^{\dagger} \tau(E) = -1, \tag{92}$$

for $\tau(E)$ with appropriate boundary conditions; here $L_{\rm FP}^{\dagger}$ is [18, 23] the adjoint Fokker–Planck operator associated with Eq. (82). The MFPT is the average time needed to reach the separatrix for the *first* time from a starting point E_0 inside the initial domain of attraction [4]. In the VLD limit, this MFPT $\tau(E_0)$ becomes essentially independent of E_0, that is, $\tau(E_0) \simeq \tau_{\rm MFPT} = \tau$ for all starting configurations away from the neighborhood of the separatrix [4].

Following Kramers, we effectively assume that the potential near the bottom of the well is represented by that of a harmonic oscillator, where $\omega_{E_A} = \omega_A$ which

is independent of E (ω_A is defined by the small oscillation frequency Eq. 2). Thus we may estimate the value of the inner integral in Eq. (91) as

$$\int_{E_A}^{E} \frac{e^{-E'/kT}}{\omega_{E'}} dE' \simeq \frac{1}{\omega_A} \int_{E_A}^{\infty} e^{-E'/kT} dE' = \frac{kT}{\omega_A} e^{-\frac{E_A}{kT}}. \tag{93}$$

In like manner the main contribution to the outer integral in Eq. (91) comes from the positive exponential factor near C which dominates the integrand there so that

$$\int_{E_A}^{E_C} \frac{e^{E/kT}}{S_E} dE \simeq \frac{1}{S_{E_C}} \int_{-\infty}^{E_C} e^{E/kT} dE = \frac{kT}{S_{E_C}} e^{\frac{E_C}{kT}}. \tag{94}$$

Substituting Eqs. (94) and (93) into Eq. (91), we obtain the VLD escape rate over the barrier

$$\Gamma_{\mathrm{VLD}} = \frac{\beta S_{E_C}}{kT} \frac{\omega_A}{2\pi} e^{-\Delta V/(kT)} = \Delta \Gamma_{\mathrm{TST}}, \tag{95}$$

(where $\Delta V = E_C - E_A$) transparently demonstrating how Δ, the ratio of the energy loss per cycle βS_{E_C} of the librating motion at the saddle energy to the thermal energy, plays a crucial role in the escape rate. Notice that S_{E_C} is always calculated via the undamped deterministic dynamics at the critical energy.

However, Eq. (95) pertains to escape from an isolated well in the VLD limit provided the particle never returns. Now, as we alluded to in our short summary of the depopulation factor in Section II, one of the most interesting situations involves escape from a double well (Fig. 6). The formula for the escape rate in this case may be written down simply by using the results of Section 4.D of Hänggi *et al.* [4]. On applying the VLD limit of Eq. (28), we have for the overall escape rate for a double-well potential [22, 23]

$$\Gamma_{\mathrm{VLD}} \sim \frac{\Delta_1 \Delta_2}{\Delta_1 + \Delta_2} \left[\frac{\omega_A(1)}{2\pi} e^{-\Delta V_1/(kT)} + \frac{\omega_A(2)}{2\pi} e^{-\Delta V_2/(kT)} \right]. \tag{96}$$

The above results which are for *point* particles will also apply to *rigid inertial rotators* as their Hamiltonians are also separable and additive. However, adjustments are often needed due to the periodic nature of the potential. The interested reader can find many examples in Chapter 10 of Reference 2.

F. Comparison of VLD Escape Rate with Longest Relaxation Time Solutions

Equation (95) is obviously an asymptotic solution valid only in the high barrier limit while Eq. (91) is the exact solution for the longest relaxation time which

is valid for all barrier heights. Therefore, if we desire a solution for the greatest relaxation time for moderate barrier heights, we [34] use the MFPT which has the same asymptotic behavior as the inverse escape rate.

The longest relaxation time τ in the VLD limit can be calculated directly from Eq. (91). However, for practical calculation purposes, it is easier to use the energy-controlled diffusion equation in the form of Eq. (83) given by Praestgaard and van Kampen [10]. Proceeding in this manner τ is now given by

$$\tau = \frac{1}{2kT\beta} \int_{E_A}^{E_C} \frac{1}{\left[E - \overline{\overline{V}}(E)\right] W_0(E)} \int_{E_A}^{E} W_0(E')dE'dE, \tag{97}$$

where $W_0(E)$ is the equilibrium solution of Eq. (83), that is, $\dot{W}_0 = 0$ and zero injected current. Equation (97) is derived noting that the quasistationary solution of Eq. (83) in the vicinity of the barrier is given by

$$W(E) = \frac{JW_0(E)}{2\beta kT} \int_{E}^{E_C} \frac{dE'}{[E' - \overline{\overline{V}}(E')]W_0(E')}.$$

For a variety of potentials τ can be evaluated analytically in terms of the elliptic functions.

Estimations of this type based on the energy-controlled diffusion method are in perfect agreement with the results of independent calculations of τ via numerical solution of the Fokker–Planck Eq. (4) in phase space. Several examples have been given in Refs. [2, 3]. These include

i. translational Brownian motion of a particle in a double-well potential, Eq. (13);
ii. rotational Brownian motion of a fixed axis rotator in a double-well potential;
iii. rotational Brownian motion of a fixed axis rotator in an asymmetrical double-well potential.

As an example, let us consider in more detail the case (i). Since $\Delta_1 = \Delta_2$ and $\Gamma_1 = \Gamma_2$ for this double-well potential with two equivalent wells 1 and 2, the VLD escape rate can be estimated in the high barrier limit ($\Delta V \gg kT$) from the asymptotic Eq. (96) as

$$\Gamma_{\mathrm{VLD}} = \frac{\beta S}{kT} \frac{\omega_A}{2\pi} e^{-\Delta V/(kT)} \sim \frac{8\sqrt{2}\beta Q}{3\pi} e^{-Q}, \tag{98}$$

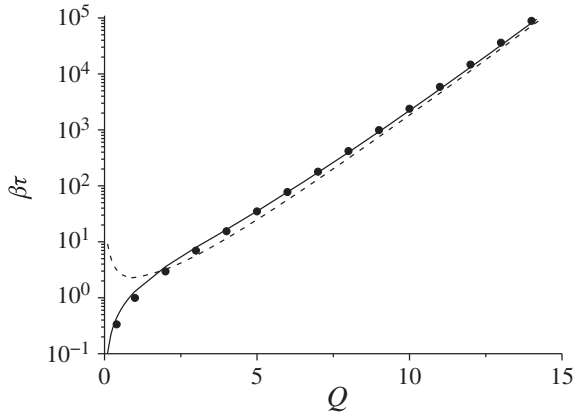

Figure 7. $\beta\tau$, $\beta/\Gamma_{\rm VLD}$ and β/λ_1 versus Q. Filled circles: numerical solution for the inverse of the smallest nonvanishing eigenvalue β/λ_1 of the Fokker–Planck operator, Eq. (4) [2]. Dashed line: the VLD Eq. (98). Solid line: τ from Eq. (99).

where $Q = \Delta V/(kT)$, $\omega_A \sim 2\eta^{-1}\sqrt{Q}$, and $\beta S/(kT) \sim 8\beta'\sqrt{2Q}/3$ [2]. Now the VLD longest relaxation time τ for this double-well potential is calculated in Appendix A and is given by

$$\tau_{\rm MFPT} = \frac{3Q}{4\beta}\int_{-1}^{0} \frac{e^{Qz}\sqrt{1+\sqrt{1+z}}\int_{-1}^{z}\frac{e^{-Qz'}}{\sqrt{1+\sqrt{1+z'}}}K\left(\frac{2\sqrt{1+z'}}{1+\sqrt{1+z'}}\right)dz'}{zK\left(\frac{2\sqrt{1+z}}{1+\sqrt{1+z}}\right)+\left(1+\sqrt{1+z}\right)E\left(\frac{2\sqrt{1+z}}{1+\sqrt{1+z}}\right)}dz, \quad (99)$$

where $K(m)$ and $E(m)$ are complete elliptic integrals of the first and second kind, respectively [35]. Equation (99) is valid for all Q. The longest relaxation time $\sim \Gamma_{\rm VLD}^{-1}$ predicted by the asymptotic Eq. (98), τ from Eq. (99) and the inverse of the smallest nonvanishing eigenvalue λ_1 of the Fokker–Planck operator, Eq. (4),calculated numerically by the matrix continued fraction method [2] are shown in Fig. 7 as functions of the barrier height Q. Apparently, λ_1^{-1} and τ are very close to each other for all Q while in the high barrier limit, the asymptotic Eq. (98) provides a good approximation to both λ_1^{-1} and τ. The merit of Eq. (99) is that it yields the VLD longest relaxation time valid for *all barrier heights* including *low* barriers ($0 \le Q \le 2$), where asymptotic escape rate equations obtained in the high barrier limit are not applicable.

Regarding now the inertial rotational Brownian motion which for fixed axis rotators take place on a circle the calculations are exactly the same as for a particle moving in one dimension as the Hamiltonian is still separable and additive as indeed is also true for rotation in space. Details of all these calculations are given in

Chapter 10 of Ref. [2] and in Section II of Ref. [3]. Moreover, the three dimensional inertial rotational Brownian motion of rod-like molecules in an axially symmetric potential with nonequivalent wells has been exhaustively treated in Chapter 11 of Ref. [2] exhibiting, along with the ubiquitous Kramers overbarrier relaxation, the high frequency resonance process in the wells. In addition, of course, a fast relaxation process also arises due to rapid decays in the wells themselves. However, we shall not reproduce the details of any of these investigations here as the main objective of this review is merely to clarify the calculation of the VLD rate and its relation to the high frequency resonant process.

IV. ENERGY-CONTROLLED DIFFUSION OF CLASSICAL SPINS

Experimental success [21, 36–38] in isolating *individual* single domain ferromagnetic particles (containing circa 10^5 spins which behave as a single giant spin hence the generic title superparamagnetism), in making measurements of the reversal time of the magnetization **M** of an individual particle, and in verifying [36] the behavior of the reversal time as a function of the damping parameter predicted by the Néel–Brown [39, 40] theory have stimulated renewed interest in the Kramers escape rate theory for classical spins. The Néel–Brown [39, 40] theory is in effect an adaptation of the Kramers theory to macrospin relaxation governed by a gyromagnetic-like equation so that the verification [36] of that theory in effect confirms the Kramers conception of a thermal relaxation process over a potential barrier. Yet another adaptation of the Kramers VLD theory is its use in the relatively new subject of spintronics which has been reviewed by Dunn *et al.* [19]. It is the purpose of this section to outline how the VLD rate may be calculated in substantially the same manner as for particles using the energy-controlled diffusion equation for spins given by Dunn *et al.* [19].

Néel's original estimate [39] of the relaxation time over an internal anisotropy barrier in a single domain ferromagnetic particle with axially symmetric (functions of the latitude only) potentials (per unit volume) of the magnetocrystalline anisotropy

$$V = -K\cos^2\vartheta, \tag{100}$$

(K is an anisotropy constant) like that shown schematically in Fig. 8 was based on TST. Thus the relaxation time over a barrier is given by

$$\tau = \tau_0 e^{vK/(kT)}, \tag{101}$$

where v is the volume of the particle and τ_0^{-1} is the attempt frequency which is of the order of the gyromagnetic precession frequency. Thus τ_0 lies between 10^{-10} to 10^{-11} seconds. However, since the volume of the particle is involved

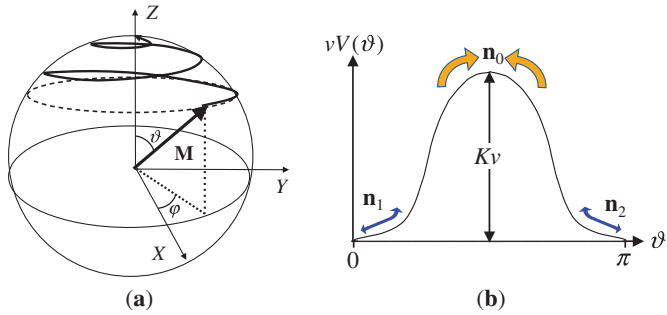

Figure 8. (**a**) Magnetization **M** with spherical polar coordinates ϑ and φ. In the absence of thermal agitation (if there is no damping), **M** will precess along orbits of constant energy called Stoner–Wohlfarth orbits [41] (dashed line). According to Eq. (105), if damping is involved, the precession will slowly collapse by spiraling toward an energy minimum (solid line). (**b**) Néel's conception of the superparamagnetic relaxation time as illustrated in profile for a single-domain particle with uniaxial anisotropy giving rise to axial symmetry, for which the anisotropy potential is $V = -K\cos^2\vartheta$ (see also Fig. 11a), the magnetization **M** has two stable orientations, $\mathbf{n}_1$ and $\mathbf{n}_2$, at the north ($\vartheta = 0$) and south ($\vartheta = \pi$) poles of the sphere, respectively, and an unstable one at the equator. The reversal time over the barrier at the equator is $\tau = \tau_0 e^{vK/(kT)}$.

in the exponential, the relaxation time can vary from as little as 10^{-9} seconds to geological epochs. However, Brown [40] criticized Néel's original TST-based treatment of the overbarrier time because gyromagnetic effects were not explicitly included. Moreover, the dissipation dependence of the prefactor is not taken into account just as we described in the Kramers theory for point particles. The key to a more precise treatment of the problem is the construction of a Langevin equation for the evolution of the magnetization **M** which will then allow us to generalize the Kramers theory to the spin relaxation (over a potential barrier) of single-domain particles.

A. Magnetization Evolution Equations: Brown's Langevin and Fokker–Planck Equations

Our starting point for the explicit inclusion of gyromagnetic effects is the equation given by Landau and Lifshitz in 1935 [20] who postulated that, in the absence of damping, the magnetization **M** of a single domain ferromagnetic particle or macrospin precesses about an effective magnetic field **H** according to the gyromagnetic equation

$$\dot{\mathbf{M}} = \gamma[\mathbf{H} \times \mathbf{M}]. \tag{102}$$

This is just the Larmor equation for a single spin generalized to the coherent rotation of a macrospin [20] where γ is the gyromagnetic ratio. The effective

magnetic field **H** is proportional to the negative gradient of the free energy density $V(\vartheta, \varphi)$, namely,

$$\mathbf{H} = -\frac{\partial V}{\partial \mathbf{M}}. \tag{103}$$

Assuming that the single domain ferromagnetic particle is at its saturation magnetization M_S so that only the direction of **M** can change, we can write Eq. (102) in terms of a unit vector $\mathbf{u} = \mathbf{M}/M_S$ and in terms of the gradient of the scalar magnetic potential so that the kinematic equation is simply that defining angular velocity $\mathbf{\Omega}(t)$, namely,

$$\dot{\mathbf{u}}(t) = \mathbf{\Omega}(t) \times \mathbf{u}(t), \tag{104}$$

where

$$\mathbf{\Omega} = -\frac{\gamma}{M_S}\frac{\partial V}{\partial \mathbf{u}}.$$

Invariably the potential energy density V comprises an anisotropy potential plus the Zeeman energy due to an external applied magnetic field. Taking as example a bistable potential, a giant spin will orbit at constant energy in one of the wells. If the applied field is strong enough, however, the orbital precession will be *reversed*, that is, cross over into the other potential well, as shown schematically by the dashed line in Fig. 9. Switching of the direction of precession in this way represents the process of erasure of magnetic recordings by Oersted fields.

Now the evolution of the magnetization as described by the gyromagnetic Eq. (104) is a *conservative* process so there is no energy lost in the motion of the magnetization to the surrounding environment. Therefore, **M** must follow

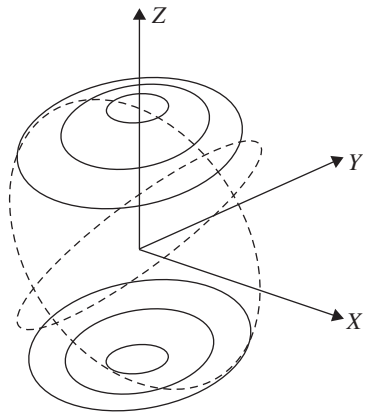

Figure 9. Stoner–Wohlfarth orbits encircling an energy minimum along the polar positive and negative *Z*-axis (solid lines) or crossing a potential barrier lying in the *XY* plane (dashed lines).

paths of *constant* energy, that is, the Stoner–Wohlfarth orbits [19, 41, 42] (Fig. 9) and so will continue to precess *ad infinitum* in a well of the potential provided that the energy of the applied field is less than the barrier height. However, in practice, the nanomagnet loses energy to the microscopic degrees of freedom of its surroundings. In order to model this effect of the energy dissipation, Landau and Lifshitz in 1935 and Gilbert in 1955 [2, 20] introduced a damping torque which opposes the precession so that the gyromagnetic equation becomes

$$\dot{\mathbf{u}} = \frac{\gamma}{M_S}\left[\mathbf{u} \times \frac{\partial V}{\partial \mathbf{u}}\right] + \alpha[\mathbf{u} \times \dot{\mathbf{u}}]. \tag{105}$$

The above equation which tends to make **M** spiral toward the *Z*-axis in Fig. 8a is known as the Landau–Lifshitz–Gilbert (LLG) equation. In Gilbert's model, which reduces to that of Landau–Lifshitz in the VLD limit, the energy of the system is no longer conserved and will continuously be dissipated by the drag torque so that the Stoner–Wohlfarth orbits centered on the energy minima will start to collapse until they become a singularity (see Figs. 8 and 9). Thus Gilbert's equation describes a transient precession that will ultimately cease.

The LLG equation takes no account of thermal fluctuations which arise as the nanomagnet is at a finite temperature *T*. If these are included the precessional motion would be maintained by energy provided by the heat bath. In order to do this Brown [40] in 1963 added a random isotropic noise field **F** to the dissipative field that would be a source of energy to the system

$$\dot{\mathbf{u}} = \frac{\gamma}{M_S}\left[\mathbf{u} \times \left(\frac{\partial V}{\partial \mathbf{u}} - M_S\mathbf{F}\right)\right] + \alpha[\mathbf{u} \times \dot{\mathbf{u}}]. \tag{106}$$

This random magnetic field is treated as spatially isotropic Gaussian white noise and has the properties [2] of Section III.B

$$\overline{F_i(t_1)} = 0,\ \overline{F_i(t_1)F_j(t_2)} = 2D\delta_{i,j}\delta(t_1 - t_2), \tag{107}$$

where the constant

$$D = \frac{\alpha kT}{v\gamma M_S}, \tag{108}$$

is determined by imposing the Boltzmann equilibrium distribution of orientations (details in [2, 40]) and $i,j = 1,2,3$ represent the Cartesian axes of the laboratory coordinate system (see Fig. 8). In other words, the expected value of **F** is zero and **F** is uncorrelated in both space and time while Isserlis' theorem (Eqs. 41 and 43) is still obeyed. Equation (106) is known as the *magnetic Langevin equation*.

Since the random torque counteracts the damping torque it can, if the temperature is high enough, reverse the direction of precession. The time for the reversal of the direction of precession (magnetization) over the anisotropy-Zeeman energy barrier is known as the magnetization (superparamagnetic) relaxation time. Brown's magnetic Langevin equation describes how magnetic recordings may degrade in a heat bath because thermal fluctuations cause unwanted magnetic reversal so that data stored in magnetic recordings is ultimately lost.

Brown then derived from Eq. (106), the appropriate Fokker–Planck equation for the distribution function $W(\vartheta, \varphi, t)$ of the orientations of the magnetization vector **M** on the surface of the unit sphere (see Refs. [40] and [43] for details)

$$\frac{\partial}{\partial t}W = \mathrm{L}_{FP}W = \frac{1}{2\tau_{\mathrm{N}}\sin\vartheta}\frac{\partial}{\partial\vartheta}\left\{\sin\vartheta\left[\frac{\partial W}{\partial\vartheta} + \frac{v}{kT}W\left(\frac{\partial V}{\partial\vartheta} + \frac{\alpha^{-1}}{\sin\vartheta}\frac{\partial V}{\partial\varphi}\right)\right]\right\} + \frac{1}{2\tau_{\mathrm{N}}\sin^2\vartheta}\frac{\partial}{\partial\varphi}\left[\frac{\partial W}{\partial\varphi} + \frac{v}{kT}W\left(\frac{\partial V}{\partial\varphi} - \alpha^{-1}\sin\vartheta\frac{\partial V}{\partial\vartheta}\right)\right], \tag{109}$$

where

$$\tau_{\mathrm{N}} = \frac{vM_S(\alpha^{-1} + \alpha)}{2\gamma kT}, \tag{110}$$

is the free diffusion time of the magnetization (τ_{N} is of the order of 10^{-11}–10^{-8} s), L_{FP} is the Fokker–Planck operator, the operators Δ and $\partial/\partial\mathbf{u}$ are, respectively, the Laplacian and the gradient on the surface of the unit sphere defined in the spherical coordinates shown in Fig. 10 as

$$\Delta = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}. \tag{111}$$

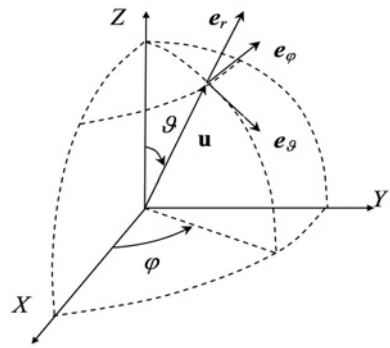

Figure 10. Spherical polar coordinate system.

$$\frac{\partial}{\partial \mathbf{u}} = \frac{\partial}{\partial \vartheta}\mathbf{e}_\vartheta + \frac{1}{\sin\vartheta}\frac{\partial}{\partial \varphi}\mathbf{e}_\varphi. \tag{112}$$

A detailed discussion of the assumptions made in the derivation of the Fokker–Planck and Gilbert equations is given elsewhere (e.g., [2, 25, 40, 43]). We remark in passing that in developing his theory of the magnetization relaxation for superparamagnets (classical spins) Brown obviously used by analogy ideas originating in the Debye theory of dielectric relaxation of polar dielectrics [2, 6, 7, 44]. In Eq. (109), the term in α^{-1} corresponds to the *precessional* (gyromagnetic) term in Eq. (106), giving rise to ferromagnetic resonance (usually in the GHz range). When $\alpha \to \infty$ (i.e., ignoring the gyromagnetic term) Brown's Fokker–Planck equation (109) has the same mathematical form as the *noninertial* rotational diffusion equation for a rigid body in an external potential known as the Smoluchowski equation in configuration space (ϑ, φ) (see, e.g., Ref. [2], Chapter 1 for details).

Referring to magnetic relaxation, in his earliest calculations of the reversal time of the magnetization τ, *which may be defined as the inverse of the smallest nonvanishing eigenvalue* λ_1 *of the Fokker–Planck operator* $\mathrm{L_{FP}}$ in Eq. (109), Brown confined himself to *axially symmetric potentials* of the magnetocrystalline anisotropy and Zeeman energy [40]. Hence *no dynamical coupling between the longitudinal and the transverse modes of motion exists* so that the longitudinal modes are governed by a *single* state variable, namely, the colatitude ϑ, that is, the polar angle of $\mathbf{M}$. The second state variable, namely the azimuthal angle φ of $\mathbf{M}$, gives rise only to a steady precession of that vector. Noting the decoupling between the transverse and longitudinal modes existing for axial symmetry, which results in an exact single-variable Fokker–Planck equation in the colatitude ϑ, Brown [40] demonstrated that the Kramers escape rate theory for point particles may be easily adapted to yield an expression for the escape rate for spins in axially symmetric potentials which is valid for all values of the damping parameter α. We remark, however, that the *exact* Fokker–Planck equation in the single variable ϑ arises not from strong damping of the momentum (which in the Brownian motion of point particles or rigid bodies, governed by the Klein–Kramers equation in the Euler angles and corresponding angular momenta, gives rise to the *approximate* noninertial Smoluchowski equation [2]) rather it follows from the *axial symmetry* of the potential.

As a consequence of this very particular result valid for axially symmetric problems alone the complete analogy with the Kramers theory for separable and additive Hamiltonians only becomes fully apparent when an attempt [20] is made to treat *non-axially-symmetric potentials* of the magnetocrystalline anisotropy which are functions of both the colatitude ϑ and longitude φ (examples in Fig. 11b–d). Here all the particular cases of the escape rate as a function of the friction considered by Kramers for point particles will appear as well as the turnover region (see Sections II.A and II.B). In the non-axially symmetric context, Brown

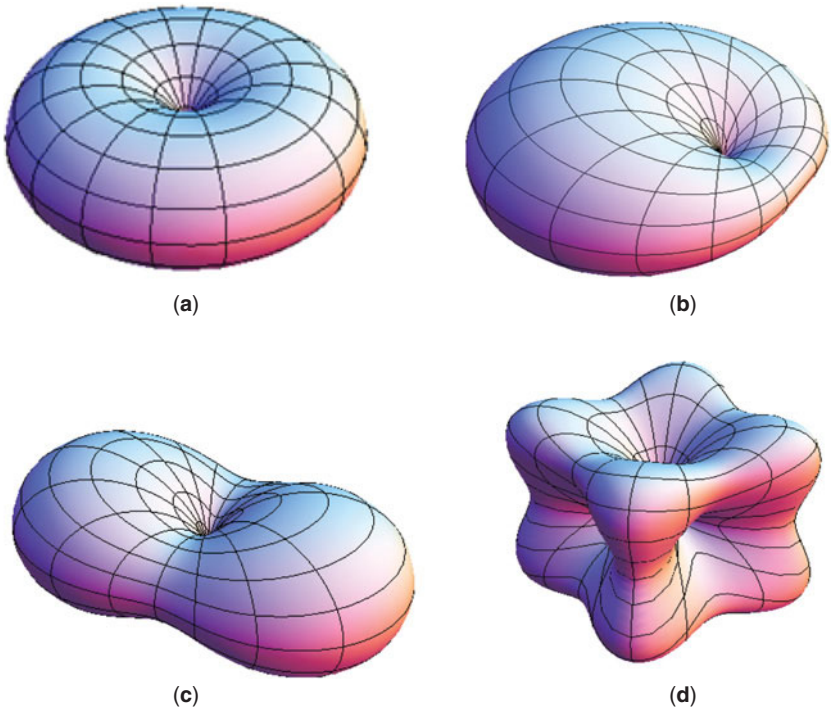

Figure 11. (**a**) Uniaxial anisotropy potential without external field: $vV/(kT) = \sigma \sin^2 \vartheta$; (**b**) uniaxial potential with external field: $vV/(kT) = \sigma \sin^2 \vartheta - \xi(\cos\psi \cos\vartheta + \sin\psi \sin\vartheta \cos\varphi)$; (**c**) biaxial anisotropy potential: $vV/(kT) = \sigma(-\cos^2 \vartheta + \delta \sin^2 \vartheta \cos^2 \varphi)$; and (**d**) cubic anisotropy potential $vV/(kT) = \sigma(\sin^4 \vartheta \sin^2 2\varphi + \sin^2 2\vartheta)$. Here, σ and δ are, respectively, the barrier height and biaxiality parameters, ξ is the external field parameter, and ψ is the angle between the easy axis and the external field. For a color version of this figure, see the color plate section.

[20, 43] succeeded in giving a formula for the greatest relaxation time for single-domain particles (spins) in the IHD limit which is the exact analog of the Kramers IHD formula for point particles or rigid rotators. For example, taking the potential Fig. 11b the greatest relaxation time is the reciprocal of the sum of the escape rates from each well of the potential. However, the calculation is very much more involved [20] than that for point particles by virtue of the facts that it must be carried out in spherical polar co-ordinates, that the undamped motion is *rotational* (precessional) [27, 29] so that large oscillations comprising libration in the direction of precession at the barrier energy before escape (representing in this case reversal of the direction of precession) from a well are involved, and that the inertia of the particle plays no role. The role of the latter being mimicked [3] by the gyromagnetic term in the equation of motion of the magnetization (see Eq. 106).

Moreover, the Hamiltonian comprising the anisotropy and Zeeman energy is not separable. Furthermore, the phase space orbits at constant energy inside the well in the original one degree of freedom Kramers problem are approximate ellipses while the corresponding quantities in the magnetization problem which pertain to the two degrees of freedom (ϑ, φ), namely the Stoner–Wohlfarth [19, 41] orbits, are very much more complicated as they exist in the domain of a sphere of constant radius.

Brown's calculation for non-axially symmetric potentials only applies in the IHD limit like its counterpart for point particles. Now we saw that for point particles, Kramers [1] showed (by essentially treating the low-damping case as a perturbation of the zero-damping case and constructing a diffusion equation for the energy) how a simple formula (Eq. 95) for the inverse overbarrier relaxation time (escape rate) could be obtained in the VLD limit, where $\Delta \ll 1$. Thus a VLD escape rate is also required for spins. This defect was remedied by Klik and Gunther [25,26] who used the theory of first passage times to obtain the magnetic analogue of the Kramers low-damping formula so bypassing the Kramers energy-controlled diffusion method entirely. Their calculation (since it involves an extension to spins of the uniform asymptotic method for the calculation of first passage times which Matkowsky *et al.* [24] formulated for the original Kramers problem) involves complicated mathematical manipulations [22, 23]. However, Dunn *et al.* [19] have very recently given, essentially using the Stratonovich method already described in the previous sections, an energy-controlled diffusion equation for spins. They did not, however, derive the Kramers escape rate using their equation. Here, we demonstrate how the VLD Kramers rate for spins follows naturally from this equation exactly as we have just discussed for point particles. Thus, the mathematical complications associated with the first passage time method of Matkowsky *et al.* [24] as adapted to spins are avoided. Moreover, it becomes readily apparent how the Mel'nikov approach to the turnover problem as adapted to bistable potentials by Mel'nikov and Meshkov [33] may be extended to spins [20, 45]. It should be noted from Fig. 11 that the single-domain particle of volume v will in general involve several states of stability, e.g., for uniaxial anisotropy with a uniform magnetic field the potential is bistable and so on. The detailed calculations of the escape rate for all values of the damping have been given in Refs. [2] and [3] for the various potentials. However, since the purpose of this chapter is simply to explain in reasonable detail how the VLD rate is calculated in novel fashion from the energy-controlled diffusion equation given by Dunn *et al.* [19], we will mainly confine ourselves to escape from a single well. For a symmetric double-well potential, the overall escape rate can be determined by calculating that for a single well (see Eq. 96). Many examples are given in Refs. [2] and [3]. We emphasize throughout that unlike point particles the Hamiltonian is nonseparable and nonadditive, typical examples being shown in Fig. 11. Just as with particles we will first consider the nonstochastic case.

B. Undamped Motion of Classical Spins

Inspired by our previous treatment of the lightly damped motion for point particles we shall parameterize the instantaneous magnetization direction by the slow energy variable $E = vV$ (v is the volume of the particle and V represents the energy density) and the fast precessional variable ϕ with period 2π running uniformly along a closed Stoner–Wohlfarth orbit of energy E. We assume that E varies very slow compared to ϕ. We denote the energy-dependent precession period as

$$T_E = \frac{2\pi}{\Omega_E}, \tag{113}$$

where Ω_E is the precession frequency at a given energy in radians per second. The time dt to reach a given point along a Stoner–Wohlfarth orbit is then given by

$$d\phi = \frac{2\pi}{T_E} dt = \Omega_E dt. \tag{114}$$

Now we can express dt in terms of a change in magnetization $d\mathbf{M}$. To achieve this, we write the evolution equation for the magnetization in the absence of damping, considering only the gyromagnetic term

$$\dot{\mathbf{M}} = \gamma[\mathbf{H} \times \mathbf{M}]. \tag{115}$$

Now taking scalar products $(\dot{\mathbf{M}} \cdot [\mathbf{H} \times \mathbf{M}]) = \gamma |\mathbf{H} \times \mathbf{M}|^2$ and rearranging them we have the time dt along an element of orbit $d\mathbf{M}$, namely,

$$dt = \frac{([\mathbf{H} \times \mathbf{M}] \cdot d\mathbf{M})}{\gamma |\mathbf{H} \times \mathbf{M}|^2}. \tag{116}$$

Hence, we can find the precession period explicitly by taking a closed line integral along a Stoner–Wohlfarth orbit of constant energy E, namely,

$$T_E = \gamma^{-1} \oint_E \frac{([\mathbf{H} \times \mathbf{M}] \cdot d\mathbf{M})}{|\mathbf{H} \times \mathbf{M}|^2}. \tag{117}$$

Equation (117) can also be rewritten in terms of polar and azimuthal angles as

$$T_E = \frac{M_S}{\gamma} \oint_E \left[\frac{1}{\sin^2 \vartheta} \left(\frac{\partial V}{\partial \varphi} \right)^2 + \left(\frac{\partial V}{\partial \vartheta} \right)^2 \right]^{-1} \left(\sin \vartheta \frac{\partial V}{\partial \vartheta} d\varphi - \frac{1}{\sin \vartheta} \frac{\partial V}{\partial \varphi} d\vartheta \right). \tag{118}$$

As an example, we consider the uniaxial potential $vV(\vartheta) = -\sigma kT\cos^2\vartheta$. By substituting $V(\vartheta)$ into the general Eq. (118), we have

$$T_E = \frac{vM_S}{2\gamma\sigma kT}\oint_E \frac{d\varphi}{\cos\vartheta} = \frac{vM_S}{2\gamma\sigma kT\cos\vartheta_E}\int_0^{2\pi} d\varphi = \frac{\pi vM_S}{\gamma\sigma kT\cos\vartheta_E}. \quad (119)$$

This result can be verified by direct solution of the gyromagnetic equation of motion (115) which in our example of a uniaxial potential is the following set of equations

$$\dot{\vartheta}(t) = 0 \quad (120)$$

$$\dot{\varphi}(t) = \frac{2\gamma\sigma kT}{vM_S}\cos\vartheta(t). \quad (121)$$

The solution is

$$\vartheta(t) = \vartheta_E \quad (122)$$

$$\varphi(t) = \frac{2\gamma\sigma kT\cos\vartheta_E}{vM_S}t + \varphi(0). \quad (123)$$

Thus the vector $\mathbf{M}$ precesses at a constant angle ϑ_E. The period of this precessional motion is by definition

$$T_E = \frac{2\pi}{\dot{\varphi}(t)} = \frac{\pi vM_S}{\gamma\sigma kT\cos\vartheta_E}. \quad (124)$$

Clearly Eq. (124) is in full agreement with Eq. (119).

In the analysis which follows, we will need $\frac{\partial\mathbf{M}}{\partial\phi}$ and $\frac{\partial\mathbf{M}}{\partial E}$. Now $\frac{\partial\mathbf{M}}{\partial\phi}$ can be obtained using Eqs. (114) and (115) yielding

$$\frac{\partial\mathbf{M}}{\partial\phi} = \frac{\dot{\mathbf{M}}}{\dot{\phi}} = \frac{\gamma}{\Omega_E}[\mathbf{H}\times\mathbf{M}], \quad (125)$$

while $\frac{\partial\mathbf{M}}{\partial E}$ can be obtained as follows. On cross multiplying the equation $\mathbf{H} = -\frac{1}{v}\frac{\partial E}{\partial\mathbf{M}}$ by $\mathbf{M}$ and taking the scalar vector product with $[\mathbf{H}\times\mathbf{M}]$ we have

$$|[\mathbf{H}\times\mathbf{M}]|^2 = -\frac{1}{v}\left(\left[\frac{\partial E}{\partial\mathbf{M}}\times\mathbf{M}\right]\cdot[\mathbf{H}\times\mathbf{M}]\right). \quad (126)$$

Using the scalar triple product [46], we rearrange Eq. (126) as

$$|[\mathbf{H}\times\mathbf{M}]|^2 = -\frac{1}{v}\left(\frac{\partial E}{\partial\mathbf{M}}\cdot[\mathbf{M}\times[\mathbf{H}\times\mathbf{M}]]\right).$$

or

$$1 = -\left(\frac{\partial E}{\partial \mathbf{M}} \cdot \frac{[\mathbf{M} \times [\mathbf{H} \times \mathbf{M}]]}{\nu |[\mathbf{H} \times \mathbf{M}]|^2}\right). \tag{127}$$

Since $\left(\frac{\partial E}{\partial \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial E}\right) = 1$ we then have by inspection

$$\frac{\partial \mathbf{M}}{\partial E} = -\frac{[\mathbf{M} \times [\mathbf{H} \times \mathbf{M}]]}{\nu |[\mathbf{H} \times \mathbf{M}]|^2}. \tag{128}$$

Clearly the new coordinates (E, ϕ) are *locally* orthogonal because

$$\left(\frac{\partial \mathbf{M}}{\partial E} \cdot \frac{\partial \mathbf{M}}{\partial \phi}\right) = -\frac{\gamma}{\nu \Omega_E |[\mathbf{H} \times \mathbf{M}]|^2}([\mathbf{M} \times [\mathbf{H} \times \mathbf{M}]] \cdot [\mathbf{H} \times \mathbf{M}]) = 0. \tag{129}$$

It is also useful to give a geometrical interpretation of the periodic time T_E as [19]

$$T_E = \frac{v}{\gamma M_S} \frac{dA_E}{dE} = \frac{v}{\gamma M_S^2} \oint_{R_E} \left(\mathbf{M} \cdot \left[\frac{\partial \mathbf{M}}{\partial E} \times d\mathbf{M}\right]\right), \tag{130}$$

where A_E is the portion of the area of the sphere that is enclosed by a Stoner–Wohlfarth orbit with energy E. Substituting for $\frac{\partial \mathbf{M}}{\partial E}$ from Eq. (128) and noticing that

$$\left(\mathbf{M} \cdot \left[\frac{\partial \mathbf{M}}{\partial E} \times d\mathbf{M}\right]\right) = \left(\left[\mathbf{M} \times \frac{\partial \mathbf{M}}{\partial E}\right] \cdot d\mathbf{M}\right)$$

and

$$[\mathbf{M} \times [\mathbf{M} \times [\mathbf{H} \times \mathbf{M}]]] = M_S^2 [\mathbf{M} \times \mathbf{H}],$$

we have

$$\begin{aligned} \frac{v}{\gamma M_S^2} \oint_{R_E} \left(\mathbf{M} \cdot \left[\frac{\partial \mathbf{M}}{\partial E} \times d\mathbf{M}\right]\right) &= \oint_{R_E} \frac{([\mathbf{M} \times [\mathbf{M} \times [\mathbf{H} \times \mathbf{M}]]] \cdot d\mathbf{M})}{\gamma M_S^2 |[\mathbf{H} \times \mathbf{M}]|^2} \\ &= \frac{1}{\gamma} \oint_{R_E} \frac{([\mathbf{M} \times \mathbf{H}] \cdot d\mathbf{M})}{|[\mathbf{H} \times \mathbf{M}]|^2}. \end{aligned}$$

so proving Eq. (130). Thus we now have a useful geometrical interpretation of the periodic time T_E as the rate of change of the portion of the area of the sphere enclosed by a Stoner–Wohlfarth orbit of a constant energy. Again we consider

the uniaxial potential as an example. The portion of the area of the sphere that is enclosed by the orbit of the precessing vector $\mathbf{M}$ is then

$$A_E = 2\pi M_S^2(1 - \cos\vartheta_E). \tag{131}$$

while the orbital energy is

$$E = -\sigma kT\cos^2\vartheta_E + \text{const.} \tag{132}$$

Consequently, the periodic time is then

$$T_E = \frac{v}{\gamma M_S}\frac{dA_E}{d\vartheta_E}\frac{d\vartheta_E}{dE} = \frac{\pi v M_S}{\gamma\sigma kT\cos\vartheta_E}, \tag{133}$$

which is again in agreement with Eqs. (119) and (124).

C. Mean Energy Loss per Cycle of a Stoner–Wohlfarth Orbit

Just as accomplished for point particles in the absence of thermal agitation, we can rewrite the vector equation of motion, Eq. (105), as equations of motion for the state variables E and ϕ. Subsequently, we shall invariably neglect all terms of order α^2 thereby assuming the VLD limit, namely, $\alpha \ll 1$. We will then have

$$\dot{E} = \left(\frac{\partial E}{\partial \mathbf{M}}\cdot\dot{\mathbf{M}}\right) = -v(\mathbf{H}\cdot\dot{\mathbf{M}}). \tag{134}$$

Now, comparing Eq. (105), the only way E can alter is via the nonconservative Gilbert damping term $\alpha[\mathbf{u}\times\dot{\mathbf{u}}]$ in Eq. (105) so that by the properties of the triple scalar product [46]

$$\begin{aligned}\dot{E} &= -\frac{v\alpha}{M_S}(\mathbf{H}\cdot[\mathbf{M}\times\dot{\mathbf{M}}]) = -\frac{v\alpha}{M_S}(\dot{\mathbf{M}}\cdot[\mathbf{H}\times\mathbf{M}])\\ &= -\frac{v\alpha}{\gamma M_S}(\dot{\mathbf{M}}\cdot\dot{\mathbf{M}}) = -\frac{v\alpha}{\gamma M_S}|\dot{\mathbf{M}}|^2,\end{aligned} \tag{135}$$

which is essentially similar to the corresponding expression Eq. (33) for point particles. In (135), the term $\dot{\mathbf{M}}$ is understood in the (conservative) sense $\dot{\mathbf{M}} = \gamma[\mathbf{H}\times\mathbf{M}]$ because we assume the very low damping limit, $\alpha \ll 1$. Notice that, just as with the (conservative) inertial term for particles, the gyromagnetic term does not contribute to $\dot{E}$ so the only contribution to $\dot{E}$ in the non-stochastic case is from the Gilbert damping term which is the origin of the instantaneous power loss. The equation of motion of ϕ can be obtained from Eq. (125) which we rewrite as

$$\dot{\mathbf{M}} = \frac{\gamma}{\Omega_E}[\mathbf{H}\times\mathbf{M}]\dot{\phi}. \tag{136}$$

By taking the scalar product of both sides with $[\mathbf{H}\times\mathbf{M}]$ we have

$$\dot{\phi} = \frac{\Omega_E}{\gamma}\frac{([\mathbf{H}\times\mathbf{M}]\cdot\dot{\mathbf{M}})}{|[\mathbf{H}\times\mathbf{M}]|^2} = \Omega_E. \tag{137}$$

We can now, just as with particles, evaluate the mean power loss per period of a Stoner–Wohlfarth orbit from Eq. (135). We have

$$\overline{\dot{E}} = -\frac{\alpha v\Omega_E}{2\pi\gamma M_S}\int_0^{T_E}(\dot{\mathbf{M}}\cdot\dot{\mathbf{M}})dt, \tag{138}$$

where the overbar represents the average over a period. Since the time is measured on a *closed* orbit, we have

$$\overline{\dot{E}} = -\frac{\alpha v\Omega_E}{2\pi M_S\gamma}\oint_{R_E}(\dot{\mathbf{M}}\cdot d\mathbf{M}). \tag{139}$$

Since $\overline{\dot{E}}$ is the mean power loss in a precessional cycle, we have

$$\overline{\dot{E}} = -\frac{\Omega_E\overline{\overline{\delta E}}}{2\pi} = -\frac{\overline{\overline{\delta E}}}{T_E}, \tag{140}$$

where $\overline{\overline{\delta E}}$ is the mean energy loss in such a cycle. Therefore,

$$\overline{\overline{\delta E}} = \frac{\alpha v}{\gamma M_S}\oint_{R_E}(\dot{\mathbf{M}}\cdot d\mathbf{M}), \tag{141}$$

which is the magnetic analog to Eq. (38).

D. Stochastic Motion of Classical Spins in the VLD Limit

To treat the stochastic case, following Brown [40] and Dunn *et al.* [19], we simply use Eq. (106) with a spatially isotropic Gaussian white noise term $\mathbf{F}$ (with properties given by Eq. 107) and neglect all terms of the order of $O(\alpha^2)$. Thus, we have from Eq. (134)

$$\dot{E} = -v(\mathbf{H}\cdot\dot{\mathbf{M}}) - v\gamma(\mathbf{H}\cdot[\mathbf{F}\times\mathbf{M}]) = -v(\mathbf{H}\cdot\dot{\mathbf{M}}) + v(\mathbf{F}\cdot\dot{\mathbf{M}}). \tag{142}$$

As in the deterministic case, only the Gilbert damping term is involved in the $\dot{\mathbf{M}}$ in the first term on the right-hand side and the multiplicative noise term can be expressed using Eq. (114) as [cf. Eq. (135)]

$$\dot{E} = -\frac{v\alpha}{\gamma M_S}(\dot{\mathbf{M}} \cdot \dot{\mathbf{M}}) + v\Omega_E \left(\mathbf{F} \cdot \frac{\partial \mathbf{M}}{\partial \phi} \right). \tag{143}$$

Similarly for $\dot{\phi}$, one has from Eq. (137)

$$\dot{\phi} = \Omega_E + \gamma \Omega_E \frac{([\mathbf{F} \times \mathbf{M}] \cdot \dot{\mathbf{M}})}{(\dot{\mathbf{M}} \cdot \dot{\mathbf{M}})} = \Omega_E - v\Omega_E \left(\mathbf{F} \cdot \frac{\partial \mathbf{M}}{\partial E} \right). \tag{144}$$

E and ϕ are now random variables and we easily see that multiplicative noise terms are again involved as for particles. In Eqs. (143) and (144) and below, the term $\dot{\mathbf{M}}$ is again understood in the sense $\dot{\mathbf{M}} = \gamma[\mathbf{H} \times \mathbf{M}]$ because we assume the very low damping limit, $\alpha \ll 1$.

We can now write from Eqs. (143) and (144), the equations of motion as Langevin equations with multiplicative noise for the state variables $\xi_1 = E$ and $\xi_2 = \phi$, namely,

$$\dot{\xi}_i = h_i + (\mathbf{g}_i \cdot \mathbf{F}) \; (i = 1, 2) \tag{145}$$

where

$$h_1 = -\frac{v\alpha}{\gamma M_S}(\dot{\mathbf{M}} \cdot \dot{\mathbf{M}}), \; h_2 = \Omega_E \tag{146}$$

and

$$\mathbf{g}_1 = v\Omega_E \frac{\partial \mathbf{M}}{\partial \phi} = v\dot{\mathbf{M}}, \; \mathbf{g}_2 = -v\Omega_E \frac{\partial \mathbf{M}}{\partial E}. \tag{147}$$

The Langevin equation, Eq. (145), now allows one [19] to write a Fokker–Planck equation for the probability density $W(E, \phi, t)$ using the Stratonovich method as described in Section III.C for point particles.

E. Fokker–Planck Equation

We have formally

$$\dot{W} = -\frac{\partial}{\partial E}\left[D_1^{(1)} W - \sum_j \frac{\partial}{\partial \xi_j}\left(D_{1,j}^{(2)} W \right) \right] - \frac{\partial}{\partial \phi}\left[D_2^{(1)} W - \sum_j \frac{\partial}{\partial \xi_j}\left(D_{2,j}^{(2)} W \right) \right]. \tag{148}$$

where the drift and the diffusion coefficients are (cf. [47])

$$D_i^{(1)} = h_i + D\sum_k \left(\mathbf{g}_k \cdot \frac{\partial \mathbf{g}_i}{\partial \xi_k}\right). \tag{149}$$

$$D_{i,j}^{(2)} = D(\mathbf{g}_i \cdot \mathbf{g}_j), \tag{150}$$

and D is the free diffusion coefficient of the magnetization defined by Eq. (108).

In order to write the Fokker–Planck equation in explicit form, we notice at first that according to the orthogonality property Eq. (129) and then Eq. (147), we have

$$\frac{\partial}{\partial \xi_i}(\mathbf{g}_1 \cdot \mathbf{g}_2) = \left(\mathbf{g}_1 \cdot \frac{\partial \mathbf{g}_2}{\partial \xi_i}\right) + \left(\mathbf{g}_2 \cdot \frac{\partial \mathbf{g}_1}{\partial \xi_i}\right) = 0,$$

so that

$$\left(\mathbf{g}_2 \cdot \frac{\partial \mathbf{g}_1}{\partial \xi_i}\right) = -\left(\mathbf{g}_1 \cdot \frac{\partial \mathbf{g}_2}{\partial \xi_i}\right). \tag{151}$$

and

$$\frac{\partial \mathbf{g}_2}{\partial \phi} = \frac{\partial}{\partial \phi}\left(-v\Omega_E \frac{\partial \mathbf{M}}{\partial E}\right) = -v\left[\frac{\partial}{\partial E}\left(\Omega_E \frac{\partial \mathbf{M}}{\partial \phi}\right) - \frac{\partial \mathbf{M}}{\partial \phi}\frac{\partial \Omega_E}{\partial E}\right] = -\frac{\partial \mathbf{g}_1}{\partial E} + \mathbf{g}_1 \frac{\partial \ln \Omega_E}{\partial E}. \tag{152}$$

Due to Eqs. (151) and (152), the noise-induced contribution to the drift coefficient $D_1^{(1)}$ can then be written using

$$\sum_j \left(\mathbf{g}_j \cdot \frac{\partial \mathbf{g}_1}{\partial \xi_j}\right) = 2\left(\mathbf{g}_1 \cdot \frac{\partial \mathbf{g}_1}{\partial E}\right) - \frac{\partial \ln \Omega_E}{\partial E}(\mathbf{g}_1 \cdot \mathbf{g}_1) = \frac{\partial |\mathbf{g}_1|^2}{\partial E} - \frac{\partial \ln \Omega_E}{\partial E}|\mathbf{g}_1|^2, \tag{153}$$

while the noise-induced contribution to the drift $D_2^{(1)}$ can be written using

$$\sum_j \left(\mathbf{g}_j \cdot \frac{\partial \mathbf{g}_2}{\partial \xi_j}\right) = (\mathbf{g}_2 \cdot \mathbf{g}_1)\frac{\partial \ln \Omega_E}{\partial E} + 2\left(\mathbf{g}_2 \cdot \frac{\partial \mathbf{g}_2}{\partial \phi}\right) = 2\left(\mathbf{g}_2 \cdot \frac{\partial \mathbf{g}_2}{\partial \phi}\right) = \frac{\partial}{\partial \phi}|\mathbf{g}_2|^2. \tag{154}$$

Moreover, the diffusion terms can also be simplified using the orthogonality property, Eq. (129); we have

$$\sum_j \frac{\partial}{\partial \xi_j} D^{(2)}_{1,j} W = \frac{\partial}{\partial E}\left(D^{(2)}_{1,1} W\right) = D\frac{\partial}{\partial E}\left(|\mathbf{g}_1|^2 W\right) \tag{155}$$

$$\sum_j \frac{\partial}{\partial \xi_j} D^{(2)}_{2,j} W = \frac{\partial}{\partial \phi}\left(D^{(2)}_{2,2} W\right) = D\frac{\partial}{\partial \phi}\left(|\mathbf{g}_2|^2 W\right). \tag{156}$$

Substituting Eqs. (153)–(156) into Eq. (148) then yields the Fokker–Planck equation in the two state variables E and ϕ

$$\begin{aligned}\dot{W} = {} & \frac{\partial}{\partial E}\left[\left(\frac{\alpha v}{\gamma M_S}|\dot{\mathbf{M}}|^2 - D\frac{\partial}{\partial E}|\mathbf{g}_1|^2 + D\frac{\partial \ln \Omega_E}{\partial E}|\mathbf{g}_1|^2\right) W + D\frac{\partial}{\partial E}\left(|\mathbf{g}_1|^2 W\right)\right] \\ & -\frac{\partial}{\partial \phi}\left[\left(\Omega_E + D\frac{\partial}{\partial \phi}|\mathbf{g}_2|^2\right) W - D\frac{\partial}{\partial \phi}\left(|\mathbf{g}_2|^2 W\right)\right].\end{aligned} \tag{157}$$

This equation may be further simplified by expanding $\frac{\partial}{\partial E}(|\mathbf{g}_1|^2 W)$ and $\frac{\partial}{\partial \phi}(|\mathbf{g}_2|^2 W)$ and then using Eq. (147) so that

$$D|\mathbf{g}_1|^2 = Dv^2|\dot{\mathbf{M}}|^2. \tag{158}$$

Thus we have the final form of the Fokker–Planck equation for the joint probability density function $W(E, \phi, t)$ analogous to Eq. (68) for particles, namely,

$$\begin{aligned}\dot{W} = {} & \frac{\partial}{\partial E}\left[\frac{\alpha v}{\gamma M_S}|\dot{\mathbf{M}}|^2\left(1 + kT\frac{\partial \ln \Omega_E}{\partial E} + kT\frac{\partial}{\partial E}\right) W\right] \\ & +\frac{\partial}{\partial \phi}\left[-\Omega_E W + \frac{v\alpha kT}{\gamma M_S}\Omega_E^2\left|\frac{\partial \mathbf{M}}{\partial E}\right|^2 \frac{\partial W}{\partial \phi}\right]\end{aligned} \tag{159}$$

This equation, because the two state variables E and ϕ are again involved, is difficult to treat and cannot be solved by quadratures. However, because on long timescales, $t \gg T_E$, ϕ is a fast variable and E is slow and is almost conserved, we can reduce Eq. (159) to a one dimensional equation in the energy variable just as with the Stratonovich calculation in Section III.D for point particles with separable and additive Hamiltonians.

F. Energy Diffusion Equation

Following Dunn *et al.* [19], we eliminate the fast variable by exploiting the periodicity of W in ϕ along a precessional orbit to write the Fourier series

$$W(E,\phi,t) = \sum_{m=-\infty}^{\infty} W_m(E,t)e^{im\phi} \tag{160}$$

Now on long timescales, $t \gg T_E$, $W(E,\phi,t)$ nearly equilibrates in ϕ and slowly evolves in E. Therefore, on these timescales, the density is dominated by the Fourier component $W_0(E,t)$ that does not depend on ϕ. In other words on this timescale, $W(E,\phi,t) \simeq W_0(E,t)$, thus eliminating the ϕ dependence which corresponds to averaging over a period, we then find that Eq. (159) yields a Fokker–Planck equation for $W_0(E,t)$

$$\dot{W}_0 = \frac{\partial}{\partial E}\left[\frac{\Omega_E\overline{\overline{\delta E}}}{2\pi}\left(1 + kT\frac{\partial \ln \Omega_E}{\partial E} + kT\frac{\partial}{\partial E}\right)W_0\right] \tag{161}$$

since [cf. Eq. 138]

$$\frac{v\alpha}{2\pi\gamma M_S}\int_0^{2\pi}|\dot{\mathbf{M}}|^2 d\phi = \frac{v\alpha\Omega_E}{2\pi\gamma M_S}\int_0^{T_E}|\dot{\mathbf{M}}|^2 dt = \frac{\Omega_E\overline{\overline{\delta E}}}{2\pi} \tag{162}$$

Equation (161) represents the continuity equation

$$\dot{W}_0 + \frac{\partial J}{\partial E} = 0, \tag{163}$$

where J is the probability current. Thus we have a one-dimensional evolution equation in the distribution function in the energy E exactly analogous to that previously derived for point particles.

The time-independent solutions of Eq. (163) will be of particular interest to us. Setting $\dot{W}_0 = 0$, the possible solutions are $J = 0$ or $J =$ constant. The solution $J = 0$ yields the equilibrium distribution while $J =$ constant represents the quasistationary solution. The latter solution will be considered when we discuss the VLD escape rate in Section IV.H. The equilibrium distribution satisfies, by inspection of Eq. (161),

$$\frac{\partial W_0}{\partial E} + \left(\frac{1}{kT} + \frac{\partial \ln \Omega_E}{\partial E}\right)W_0 = 0, \tag{164}$$

so that

$$W_0(E) = \frac{1}{Z} e^{-\frac{1}{kT}(E + kT \ln \Omega_E)} = \frac{e^{-E/(kT)}}{Z\Omega_E}, \tag{165}$$

where Z is the partition function given by

$$Z = \int \frac{e^{-E'/(kT)}}{\Omega_{E'}} dE'. \tag{166}$$

Here, the dependence on the entropy $kT \ln \Omega_E^{-1}$ is obvious. Notice that the origin of the entropy term in our Fokker–Planck approach is due to the multiplicative noise terms in the Langevin equations (143) and (144).

G. Very Low Damping Escape Rate

The Kramers very low damping escape rate for spins (which we shall now determine via the quasistationary solution of Eq. 163) was first derived by Klik and Gunther [25,26] using the first-passage time method originally developed for point particles by Matkowsky *et al.* [24]. This was extended to classical spins by Klik and Gunther [25,26] and the details of the calculation were provided by McCarthy and Coffey [22] and Coffey *et al.* [23, 45]. However, the latter method involves rather long calculations and the VLD escape rate may be much more transparently derived from the energy-controlled diffusion Eq. (161). Moreover, the escape rate so obtained may be compared with the VLD solutions of Eq. (161) obtained using the MFPT. This is so because in the VLD limit, the energy-controlled diffusion equation is a Fokker–Planck equation in a single space variable. Thus, the MFPT in this limit may be exactly calculated by quadratures as shown in Eq. (172). The latter method has been extensively applied to point particles and rigid rotators in Ref. [2].

We now derive the VLD rate from Eq. (161). First recall that the steady state probability current J is given by

$$J = -\frac{\Omega_E \overline{\overline{\delta E}}}{2\pi} \left(1 + kT \frac{\partial \ln \Omega_E}{\partial E} + kT \frac{\partial}{\partial E} \right) W_0. \tag{167}$$

As in the Kramers calculation for particles, the first integral of Eq. (161) with a steady injected probability current satisfies the first-order linear differential equation

$$\frac{\partial W_0}{\partial E} + \left(\frac{1}{kT} + \frac{\partial \ln \Omega_E}{\partial E} \right) W_0 = -\frac{2\pi J}{kT\Omega_E \overline{\overline{\delta E}}}. \tag{168}$$

Considering the behavior of $W_0(E)$ at E_C and, following Kramers, assuming that $W_0(E_C) = 0$ (all spins that reach the barrier go over) we have by quadratures the particular solution

$$W_0(E) = \frac{2\pi J}{kT} \frac{e^{-\frac{E}{kT}}}{\Omega_E} \int_E^{E_C} \frac{e^{\frac{E'}{kT}} dE'}{\overline{\overline{\delta E}}_{E'}}. \tag{169}$$

Let N denote the number of precessional orbits in the well that is

$$N = \int_{E_A}^{E_C} W_0(E) dE = \frac{2\pi J}{kT} \int_{E_A}^{E_C} \frac{e^{-\frac{E}{kT}}}{\Omega_E} \int_E^{E_C} \frac{e^{\frac{E'}{kT}} dE'}{\overline{\overline{\delta E}}_{E'}} dE, \tag{170}$$

we then have the escape rate as the flux-over-population

$$\Gamma = \frac{J}{N} = \left(\frac{2\pi}{kT} \int_{E_A}^{E_C} \frac{e^{-\frac{E}{kT}}}{\Omega_E} \int_E^{E_C} \frac{e^{\frac{E'}{kT}} dE'}{\overline{\overline{\delta E}}_{E'}} dE \right)^{-1}. \tag{171}$$

We remark in passing that, just as with point particles, we can derive by integrating by parts an equation for the longest relaxation (reversal) time $\tau = 1/\Gamma$, namely,

$$\tau = \frac{2\pi}{kT} \int_{E_A}^{E_C} \frac{e^{\frac{E}{kT}}}{\overline{\overline{\delta E}}_E} \int_{E_A}^{E} \frac{e^{-\frac{E'}{kT}} dE'}{\Omega_{E'}} dE. \tag{172}$$

Again, just as with point particles, the main contribution to the inner integral of Eq. (172) comes from near the bottom of the well because the negative exponential dominates there. Furthermore, near the bottom of the well the precession frequency $\Omega_{E_A} \simeq \Omega_A$, which is independent of E because of the paraboloid approximation for the potential near the bottom of the well [Ω_A is defined by Eq. (184)]. Thus

$$\int_{E_A}^{E} \frac{e^{-\frac{E'}{kT}}}{\Omega_{E'}} dE' \simeq \frac{1}{\Omega_A} \int_{E_A}^{\infty} e^{-\frac{E'}{kT}} dE' = \frac{kT}{\Omega_A} e^{-\frac{E_A}{kT}}. \tag{173}$$

With regard to the physical meaning of the frequency Ω_A in Eq. (173), this is the precessional angular frequency in accordance with the original conjectures of Néel and is effectively independent of the energy. The main contribution to the

outer integral of Eq. (172) comes from the positive exponential factor dominating the integrand near the saddle point of the potential. Therefore,

$$\int_{E_A}^{E_C} \frac{e^{\frac{E}{kT}} dE}{\overline{\overline{\delta E}}_E} \simeq \frac{1}{\overline{\overline{\delta E}}_{E_C}} \int_{-\infty}^{E_C} e^{\frac{E}{kT}} dE = \frac{kT}{\overline{\overline{\delta E}}_{E_C}} e^{\frac{E_C}{kT}}. \tag{174}$$

Here, we have neglected the energy dependence of $\overline{\overline{\delta E}}_{E'}$. Using Eqs. (174) and (173) in Eq. (171) yields the VLD escape rate

$$\Gamma_{\mathrm{VLD}} = \Delta \frac{\Omega_A}{2\pi} e^{-\frac{\Delta V}{kT}} = \Delta \Gamma_{\mathrm{TST}}, \tag{175}$$

where $\Delta V = (E_C - E_A)$ and

$$\Delta = \frac{\overline{\overline{\delta E}}_{E_C}}{kT}. \tag{176}$$

To compare the escape rate equation for spins with that for point particles, we may also rewrite Eq. (176) noting Eq. (141) in terms of an action S_{E_C} at the saddle point energy as

$$\Delta = \frac{\alpha S_{E_C}}{kT}, \tag{177}$$

with

$$S_{E_C} = \frac{v}{M_S} \oint_{R_{E_C}} ([\mathbf{H} \times \mathbf{M}] \cdot d\mathbf{M}) = v \oint_{R_{E_C}} \left(\left[\mathbf{u} \times \frac{\partial V}{\partial \mathbf{u}} \right] \cdot d\mathbf{u} \right), \tag{178}$$

where $\mathbf{u}$ is a unit vector in the direction of $\mathbf{M}$, $\mathbf{u} = \mathbf{M}/M_S$. In spherical polar coordinates (see Fig. 10)

$$\mathbf{u} = \mathbf{e}_r, \; d\mathbf{u} = \mathbf{e}_\vartheta d\vartheta + \mathbf{e}_\varphi \sin\vartheta d\varphi, \tag{179}$$

so that Eq. (178) becomes

$$S_{E_C} = -v \oint_{R_{E_C}} \left[\frac{\partial V}{\partial \varphi} \frac{1}{\sin\vartheta} d\vartheta - \frac{\partial V}{\partial \vartheta} \sin\vartheta d\varphi \right]. \tag{180}$$

The contour integral is taken along the critical energy trajectory on which the magnetization (direction of precession) may reverse by passing through the saddle points. Hence, we have the VLD escape rate, given by Klik and Gunther [25, 26], for spins in the same manner as the escape rate for point particles.

Now, in order to evaluate Γ_{VLD}, we require explicit equations for Ω_A and Δ. The latter can be calculated from Eq. (180). In order to calculate Ω_A, it is supposed [2, 20] that the free energy per unit volume $V(\mathbf{M})$ of a single-domain particle has a multistable structure with a minimum at $\mathbf{n}_A$ separated by a potential barrier with a saddle point at $\mathbf{n}_C$. If $\mathbf{M}$ is close to a stationary point $\mathbf{n}_A$ and $(u_1^{(A)}, u_2^{(A)}, u_3^{(A)})$ denote the direction cosines of $\mathbf{M}$, then $V(\mathbf{M})$ can be approximated to second order in $u_1^{(A)}$ and $u_2^{(A)}$ via the Taylor series

$$\frac{vV}{kT} = \frac{vV_A}{kT} + \frac{1}{2}\left[c_1^{(A)}\left(u_1^{(A)}\right)^2 + c_2^{(A)}\left(u_2^{(A)}\right)^2\right] + \cdots \tag{181}$$

To determine the expansion coefficients $c_1^{(A)}, c_2^{(A)}$, and V_A, we recall that the transformation matrix $\mathbf{R}^{(A)}$ relating the basic polar coordinate system P and a new polar coordinate system P' with the origin at the stationary point $\mathbf{n}_A$, is defined as [2, 20]

$$\mathbf{R}^{(A)} = \begin{pmatrix} \cos\varphi_A \cos\vartheta_A & \sin\varphi_A \cos\vartheta_A & -\sin\vartheta_A \\ -\sin\varphi_A & \cos\varphi_A & 0 \\ \cos\varphi_A \sin\vartheta_A & \sin\varphi_A \sin\vartheta_A & \cos\vartheta_A \end{pmatrix},$$

so that the relationship between the direction cosines $u_n^{(A)}$ and $u_m'^{(A)}$ in the systems P and P' is given by

$$u_n^{(A)} = R_{1n}^{(A)} u'^{(A)}_1 + R_{2n}^{(A)} u'^{(A)}_2 + R_{3n}^{(A)} u'^{(A)}_3, \tag{182}$$

$(n = 1, 2, 3)$. Because

$$u'^{(A)}_3 = \left(1 - u'^{(A)2}_1 - u'^{(A)2}_2\right)^{1/2} \approx 1 - \left(u'^{(A)2}_1 + u'^{(A)2}_2\right)/2,$$

$c_1^{(A)}, c_2^{(A)}$, and V_A, can be evaluated from Eqs. (181) and (182) as

$$V_A = V_A(u_1^{(A)}, u_2^{(A)})\Big|_{u'^{(p)}_1, u'^{(p)}_2 = 0}, \quad c_1^{(A)} = \frac{v}{kT}\left.\frac{\partial^2 V}{\partial u'^{(A)2}_1}\right|_{u'^{(A)}_1, u'^{(A)}_2 = 0}, \quad c_2^{(A)} = \frac{v}{kT}\left.\frac{\partial^2 V}{\partial u'^{(A)2}_2}\right|_{u'^{(A)}_1, u'^{(A)}_2 = 0}. \tag{183}$$

The well angular frequency is then defined as [2, 20]

$$\Omega_A = \frac{\gamma kT}{vM_S}\sqrt{c_1^{(A)}c_2^{(A)}}. \tag{184}$$

An example of the calculation of Ω_A for biaxial anisotropy is given in Section IV.H. For particular anisotropies, the coefficients $c_1^{(A)}$ and $c_2^{(A)}$ may sometimes be equal to zero [2, 20]. In those cases, the next term in the expansion, Eq. (181), must be considered.

We remark that the VLD escape rate Eq. (175) has been derived under the assumption that all spins are absorbed at the boundary, that is, having reached the separatrix they never return to their original direction of precession. In practice, we saw that a potential in single domain ferromagnetic particles will have several states of stability (see Fig. 11). Hence, the multiwell nature of the potential must be taken account of just as with the corresponding problem for point particles. Moreover, since the escape rates have essentially the same mathematical form as those of the original Kramers problem, the results of Mel'nikov and Meshkov [33] should also apply to the magnetic problem. This has been justified rigorously by Déjardin *et al.* [45] provided the departures from axial symmetry are significant. The case of small departures from axial symmetry has been considered by Coffey *et al.* [23] (see also [48]). A particular example of a uniaxial crossover is considered in Section IV.H.

Now considering, for example, a bistable potential with a field at an angle to the easy axis of magnetization (see Fig. 11b) the escape rate for all values of the damping is given by

$$\Gamma = \left(\Gamma_1^{\mathrm{IHD}} + \Gamma_2^{\mathrm{IHD}}\right)\frac{A(\Delta_1)A(\Delta_2)}{A(\Delta_1+\Delta_2)}, \tag{185}$$

which is of the same form as the corresponding equation for point particles in an asymmetric double-well potential, Eq. (28). The calculation of the IHD escape rates Γ_1^{IHD} and Γ_2^{IHD} is, however, more complicated due to the nonseparable form of the anisotropy-Zeeman energy density which renders the determination of the IHD rates significantly more difficult. However, the interested reader can find the details in Coffey and Kalmykov [2, 20] since our purpose here is merely to explain simply how the VLD rate may be obtained from an energy-controlled diffusion equation rather than from the more complicated first passage time method. Also in non-axially symmetric problems, the phenomena of high frequency (ferromagnetic) resonance and low frequency overbarrier (Néel) relaxation behavior alluded to in our introductory sections will always be evident because of the *coupling between the longitudinal and transverse modes of magnetization which occurs for non-axially symmetric potentials of the magnetocrystalline-Zeeman energy*. The reader

can find several examples of this in Chapter 9 of Ref. [2]. The salient point is that the high frequency ferromagnetic resonance behavior is essentially due to the almost harmonic motion in the bottom of the potential wells while the overbarrier relaxation is just as with particles due to the anharmonic part of the well dynamics and of course is influenced by the well frequency via the TST limit.

H. Reversal Time and Escape Rate for Biaxial and Uniaxial Anisotropies

As an example, we consider the biaxial potential in the form shown in Fig. 11c yielding

$$E = vV(\vartheta, \varphi) = \sigma kT(-\cos^2\vartheta + \delta \sin^2\vartheta \cos^2\varphi). \tag{186}$$

Here σ and δ are, respectively, barrier height and biaxiality parameters. The potential, Eq. (186), has two *equivalent wells* and two *equivalent saddle points*. The biaxial anisotropy may yield an appreciable contribution to the free energy density of magnetic nanoparticles [42]. In particular, Eq. (186) describes the magnetic anisotropy energy of a spheroidal single-domain particle, with the axis of symmetry inclined at a certain angle to the easy anisotropy axis of the particle as well that of elongated particles, where easy- and hard-axis anisotropy terms are present [49]. Furthermore, the bistable potential in the form of Eq. (186) is commonly used in spintronic applications [42, 50] in order to represent the free energy density of a nanopillar in the standard form of superimposed easy-plane and in-plane easy axis anisotropies.

In accordance with Eq. (172) (see details in Appendix B), the magnetization reversal time can be calculated in the VLD limit as

$$\tau = \frac{\tau_N}{2} \int_{-1}^{0} \frac{e^{\sigma\varepsilon}}{\sqrt{\delta - \varepsilon}\left[E\left(\frac{\delta+\delta\varepsilon}{\delta-\varepsilon}\right) + \varepsilon K\left(\frac{\delta+\delta\varepsilon}{\delta-\varepsilon}\right)\right]} \int_{-1}^{\varepsilon} \frac{K\left(\frac{\delta+\delta\varepsilon'}{\delta-\varepsilon'}\right) e^{-\sigma\varepsilon'}}{\sqrt{\delta - \varepsilon'}} d\varepsilon' d\varepsilon \tag{187}$$

where $K(m)$ and $E(m)$ are the complete elliptic integrals of the first and second kind, respectively [35, 51], $\tau_N \approx vM_S/(2\alpha\gamma kT)$ is the free diffusion time, and $\varepsilon = E/(\sigma kT)$, $-1 \le \varepsilon \le \delta$, is the normalized free energy of the initial state of the magnetization.

Now we can compare this result both with the exact numerical solution obtained via matrix continued fractions and with the VLD escape rate formula for the biaxial

potential. For biaxial anisotropy, Eq. (186), Eq. (183) yields $c_1^{(A)} = 2\sigma$, $c_2^{(A)} = 2\sigma(1+\delta)$ [2, 20] so that

$$\Omega_A = \frac{2\gamma kT\sigma}{vM_S}\sqrt{(1+\delta)}. \tag{188}$$

Furthermore, the dimensionless action Δ is given by the contour integral, Eq. (180), taken along the separatrixes $\cos\vartheta(\varphi)|_{E=E_C}$, which are determined by the equation $vV(\vartheta,\varphi)/(kT) = E_C$, where $E_C = 0$ is the value of energy at the saddle points. The separatrixes satisfy the trigonometric equation

$$-\cos^2\vartheta + \delta(1-\cos^2\vartheta)\cos^2\varphi = 0$$

with solution

$$\cos\vartheta(\varphi)|_{E=E_C} = \frac{\delta\cos^2\varphi}{1+\delta\cos^2\varphi} \tag{189}$$

Thus, we have from Eqs. (180) and (189)

$$\Delta = \alpha 2\sigma\sqrt{\delta}(1+\delta)\int_0^{2\pi}\sqrt{\frac{\cos^2\varphi}{(1+\delta\cos^2\varphi)^3}}d\varphi = 8\sigma\alpha\sqrt{\delta} \tag{190}$$

Noting that the well energy $E_A = -\sigma$ and the barrier height parameter $v\Delta V/(kT) = \sigma$, we obtain from Eq. (175) the VLD asymptote for the longest relaxation time for biaxial anisotropy, namely,

$$\tau_{\mathrm{VLD}} = \frac{1}{\Gamma_{\mathrm{VLD}}} \sim \frac{\tau_N\pi e^\sigma}{4\sigma^2\sqrt{\delta(1+\delta)}},\ \sigma \ll 1. \tag{191}$$

The longest relaxation time $\sim \Gamma_{\mathrm{VLD}}^{-1}$ predicted by Eq. (191), τ from Eq. (187), and the inverse of the smallest nonvanishing eigenvalue λ_1 of the Fokker–Planck operator, Eq. (109), calculated numerically by the matrix continued fraction method [2, 20] are shown in Fig. 12 as functions of the barrier height σ. Apparently, λ_1^{-1} and τ are very close to each other for virtually all σ while in the high barrier limit, $\sigma \gg 1$ and $\sigma\delta > 1$, the asymptotic Eq. (191) provides an accurate approximation to both λ_1^{-1} and τ.

However, for $\delta \to 0$, the (asymptotic) escape rate Eq. (191) cannot be used to determine the longest relaxation time. In contrast this limit corresponds to the uniaxial anisotropy given by Eq. (100) and can be treated via the general Eq. (187)

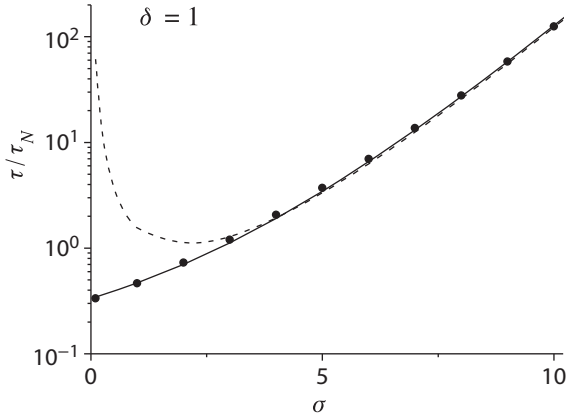

Figure 12. Normalized times τ/τ_N, $1/(\tau_N\Gamma_{\rm VLD})$ and $1/(\tau_N\lambda_1)$ versus the barrier height (inverse temperature) parameter σ for *biaxial anisotropy*, Eq. (186), with $\delta = 1$. Filled circles: numerical solution for the inverse of the smallest nonvanishing eigenvalue $1/(\tau_N\lambda_1)$ of the Fokker–Planck operator in Eq. (109) [2]. Dashed line: the VLD asymptotic Eq. (191). Solid line: τ from Eq. (187).

in the limit $\delta \to 0$ yielding

$$\tau = \frac{\tau_N}{2}\int_{-1}^{0}\frac{e^{\sigma\varepsilon}}{(1+\varepsilon)\sqrt{-\varepsilon}}\int_{-1}^{\varepsilon}\frac{e^{-\sigma\varepsilon'}}{\sqrt{-\varepsilon'}}d\varepsilon' d\varepsilon$$
$$= \frac{\tau_N\sqrt{\pi}}{2}\int_0^{\sigma}\frac{e^{-z}\left[\mathrm{erfi}(\sqrt{\sigma})-\mathrm{erfi}(\sqrt{z})\right]}{(\sigma-z)\sqrt{z}}dz. \tag{192}$$

Here $\mathrm{erfi}(z) = \frac{1}{\sqrt{\pi}}\int_0^z e^{t^2}dt$ is the error function of imaginary argument [35] and we have used $E(0) = K(0) = \pi/2$ [35]. The high barrier asymptote, $\sigma \gg 1$, τ from Eq. (192) is now closely approximated by Brown's formula for the longest relaxation time [20]

$$\tau_{\rm VLD} \sim \frac{\tau_N\sqrt{\pi}e^{\sigma}}{2\sigma^{3/2}},\ \sigma \gg 1. \tag{193}$$

The τ from Eq. (192), $\tau_{\rm VLD}$ predicted by the asymptotic Eq. (193), and the inverse of the smallest nonvanishing eigenvalue λ_1 of the Fokker–Planck operator, Eq. (109), calculated numerically by the matrix continued fraction method [2, 20] are shown in Fig. 13 as functions of the barrier height σ. Again λ_1^{-1} and τ are very close to each other for all σ while in the high barrier limit, $\sigma \gg 1$, Eq. (193) provides an accurate approximation both to λ_1^{-1} and τ.

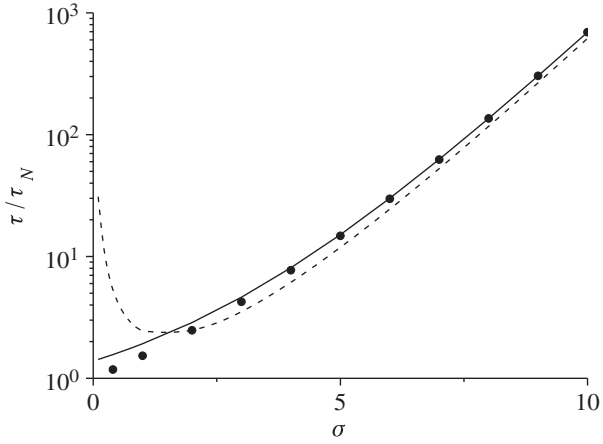

Figure 13. Normalized times $\tau_{\mathrm{MFPT}}/\tau_N$, $1/(\tau_N \Gamma_{\mathrm{VLD}})$, and $1/(\tau_N \lambda_1)$ versus the barrier height (inverse temperature) parameter σ for *uniaxial anisotropy*, Eq. (100). Filled circles: numerical solution for the inverse of the smallest nonvanishing eigenvalue $1/(\tau_N \lambda_1)$ of the Fokker–Planck operator in Eq. (109) [2]. Solid line: τ from Eq. (192). Dashed line: asymptotic Eq. (193).

The merit of Eqs. (187) and (192) is that they yield the reversal time in the VLD valid for *all barrier heights* including *low* barriers ($0 \leq \sigma \leq 3$), where asymptotic methods (like escape rate equations in the high barrier limit) are not applicable.

V. CONCLUSION

In this chapter, we have reviewed the calculation of the VLD escape rate based on an energy-controlled diffusion equation for both point particles (including rigid inertial rotators) and classical spins, a topic which we believe is very often misunderstood in the literature. Confusion arises in part due to the plethora of seemingly different energy-diffusion equations involved for point particles, while for spins the escape rate problem (due to the lack of an energy-controlled diffusion equation for the latter) has hitherto been treated indirectly using the uniform asymptotic expansion method for the calculation of first passage times [24–26]. This method, although correct in every detail, does not explicitly involve an energy-controlled diffusion equation. Consequently for spins the basic relationship with the original VLD calculation of Kramers for point particles, *a fortiori* with his IHD solution and the general theory of the decay of metastable states [2, 4], is somewhat obscured, particularly for the uninitiated reader. As well as circumventing these difficulties, the availability of an energy-controlled diffusion equation for spins transparently shows how the Mel'nikov and Meshkov [11, 33] formalism for the escape rates for all values of the dissipation for point particles carries over to

classical spins yielding the spin escape rate in the entire damping range. Now, although on cursory inspection, the particle and spin problems appear to be quite different since for particles the Hamiltonian is *separable* and *additive* and the domain is the *real line* while for spins the Hamiltonian is *nonseparable* and *nonadditive* and the domain is the *unit sphere* (a feature which is shared with rigid rotators), in reality the exact expressions for the VLD MFPT, namely, Eqs. (91) and (172), are essentially similar. The commonality of the two problems is emphasized by the elegant Stratonovich method [16]. This consists of reduction to a one dimensional diffusion problem based on the concept of transforming the lightly damped Langevin equation, consequently the Fokker–Planck equation to *slow* energy and *fast* configuration (phase) variables and then averaging the subsequent noise induced drift, the latter being determined using his interpretation of the Langevin equation. The Stratonovich method allows one to transparently derive the energy-controlled diffusion equation for both cases by averaging over the fast configuration variable while at the same time removing the obscurities which have been associated with the derivation of such equations for point particles with the bonus of the diffusion equation for spins. The VLD results for spins, embodied in Eq. (172) (just as with particles) are valuable as they serve as a benchmark solution with which numerical calculations of the greatest relaxation time from the relevant Fokker–Planck equation in the VLD limit must agree. We remark that in order to calculate the VLD escape rate, knowledge of the *deterministic dynamics in the given potential* is always required. In general, the calculation of the VLD rate due to the action integrals, etc. involved always reduces to the solution of a problem in the classical mechanics [27–29] of particles (including rigid rotators) governed by Newton's or Euler's equations or spins governed by the Larmor equation which is simply the kinematic equation, Eq. (104). The study of the deterministic dynamics usually governed by the Jacobian doubly periodic elliptic functions [35, 52–54] does not, due to the form of the action integrals which are involved, pose of itself an insuperable problem with the exception of spintronic [42] or Josephson junction problems [18], where an injected current is present. Such dynamical systems driven by an external current exhibit behavior [50] in marked contrast to the conventional steady state characterized by the Boltzmann equilibrium distribution which arises when the current is omitted.

We have derived the energy controlled diffusion equation for classical spins using the Stratonovich method. However that equation was originally given by Apalkov and Visscher [55] using a method essentially similar to that of Kramers in his original justification [1] of the corresponding VLD equation for point particles. Furthermore in our numerical demonstrations of the behavior of the VLD relaxation time we have confined ourselves to potentials of the magnetocrystalline/Zeeman energy with equivalent wells, e.g. Eq. (186). Later Coffey et al. [56] have extended the calculations to non-equivalent wells demonstrating that the results agree with those yielded by independent numerical and asymptotic methods.

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APPENDIX A: LONGEST RELAXATION TIME FOR A DOUBLE-WELL POTENTIAL, EQ. (13), IN THE VLD LIMIT

First, we introduce dimensionless variables and parameters as in Ref. [2]

$$x' = \frac{x}{\langle x^2\rangle_0^{1/2}}, \quad A = \frac{a\langle x^2\rangle_0}{2kT}, \quad B = \frac{b\langle x^2\rangle_0^2}{4kT}, \quad \beta' = \eta\beta \tag{194}$$

where $\eta = \sqrt{m\langle x^2\rangle_0/(2kT)}$ is a characteristic time and the angular brackets $\langle\ \rangle_0$ denote the statistical averages over the equilibrium distribution function. The normalization condition $\langle x'^2\rangle_0 = 1$ implies that the constants A and B are not independent [2]

$$B = B(Q) = \frac{1}{8}\left[\frac{D_{-3/2}\left(\mathrm{sgn}(A)\sqrt{2Q}\right)}{D_{-1/2}\left(\mathrm{sgn}(A)\sqrt{2Q}\right)}\right]^2 \tag{195}$$

where $Q = A^2/(4B)$ and $D_v(z)$ is the parabolic cylinder function of order v [35]. For $A < 0$ (which is the case of greatest interest), Q is equal to the barrier height.

Now, in order to specialize Eq. (97) for the MFPT, we introduce the dimensionless energy of the particle as (we retain the notation of Ref. [2])

$$\varepsilon = \eta^2\dot{x}'^2 - 2\sqrt{QB}x'^2 + Bx'^4 \tag{196}$$

and the time w (phase) measured along a closed trajectory in phase space as action-angle variables [27, 29]. The energy ε varies very slowly with time in

comparison to the phase w. By using the method of Praestgaard and van Kampen [10], that is, averaging the Fokker–Planck Eq. (4) over the *fast* phase variable w, we have, as already seen, a single variable Fokker–Planck Eq. (83) for the probability distribution function $W(\varepsilon, t)$ in energy space

$$\frac{\partial W}{\partial t} = \frac{2\beta'}{\eta}\left[\frac{\partial}{\partial \varepsilon}\left(\eta^2 \overline{\overline{\dot{x}'^2}}(\varepsilon) - \frac{1}{2}\right) + \eta^2 \frac{\partial^2}{\partial \varepsilon^2}\overline{\overline{\dot{x}'^2}}(\varepsilon)\right] W, \tag{197}$$

where the double overbar denotes averaging over the fast phase variable. Now the longest relaxation time τ from the general expressions, Eqs. (97) and (84), is formally given by

$$\tau = \frac{\eta}{2\beta'}\int_{-Q}^{0} \frac{1}{\left[\varepsilon + 2\sqrt{QB}\overline{\overline{x'^2}}(\varepsilon) - B\overline{\overline{x'^4}}(\varepsilon)\right] W_0(\varepsilon)} \int_{-Q}^{\varepsilon} W_0(\varepsilon')d\varepsilon' d\varepsilon. \tag{198}$$

We interpret Eq. (198) following Ref. [2]. Thus we first recall that in the undamped limit, the energy ε, Eq. (196), is a constant of the motion, namely, $\dot{\varepsilon} = 0$. Equation (196) can then be rearranged as the following deterministic nonlinear differential equation describing the undamped dynamics of the particle

$$\frac{\eta}{\sqrt{e_2 B}}\frac{d}{dt}z(t) = \pm\sqrt{[z^2(t) - e_1/e_2][1 - z^2(t)]}, \tag{199}$$

where $z(t) = x'(t)/\sqrt{e_2}$ and $e_{1,2} = \sqrt{Q/B}(1 \mp \sqrt{1 + \varepsilon/Q})$ are the roots of the quadratic equation $\varepsilon + 2\sqrt{QB}x' - Bx'^2 = 0$. The solution of Eq. (199) may be written [2] in terms of the Jacobian doubly periodic elliptic functions $\mathrm{cn}(u|m)$ and $\mathrm{dn}(u|m)$ [35, 52–54], namely,

$$x'(t) = \begin{cases} \pm\sqrt{e_2}\,\mathrm{dn}\left(\sqrt{Be_2}t/\eta + w \middle| m\right), & -Q \le \varepsilon \le 0 \\ \pm\sqrt{e_2}\,\mathrm{cn}\left(\sqrt{B(e_2 - e_1)}t/\eta + w\sqrt{m} \middle| m^{-1}\right), & 0 < \varepsilon < \infty \end{cases} \tag{200}$$

$$m = m(\varepsilon) = \frac{e_2 - e_1}{e_2} = \frac{2\sqrt{1 + \varepsilon/Q}}{1 + \sqrt{1 + \varepsilon/Q}} \tag{201}$$

$$w = \int_{y(0)/\sqrt{e_2}}^{1} \frac{1}{\sqrt{(x^2 - e_1/e_2)(1 - x^2)}}dx.$$

From Eq. (200) we have

$$x'^2(t) = \begin{cases} e_2\left[1 - m\mathrm{sn}^2\left(\sqrt{Be_2}t/\eta + w\middle| m\right)\right], & -Q \le \varepsilon \le 0 \\ e_2\left[1 - \mathrm{sn}^2\left(\sqrt{B(e_2 - e_1)}t/\eta + \sqrt{m}w\middle| m^{-1}\right)\right], & 0 < \varepsilon < \infty \end{cases} \tag{202}$$

Next we recall [35, 54] the identities

$$\int_0^{K(m)} \mathrm{dn}^2(u|m)\, du = E(m) \tag{203}$$

and

$$\mathrm{sn}^4(u|m) = \frac{1}{6}\frac{d^2}{du^2}\mathrm{sn}^2(u|m) - \frac{1}{3} - \frac{2}{3}(1+m)\mathrm{sn}^2(u|m). \tag{204}$$

Thus we have

$$\begin{aligned} \frac{1}{2K(m)}\int_0^{2K(m)} \mathrm{sn}^2(u|m)\, du &= \frac{1}{2mK(m)}\int_0^{2K(m)} [1 - \mathrm{dn}^2(u|m)]du \\ &= \frac{1}{m}\left(1 - \frac{E(m)}{K(m)}\right) \end{aligned} \tag{205}$$

and

$$\frac{1}{2K(m)}\int_0^{2K(m)} \mathrm{sn}^4(u|m)\, du = \frac{1}{3m^2}\left[2 + m - 2(1+m)\frac{E(m)}{K(m)}\right]. \tag{206}$$

Here, $K(m)$ and $E(m)$ are complete elliptic integrals of the first and second kind, respectively [35, 51–54].

Thus, from Eqs. (202)–(206), we can evaluate averages over the phase w. In particular for the averages $\overline{\overline{x'^2}}$ and $\overline{\overline{x'^4}}$ occurring in Eq. (198), we have in the domain of a well $-Q \le \varepsilon \le 0$, namely,

$$\overline{\overline{x'^2}}(\varepsilon) = \frac{1}{2K}\int_0^{2K} x'^2(\varepsilon, w)dw = e_2\frac{E}{K} \tag{207}$$

$$\overline{\overline{x'^4}}(\varepsilon) = \frac{e_2^2}{3}\left[m - 1 + (4 - 2m)\frac{E}{K}\right]. \tag{208}$$

Now because the stationary distribution function is the equilibrium Maxwell–Boltzmann distribution W_0, namely,

$$W_0[x'(0),\dot{x}'(0)]dx'(0)d\dot{x}'(0) = \frac{\eta}{Z\sqrt{\pi}} e^{-\eta^2\dot{x}'^2(0)+2\sqrt{QB}x'^2(0)-Bx'^4(0)} dx'(0)d\dot{x}'(0),$$

then by making the transformation of the variables $\{x'(0),\dot{x}'(0)\} \to \{w,\varepsilon\}$, and by integrating the distribution function W_0 over the phase w, we have the stationary distribution in energy space

$$W_0(\varepsilon)d\varepsilon = \frac{2^{5/4}e^{-Q/2}}{\pi Q^{1/4}D_{-1/2}\left(-\sqrt{2Q}\right)} \frac{\mathrm{Re}\{K[m(\varepsilon)]\}e^{-\varepsilon}}{\sqrt{1+\sqrt{1+\varepsilon/Q}}}d\varepsilon. \tag{209}$$

Moreover, the average of a dynamical quantity $\overline{\overline{X}}(\varepsilon)$ over the normalized energy ε is defined as, mindful of the ε ranges defined in Eqs. (200) and (202),

$$\left\langle \overline{\overline{X}} \right\rangle_0 = \int_{-Q}^{\infty} \overline{\overline{X}}(\varepsilon) W_0(\varepsilon) d\varepsilon. \tag{210}$$

In particular, we have from Eqs. (207) and (209)

$$\int_{-Q}^{\infty} W_0(\varepsilon)d\varepsilon = \frac{2^{5/4}e^{-Q/2}}{\pi Q^{1/4}D_{-1/2}\left(-\sqrt{2Q}\right)} \int_{-Q}^{\infty} \frac{\mathrm{Re}\left\{K\left[m(\varepsilon)\right]\right\} e^{-\varepsilon}}{\sqrt{1+\sqrt{1+\varepsilon/Q}}}d\varepsilon = 1,$$

and

$$\overline{\overline{\langle x'^2\rangle}}_0 = \frac{2^{11/4}Q^{1/4}e^{-Q/2}}{\pi D_{-3/2}\left(-\sqrt{2Q}\right)} \int_{-Q}^{\infty} \sqrt{1+\sqrt{1+\varepsilon/Q}}\,\mathrm{Re}\left\{E\left[m(\varepsilon)\right]\right\} e^{-\varepsilon} d\varepsilon = 1.$$

Now by using Eqs. (207)–(209) in Eq. (198), we obtain

$$\tau = \frac{3\eta}{4\beta'} \int_{-Q}^{0} \frac{e^{\varepsilon}\sqrt{1+\sqrt{1+\varepsilon/Q}}}{\varepsilon K[m(\varepsilon)] + Q(1+\sqrt{1+\varepsilon/Q})E[m(\varepsilon)]} \int_{-Q}^{\varepsilon} \frac{K[m(\varepsilon')]e^{-\varepsilon'}d\varepsilon'}{\sqrt{1+\sqrt{1+\varepsilon'/Q}}} d\varepsilon \tag{211}$$

which after some simplifications leads to Eq. (99).

APPENDIX B: UNDAMPED LIMIT FOR BIAXIAL ANISOTROPY

For the biaxial anisotropy potential, Eq. (186), the gyromagnetic Eq. (115) governing the deterministic dynamics can be rewritten in terms of the Cartesian components $u_X,\ u_Y,\ u_Z$ of the unit vector $\mathbf{u}$ along the direction of magnetization $\mathbf{M}$ as

$$\tau_0 \dot{u}_X = -u_Y u_Z. \tag{212}$$

$$\tau_0 \dot{u}_Y = (1+\delta) u_Z u_X. \tag{213}$$

$$\tau_0 \dot{u}_Z = -\delta u_X u_Y. \tag{214}$$

where $\tau_0 = M_S/(2\gamma K)$ is a characteristic time constant. The components $u_X,\ u_Y,\ u_Z$ are not independent being subject to the obvious constraint

$$u_X^2 + u_Y^2 + u_Z^2 = 1. \tag{215}$$

Furthermore, the trajectories of the precessional dynamics must satisfy the constraint (energy conservation)

$$\varepsilon = -u_Z^2 + \delta u_X^2, \tag{216}$$

where $\varepsilon = E/(\sigma kT)$, $-1 \le \varepsilon \le \delta$ is the normalized free energy of the initial state of magnetization.

In order to solve the set of Eqs. (212)–(214) in accordance with the constraints, Eqs. (215) and (216), we can introduce a function $u(t)$ which is related to $u_X(t),\ u_Y(t),\ u_Z(t)$ by the following formula

$$u_X(t) = p\sqrt{1-u^2(t)},\ u_Y(t) = p\sqrt{1+\delta}u(t)\,, \text{and } u_Z(t) = \sqrt{1-p^2-\delta p^2 u^2(t)}, \tag{217}$$

where

$$p^2 = \frac{1+\varepsilon}{1+\delta}. \tag{218}$$

By substitution of $u_X(t),\ u_Y(t),\ u_Z(t)$ from Eq. (217) into Eq. (213), we see that $u(t)$ satisfies the following differential equation

$$\frac{du}{dt} = a_\varepsilon \sqrt{(1-m_\varepsilon u^2)(1-u^2)}, \tag{219}$$

where

$$m_\varepsilon = \frac{\delta p^2}{1-p^2} = \frac{\delta + \delta\varepsilon}{\delta - \varepsilon} \tag{220}$$

$$a_\varepsilon = \frac{1}{\tau_0}\sqrt{(1-p^2)(1+\delta)} = \frac{1}{\tau_0}\sqrt{\delta - \varepsilon}. \tag{221}$$

The solution of the differential equation (219) is [51–54]

$$u(t) = \begin{cases} \mathrm{sn}(a_\varepsilon t + w|m_\varepsilon) & 0 \le m_\varepsilon \le 1 \ (-1 \le \varepsilon \le 0) \\ \frac{1}{\sqrt{m_\varepsilon}}\mathrm{sn}\left(\sqrt{m_\varepsilon}(a_\varepsilon t + w)\middle| \frac{1}{m_\varepsilon}\right) & m_\varepsilon \ge 1 \ (0 \le \varepsilon \le \delta) \end{cases} \tag{222}$$

where $\mathrm{sn}(u|m)$ is Jacobi's doubly periodic elliptic function with period $4K(m)$ [35, 51–54] and w is an integration constant (initial phase). By inserting Eq. (222) into Eqs. (217) we then obtain

$$u_X^2(t) = \begin{cases} p^2\mathrm{cn}^2(a_\varepsilon t + w|m_\varepsilon) & 0 \le m_\varepsilon \le 1 \\ p^2\mathrm{dn}^2(\sqrt{m_\varepsilon}(a_\varepsilon t + w), |1/m_\varepsilon) & m_\varepsilon \ge 1 \end{cases} \tag{223}$$

$$u_Y^2(t) = \begin{cases} p^2(1+\delta)\mathrm{sn}^2(a_\varepsilon t + w|m_\varepsilon) & 0 \le m_\varepsilon \le 1 \\ p^2[(1+\delta)/m_\varepsilon]\mathrm{sn}^2(\sqrt{m_\varepsilon}(a_\varepsilon t + w)|1/m_\varepsilon) & m_\varepsilon \ge 1 \end{cases} \tag{224}$$

$$u_Z^2(t) = \begin{cases} (1-p^2)\mathrm{dn}^2(a_\varepsilon t + w|m_\varepsilon) & 0 \le m_\varepsilon \le 1 \\ (1-p^2)\mathrm{cn}^2(\sqrt{m_\varepsilon}(a_\varepsilon t + w)|1/m_\varepsilon) & m_\varepsilon \ge 1 \end{cases} \tag{225}$$

Furthermore, the period of precession of the vector **M** is from the general Eq. (118) specialized to our biaxial potential

$$T_\varepsilon = \begin{cases} 4K(m_\varepsilon)/a_\varepsilon & 0 \le m_\varepsilon \le 1 \\ 4K(1/m_\varepsilon)/\sqrt{m_\varepsilon}a_\varepsilon & m_\varepsilon \ge 1. \end{cases} \tag{226}$$

As a check, we consider the uniaxial potential ($\delta = 0$). Noting that here $\varepsilon = -\cos^2\vartheta_E$, $m_\varepsilon = 0$, and $K(0) = \pi/2$, we have the elementary result (cf. Eq. 133)

$$T_\varepsilon = \frac{2\pi\tau_0}{\sqrt{-\varepsilon}} = \frac{\pi v M_S}{\gamma\sigma kT\cos\vartheta_E}. \tag{227}$$

The solutions for the deterministic dynamics embodied in Eqs. (223)–(226) enable one to calculate the reversal time τ in the VLD limit from the general expression Eq. (172). Noting that only the region $-1 \le \varepsilon \le 0$ is appropriate to

escape (because the energy of a separatrix trajectory is $\varepsilon_C = 0$), we can rewrite Eq. (172) specialized to the biaxial potential, namely,

$$\tau = \sigma \int_{-1}^{0} \frac{e^{\sigma\varepsilon}}{\overline{\overline{\delta\varepsilon}}} \int_{-1}^{\varepsilon} T_{\varepsilon'} e^{-\sigma\varepsilon'} d\varepsilon' d\varepsilon, \tag{228}$$

where T_ε is defined by Eq. (226) and the mean energy loss in a precessional cycle $\overline{\overline{\delta\varepsilon}}$ is given by

$$\overline{\overline{\delta\varepsilon}} = \frac{1}{\sigma kT} \overline{\overline{\delta E}}_E = \frac{2\alpha\tau_0}{M_S^2} \int_0^{T_\varepsilon} |\dot{\mathbf{M}}|^2 dt = 2\alpha\tau_0 \int_0^{T_\varepsilon} \left[\dot{u}_X^2(t) + \dot{u}_Y^2(t) + \dot{u}_Z^2(t)\right] dt. \tag{229}$$

Now by substituting the right-hand side Eqs. (212)–(214) into Eq. (229) we have

$$\begin{aligned} \overline{\overline{\delta\varepsilon}} &= \frac{2\alpha}{\tau_0} \int_0^{T_\varepsilon} \left[\delta^2 u_X^2(t) u_Y^2(t) + u_Y^2 u_Z^2(t) + (1+\delta)^2 u_Z^2 u_X^2(t)\right] dt \\ &= \frac{2\alpha}{\tau_0} \int_0^{T_\varepsilon} \left[p^2(1-p^2)(1+\delta)^2 - \delta u_Y^2(t)\right] dt, \end{aligned} \tag{230}$$

where we have used Eqs. (217). Next, to evaluate explicitly $\overline{\overline{\delta\varepsilon}}$ from Eq. (230), we now use Eqs. (205) and (224) so that

$$\overline{\overline{\delta\varepsilon}} = 8\alpha(1+\varepsilon) \begin{cases} \sqrt{\delta-\varepsilon} K(m_\varepsilon) + \delta \dfrac{E(m_\varepsilon) - K(m_\varepsilon)}{\sqrt{\delta-\varepsilon} m_\varepsilon} & (-1 \le \varepsilon \le 0) \\ \sqrt{\dfrac{\delta-\varepsilon}{m_\varepsilon}} K(1/m_\varepsilon) + \delta \dfrac{E(1/m_\varepsilon) - K(1/m_\varepsilon)}{\sqrt{m_\varepsilon(\delta-\varepsilon)}} & (0 \le \varepsilon \le \delta) \end{cases} \tag{231}$$

By substituting the first solution of Eq. (231) pertaining to the region $-1 \le \varepsilon \le 0$ into Eq. (228), we then obtain Eq. (187) for τ.

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