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Range of validity of Kramers escape rates for non-axially symmetric problems in superparamagnetic relaxation

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Abstract. The range of validity of the Kramers escape rate for non-axially symmetric problems of superparamagnetic relaxation as a function of friction is investigated. A comparison of the exact smallest non-vanishing eigenvalue of the Fokker–Planck equation with the asymptotic expressions for the Kramers escape rate in very low-damping and intermediate- to high-damping regimes is made. It is demonstrated, by calculating the smallest non-vanishing eigenvalue for the particular non-axially symmetric problem of a uniform magnetic field applied at an oblique angle to the easy axis of a particle having simple uniaxial anisotropy, that the asymptotic formulae provide an acceptable approximation in the ranges of damping for which they are expected to be valid. The range of validity of the non-axially symmetric intermediate- to high-damping formula as a function of the field angle (which is effectively a measure of the departure from axial symmetry) is also investigated.

1. Introduction

The time τ of the reversal, due to thermal agitation, of the magnetization $\boldsymbol{M}$ of a single domain ferromagnetic particle (superparamagnet) in the (generally) asymmetric multiwell potential created by the magnetocrystalline anisotropy and an applied field has recently assumed a new importance. This is in view of (a) its implications for the long term stability [1, 2] of stored information and (b) the search [3] for the macroscopic quantum tunnelling of $\boldsymbol{M}$—a mechanism of magnetization reversal originally proposed by Bean and Livingston [4]. Thus, it is imperative to have mathematically accurate asymptotic formulae for the reversal time for magnetocrystalline anisotropy potentials which are non-axially symmetric in relation to the anisotropy axis in order to achieve a reliable comparison of the theory with experiment [3]. In particular, an accurate formula for τ allows one to deduce the values of other experimental parameters, for example, the blocking temperature from measurements of τ.

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The purpose of this paper is to assess the accuracy of various non-axially symmetric asymptotic formulae based on Kramers theory [5] of escape of particles over potential barriers, and to ascertain the range of friction in which a particular asymptotic formula is valid by comparison with the exact numerical solution from the Fokker–Planck equation for the particular non-axially symmetric problem of uniaxial anisotropy with a uniform field applied at an oblique angle to the anisotropy axis. This is one of the few non-axially symmetric problems for which accurate numerical solutions are available for relatively high potential barrier heights where the asymptotic behaviour of the solution is precisely known.

The study of the reversal time, having been initiated by Néel [6] was refined by Brown [7] who, by writing down the Langevin equation for the magnetization vector $\boldsymbol{M}$ of the particle assuming *uniform* rotation of $\boldsymbol{M}$ and constructing from it the Fokker–Planck equation (FPE) for the density W of the magnetic moment orientations, showed how the problem of relaxation of the magnetization could be set in the context of the general theory of stochastic processes [1, 7–9]—with the time of reversal τ of $\boldsymbol{M}$ being essentially given in the high-barrier limit by the reciprocal of the smallest non-vanishing eigenvalue λ_1 of the FPE as dictated by the theory of first passage times [9].

Brown in his original study [7] took as his starting point the Langevin equation (which is the Gilbert equation [10] augmented by white noise terms)

$$\dot{\boldsymbol{M}} = g' M_S(\boldsymbol{M} \times \boldsymbol{H}) + h'(\boldsymbol{M} \times \boldsymbol{H}) \times \boldsymbol{M} \tag{1}$$

where

$$g' = \frac{\gamma}{(1+a^2)M_S} \qquad h' = ag'$$

and

$$a = \eta\gamma M_S \tag{2}$$

is the dimensionless damping factor. In equations (1) and (2), γ is the gyromagnetic ratio, M_S is the (constant) magnitude of $\boldsymbol{M}$ and η is a *phenomenological* damping constant arising from the heat bath. The total field $\boldsymbol{H}$ acting on a particle comprises $\boldsymbol{H}_{app}$ the applied field, $\boldsymbol{H}_A$ the anisotropy field and $\boldsymbol{h}(t)$ the random white noise field due to thermal agitation of the surroundings (heat bath).

Having written this Langevin equation Brown [7] was then able to construct, using methods familiar in the theory of stochastic processes [7–9], the FPE for the density $W(p, \phi)$ of orientations of $\boldsymbol{M}$, namely

$$\begin{aligned} 2\tau_N \frac{\partial W}{\partial t} &= \frac{\partial}{\partial p}(1-p^2)\frac{\partial W}{\partial p} + \frac{1}{1-p^2}\frac{\partial^2 W}{\partial \phi^2} \\ &\quad + \beta\frac{\partial}{\partial p}\left\{\left[(1-p^2)H_p + \frac{H_\phi}{a}\right]W\right\} + \beta\frac{\partial}{\partial \phi}\left[\left(-\frac{H_p}{a} + \frac{H_\phi}{1-p^2}\right)W\right] \end{aligned} \tag{3}$$

which has the form of a continuity equation

$$\begin{aligned} \frac{\partial W}{\partial t} = \operatorname{div}\boldsymbol{J} = \operatorname{div}(\boldsymbol{J}_D + \boldsymbol{J}_d) &= \frac{\partial}{\partial p}\left[-\dot{p}_D(\phi, p)W + \frac{1}{2\tau_N}(1-p^2)\frac{\partial W}{\partial p}\right] \\ &\quad + \frac{\partial}{\partial \phi}\left[-\dot{\phi}_D(\phi, p)W + \frac{1}{2\tau_N}\frac{1}{1-p^2}\frac{\partial W}{\partial \phi}\right] \end{aligned} \tag{4}$$

where $\boldsymbol{J}_D$ is the drift current, $\boldsymbol{J}_d$ the diffusion current and the drift coefficients are given by the Langevin equation, written in spherical polar coordinates without the noise terms, viz

$$\dot{p}_D = -h'(1-p^2)H_p - g'H_\phi \tag{5}$$

$$\dot{\phi}_D = g'H_p - h'(1-p^2)^{-1}H_\phi. \tag{6}$$

In equation (3) the colatitude ϑ and the azimuth ϕ are the polar angles describing the orientation of $\boldsymbol{M}$ on a sphere of radius M_S, where $p = \cos\vartheta$

$$\tau_N = \frac{\beta M_S}{2\gamma a}(1+a^2) = \frac{\beta}{2h'} \tag{7}$$

is the diffusional relaxation time, where $\beta = \nu/kT$, ν is the volume of the single domain particle, $H(p,\phi)$ is effectively the Hamiltonian of the system which is the Gibbs free energy

$$\nu H(p,\phi) = \nu V(\vartheta,\phi) \tag{8}$$

consisting of the anisotropy energy and the energy due to the impressed field $\boldsymbol{H}_{app}$.

If equation (4) is rewritten in an obvious notation as

$$\frac{\partial}{\partial t}W = \frac{1}{2\tau_N}L_{FP}W \tag{9}$$

then the relaxation time τ of the longest lived mode (describing the reversal of $\boldsymbol{M}$) is

$$\tau \approx \frac{2\tau_N}{\lambda_1} \tag{10}$$

where λ_1 is the smallest non-vanishing eigenvalue of the Fokker–Planck (FP) operator L_{FP}.

2. Asymptotic formula for axially symmetric problems

Brown [7] *did not solve* equation (9) rather he confined his discussion to an *asymptotic estimate* for λ_1 for *axially symmetric* bi-stable potentials $\nu V(\vartheta)$ only, so that the gyromagnetic terms (those in a^{-1}) drop out of the FPE when one considers the longitudinal relaxation. The transverse motion is then just a steady precession of the magnetic moment so that there is *no geometric coupling* between the transverse and the longitudinal relaxation modes. Brown proceeded by using [7, 9] an adaptation, to magnetization orientations specified by the spherical polar coordinate ϑ, of Kramers theory [5] of escape of particles over potential barriers. (This originally pertained to *mechanical* particles with a single degree of freedom diffusing in phase space (q, p) with $q =$ position, $p =$ momentum, with *additive* noise and obeying the particular form of the FPE known [9] as the Klein–Kramers equation that is, the FPE in (q, p) space.) Thus for an axially symmetric bi-stable potential which has minima at $\vartheta = (0, \pi)$ and a maximum at ϑ_m

$$\tau^{-1} \approx \frac{\lambda_1}{2\tau_N} \approx (\nu_{12}+\nu_{21}) \approx \frac{1}{2\tau_N}\sin\vartheta_m\left[\frac{-\beta V''(\vartheta_m)}{2\pi}\right]^{1/2}(V''(0)\exp\{-\beta[V(\vartheta_m)-V(0)]\}$$
$$+V''(\pi)\exp\{-\beta[V(\vartheta_m)-V(\pi)]\}) \tag{11}$$

where ν_{12}, ν_{21} are Kramers escape rates (transition probabilities for positive orientation 1 to negative orientation 2 and *vice versa*) on the escape paths $(0, \vartheta_m)$ and (π, ϑ_m).

Later the accuracy of the high-barrier asymptotic estimate was confirmed by Aharoni [11, 12] for simple uniaxial anisotropy with a uniform field $\boldsymbol{H}_{app}$ parallel to the polar $(\boldsymbol{k})$ axis which is taken as the easy axis of magnetization so that

$$\nu V(\vartheta) - \nu K\sin^2\vartheta - \nu H_{app}M_S\cos\vartheta \tag{12}$$

and so

$$\tau^{-1} \approx \frac{\lambda}{2\tau_N} \approx (2\tau_N)^{-1}2\pi^{-1/2}\sigma^{3/2}(1-h^2)$$
$$\times\{(1+h)\exp[-\sigma(1+h)^2]+(1-h)\exp[-\sigma(1-h)^2]\} \tag{13}$$

where, of course, the arguments of both exponentials (the barrier heights) greatly exceed unity. Here

$$\sigma = \beta K \qquad \xi = \beta M_S H_{app} \qquad h = \xi/2\sigma \tag{14}$$

are the anisotropy and field parameters, respectively. The bi-stable structure of the potential vanishes when h reaches its critical value of unity so that Néel relaxation no longer takes place.

We remark that the concept of multiplicative noise does not concern us yet as a *one-dimensional* problem with *multiplicative* noise may always be converted into a one-dimensional problem with *additive* noise [9]. We also remark that λ_1 in this problem is independent of the damping factor a.

3. Asymptotic formulae for non-axially symmetric problems

The axially symmetric asymptote for λ_1, equation (11), is by definition very restrictive, for example, for a uniform applied field, it may be used only if the field is parallel to the easy axis and there is uniaxial anisotropy. Moreover, it cannot be applied to higher order anisotropies such as cubic which are inherently non-axially symmetric. Another restriction of equation (11) is that because it arises from a *single* variable ($p = \cos\vartheta$) FPE it is valid for *all* values of the damping factor a—since a only appears in the diffusional time τ_N; thus, there is *no geometric coupling* between the transverse and longitudinal modes of the magnetization. This is not generally true because *two* reaction coordinates [13] (p, ϕ), ensuring coupling, and multiplicative noises [1, 9, 13] are involved and just as in the conventional Kramers theory [5] of escape of particles over potential barriers (for a mechanical system with a single reaction coordinate governed by the Klein–Kramers equation) the range of values of the damping factor a for which a particular escape rate formula is valid must be taken into account [13]. We remark that the axially symmetric formula equation (11) although superficially similar to the very high-damping (Smoluchowski) limit of Kramers theory (derived from Kramers intermediate- to high-damping (IHD) formula) has a *radically different* origin from the high-damping Kramers formula as it arises from *symmetry* [13–15] not from *strong damping* of the momentum as in Kramers problem. In other words, the concept of a Smoluchowski equation is irrelevant in the magnetic problem as that equation pertains to mechanical particles.

The first attempt to lift the restriction of axial symmetry was made by Smith and de Rozario [16] who derived an asymptotic formula for λ_1 for the particular case of cubic anisotropy and later for a general non-axially symmetric potential by Brown [17] (reviewed and derived in detail in Geoghegan *et al* [18]). However, neither Smith and de Rozario [16] nor Brown [17] in their formulae, which are analogous to the intermediate- to high-damping (corresponding in the Kramers problem to aperiodic to overdamped behaviour in the (inverted) harmonic oscillator potential approximation to the dynamics at the top of the barrier) limit of Kramers theory [5], addressed the problem of the range of values of a for which their results are valid, so that their papers contain no reference to a very low-damping (corresponding in the Kramers problem to the very lightly damped oscillations in the well) formula analogous to that obtained by Kramers [5] for diffusion along the energy coordinate, in a single degree of freedom mechanical system with additive noise governed by the Klein–Kramers equation in phase space.

A low-damping formula for Kramers escape rate and so an asymptotic formula for λ_1 in the energy diffusion controlled [5, 13] limit was first derived by Klik and Gunther [14, 15], who bypassed the original Kramers low-damping approach entirely, by suitably adapting

the uniform expansion of the first passage time proposed by Matkowsky *et al* [19] for the Klein–Kramers problem (in order to describe the crossover from the extremely weak damping case, that is, energy controlled diffusion to the moderate- to high-damping case, details in [13, 19]). This calculation led them *inter alia* to the concept of a range of values for a for which a particular asymptotic formula is valid in the magnetic problem. Moreover, they realised that the IHD asymptotic formula in the magnetic problem is in essence a particular example of the multireaction coordinate Kramers problem with additive white noise treated by Brinkman [20], Landauer and Swanson [21] and with the greatest degree of generality by Langer [22], reviewed in depth by Hänggi *et al* [23] (their section IV F). The calculations of Klik and Gunther and those of Brown [7, 17] have been reviewed by Coffey [13] and Geoghegan *et al* [18] so we shall merely sketch the details of the calculations insofar as they are needed for the numerical comparison with λ_1 from the FPE. Thus, in the IHD calculation Brown [17, 18] supposes that the free energy per unit volume $V = V(\boldsymbol{r})$ where

$$\boldsymbol{r} = \frac{\boldsymbol{M}}{M_S}$$

has a bi-stable structure with minima at $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ separated by a potential barrier that contains a saddle point at $\boldsymbol{n}_0$ where it is assumed that $\boldsymbol{n}_i$ are coplanar. If one denotes the plane containing $\boldsymbol{n}_i$ by Π then for each $i = 0, 1, 2$ one may define an orthogonal triad of unit vectors $E_i = (\boldsymbol{e}_1^{(i)}, \boldsymbol{e}_2^{(i)}, \boldsymbol{e}_3^{(i)})$ with $\boldsymbol{e}_1^{(i)} \perp \Pi$ and $e_2^{(i)}, e_3^{(i)} \in \Pi$ so that if

$$X_i^T = (\alpha_1^{(i)}, \alpha_2^{(i)}, \alpha_3^{(i)}) \tag{15}$$

denotes the coordinate vectors (direction cosines) of $\boldsymbol{r}$ with respect to E_i and $\boldsymbol{r}$ is close to the stationary points $\boldsymbol{n}_i$ of the potential, then $\boldsymbol{r} = E_i X_i$ and $V(\boldsymbol{r})$ can be approximated to the second order of the (supposed) small quantities $\boldsymbol{\alpha}^{(i)}$ by the Taylor series

$$V = V_i + \tfrac{1}{2}[c_1^{(i)}(\alpha_1^{(i)})^2 + c_2^{(i)}(\alpha_2^{(i)})^2]. \tag{16}$$

Now the FPE, equation (3), may be written

$$\dot{W} = g'\boldsymbol{r} \cdot (\Lambda V \times \Lambda W) + h'\Lambda \cdot (W \Lambda V) + (2\tau_N)^{-1}\Lambda^2 W \tag{17}$$

where Λ means the two-dimensional gradient operator on the surface of the unit sphere. Thus, equation (16) when substituted into equation (17) (details in [18]) yields a *linearized* FPE—*linear* in the sense that the drift coefficients are linear in the direction cosines $\alpha_1^{(i)}, \alpha_2^{(i)}$. The linearized FPE (which is akin to that of an harmonic oscillator) may be solved exactly in the vicinity of the saddle point, essentially in the same manner as described by Kramers [5] for the linearized Klein–Kramers equation to yield, after a very lengthy calculation (which is detailed fully in [18], section V) Brown's result (equation (84) of [17] or equation (5.60) of [18]), namely

$$\tau^{-1} \approx \frac{\lambda_1}{2\tau_N} \approx \frac{\Omega_0}{2\pi\omega_0}\{\omega_1 \exp[-\beta(V_0 - V_1)] + \omega_2 \exp[-\beta(V_0 - V_2)]\} \tag{18}$$

where

$$\omega_1^2 = \frac{\gamma^2}{M_S^2} c_1^{(1)} c_2^{(1)} \tag{19}$$

$$\omega_2^2 = \frac{\gamma^2}{M_S^2} c_1^{(2)} c_2^{(2)} \tag{20}$$

$$\omega_0^2 = \frac{-\gamma^2}{M_S^2} c_1^{(0)} c_2^{(0)} \tag{21}$$

are the squares of the well and saddle angular frequencies, respectively, and the (over) damped saddle angular frequency Ω_0 associated with the hyperbolic paraboloid (the corresponding quantity in the Kramers problem is an inverted oscillator potential) approximation to the potential at the top of the barrier is

$$\Omega_0 = \frac{h'}{2}\left[-c_1^{(0)} - c_2^{(0)} + \sqrt{(c_2^{(0)} - c_1^{(0)})^2 - 4a^{-2}c_1^{(0)}c_2^{(0)}}\right] \tag{22}$$

and the damping factor a is

$$a = \frac{h'}{g'} = \left[\frac{\gamma}{(1+a^2)M_S}\right]^{-1}\frac{a\gamma}{(1+a^2)M_S} = \eta\gamma M_S. \tag{23}$$

In order that equation (18) should be valid a must be large enough [5, 13] to ensure a Maxwell–Boltzmann distribution of orientations as one moves away from the saddle point. The derivation of equation (18) also requires the solution of the linearized FPE in the vicinity of the minima which is the Maxwell–Boltzmann distribution. In writing equation (18) and indeed equation (11) it is always supposed that the ratios of barrier height to thermal energy become appreciable (i.e. $\beta(V_0 - V_i) \gg 1$) so that one may assume that the density of magnetic moment orientations W rapidly achieves a state of quasi-equilibrium [7] thus the FPE, equation (17), reduces to the master equation

$$\dot{n}_1 = -\dot{n}_2 = \nu_{2,1}n_2 - \nu_{1,2}n_1$$

and

$$\lambda_1 \approx 2\tau_N(\nu_{1,2} + \nu_{2,1})$$

where ν_{ij} is the transition probability from orientation i to orientation j, n_1 is the number of particles with a positive orientation and n_2 those with a negative orientation in this case.

Equation (18) is clearly of the same form as the IHD formula derived by Kramers [5] in the context of a mechanical problem obeying the Klein–Kramers equation *consequently it is subject to the same limitations as that formula regarding the range of values of a for which it is applicable.* As we have stated a must be large enough to ensure a Maxwell–Boltzmann distribution of orientations as one moves away from the saddle point or put in yet another way; in one cycle of the motion of the orienting moments the energy dissipated must be significantly greater than the thermal energy.

Equations essentially similar to Brown equations (18)–(22) were derived by Klik and Gunther [13–15] by supposing that the saddle point and minima of the potential lie on the equator. When the Fokker–Planck equation or equivalently the Langevin equation is linearized at any point in the vicinity of the equator, the non-linear system with *multiplicative* noise so linearized behaves as a two reaction coordinate system with *additive* noise to which the formalism of Langer [22, 23] may be directly applied with the angular frequencies being given by the Hessian matrix of the energy at the stationary points [23].

We remark that [5, 23] the transition state theory result may be written by simply taking the limit as $a \to 0$ in equation (18) so that [13] the saddle angular frequency is

$$\Omega_0 = \omega_0$$

and so

$$\tau^{-1} \approx \frac{1}{2\pi}\{\omega_1 \exp[-\beta(V_0 - V_1)] + \omega_2 \exp[-\beta(V_0 - V_2)]\} \tag{24}$$

in which there is no longer any frictional dependence of the prefactor. Thus, one would have Néel relaxation in the absence of damping which is impossible. Therefore, we require a formula which reduces τ^{-1} to zero in the low-damping limit. This is accomplished by

using the uniform expansion of the first passage time technique of Matkowsky *et al* [19] (essentially used by them to treat the damping regime between the very low-damping region where equation (25) (see later) applies and (roughly) the aperiodic damping region beyond which equation (18) would be expected to apply) as adapted by Klik and Gunther [14, 15] to the magnetic problem viz (details in [13])

$$\tau^{-1} \approx \frac{a}{2\pi}\{\omega_1\beta(V_0 - V_1)\exp[-\beta(V_0 - V_1)] + \omega_2\beta(V_0 - V_2)\exp[-\beta(V_0 - V_2)]\} \tag{25}$$

which is valid if the energy loss per cycle is significantly less than the thermal energy.

4. Range of validity of asymptotic formulae as a function of the damping parameter

In order to roughly establish the range of values of a in which equations (18) and (25) are valid one may apply the criterion of Kramers [5, 23], namely, the crossover region in which neither IHD nor low-damping (LD) formulae hold, is given by

$$\tau \approx \tau_{TS}. \tag{26}$$

where τ is given by equation (25) and τ_{TS} is given by the $a = 0$ limit of equation (18), namely equation (24). This immediately leads [13] to an estimate of the range of validity of equation (18), namely the friction parameter a must satisfy the relations

$$a\beta(V_0 - V_1) > 1 \qquad a\beta(V_0 - V_2) > 1 \tag{27}$$

with of course

$$\beta(V_0 - V_1) > 1 \qquad \beta(V_0 - V_2) > 1. \tag{28}$$

In the low-damping limit, on the other hand, these criteria become

$$a\beta(V_0 - V_1) < 1 \qquad a\beta(V_0 - V_2) < 1 \tag{29}$$

and, of course, equation (27) still applies.

We remark that as well as the situation described by equations (27)–(29), it is also possible to have

$$a\beta(V_0 - V_1) \gg 1 \tag{30}$$

with

$$\beta(V_0 - V_1) \gg 1 \tag{31}$$

and

$$a\beta(V_0 - V_2) < 1 \tag{32}$$

with

$$\beta(V_0 - V_2) > 1 \tag{33}$$

corresponding to a *deep* lower minimum with barrier height given by equation (31) and a *relatively shallow* upper minimum where the barrier height is given by equation (33). If this situation arises then the IHD formula must be used to estimate the contribution to λ_1 for transitions from the lower minimum while the LD formula must be used for transitions from the upper minimum.

This discussion serves to underline an important feature of the various asymptotic formulae for λ_1: namely it is possible to identify from them the *separate* contributions to λ_1 from transitions between the upper and lower minimum and *vice versa*. This is not, in general, possible if one constructs the exact solution by numerically calculating the smallest non-vanishing eigenvalue of L_{FP}.

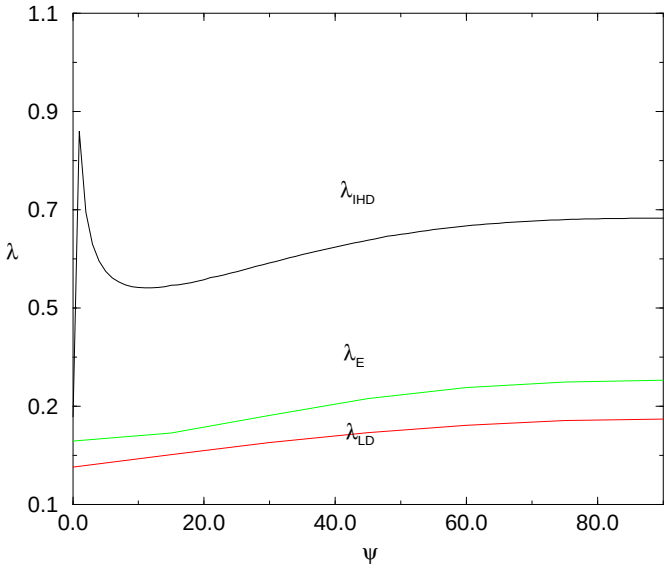

Figure 1. Smallest non-vanishing eigenvalue λ as a function of relative orientation ψ in degrees for $h = 0.1$, $a = 0.1$, $\sigma = 5$. Here the low-damping (LD) asymptote, equation (25), provides a much better approximation than the IHD formula equation (18) since $a\beta(V_0 - V_1) < 1$, $a\beta(V_0 - V_2) < 1$ by inspection of table 2.

5. Comparison of IHD and LD formulae with the exact solution from the Fokker–Planck equation

In order to test the validity criteria given earlier the approximate eigenvalue yielded by equations (18) and (25) was compared with the eigenvalue yielded by the exact solution of the FPE using the techniques described in Coffey *et al* [24] for the particular case of a uniform field applied at an oblique angle to the polar axis. Thus, the potential is of the form

$$vV(\vartheta) = Kv\sin^2\vartheta - vM_SH(\cos\vartheta\cos\psi + \sin\vartheta\cos\phi\sin\psi) \tag{34}$$

for which accurate [24] numerical solutions for λ_1 of the FPE are available. Here ψ is the colatitude of the field which is assumed to be applied in the x–z plane.

Calculation of the Taylor series expansion coefficients $c_1^{(i)}$, $c_2^{(i)}$ and the barrier heights in the Brown IHD equation (our equation (18)) for this potential is very lengthy, since it depends on finding the roots of a quartic equation. The mathematical details of the calculation are comprehensively described in pp 601–28 of [18]—with the corresponding method for the numerical calculation of λ_1 and the derivation of the differential-recurrence relation being described in [18, 24] which is used to calculate λ_1.

Thus, it is sufficient to remark here that the plane containing the relevant stationary points lies in the longitude $\phi = 0$ and that at the minima the truncated Taylor series for the potential (equation (16)) has the form [18] of an elliptic paraboloid while at the saddle point it describes a hyperbolic paraboloid (which has the appearance of a horse's saddle). The calculations are somewhat easier in the situations where the LD formula applies, as all that is required in the computation of this formula is the barrier height.

Table 1. Values of λ_E, λ_{LD} and λ_{IHD} for $h = 0.1$, $a = 0.1$, $\sigma = 5$.

ψ	λ_E	λ_{LD}	λ_{IHD}
0	0.1786	0.1260	0.2282
15	0.1953	0.1515	0.4962
30	0.2313	0.1756	0.5417
45	0.2642	0.1959	0.5880
60	0.2878	0.2111	0.6171
75	0.2993	0.2235	0.6299
90	0.3025	0.2235	0.6330

Table 2. Barrier heights for $h = 0.1$, $a = 0.1$, $\sigma = 5$.

ψ	$\beta(V_0 - V_1)$	$\beta(V_0 - V_2)$	$a\beta(V_0 - V_2)$
0	6.05	4.05	0.405
15	5.7579	3.8267	0.3827
30	5.4170	3.6871	0.3687
45	5.0503	3.6396	0.3640
60	4.6834	3.6871	0.3687
75	4.3421	3.8269	0.3827
90	4.05	4.05	0.405

Table 3. Values of λ_E, λ_{LD} and λ_{IHD} for $h = 0.1$, $a = 1.0$, $\sigma = 10$.

ψ	λ_E	λ_{LD}	λ_{IHD}
0	0.008 60	0.0073	0.0099
15	0.008 67	0.0108	0.0088
30	0.008 679	0.0142	0.0086
45	0.008 286	0.0162	0.0084
60	0.007 425	0.0166	0.0076
75	0.006 504	0.0160	0.0067
90	0.006 107	0.0156	0.0063

The results of our numerical calculations and comparison with the asymptotic formulae may be summarized as follows: in figure 1 and tables 1 and 2 we show the results for a relatively small friction situation where the LD formula equation (25) may reasonably be expected to apply: our conjecture appears to be valid here as the LD formula is a much better approximation to the exact λ_1 (denoted by λ_E) than the IHD one.

Figure 2 and tables 3 and 4 show further results for the opposite case in which the IHD formula is expected to apply. The results confirm that the IHD formula is now the best. Yet another set of results is shown in figure 3 and tables 5 and 6.

It is apparent from the above example where

$$a\beta(V_0 - V_2) \approx 1.5 \tag{35}$$

on average, that the IHD formula again provides a reasonable estimate of λ_1 even though the criteria, equation (35), for validity of the IHD formula is near unity. Figure 4, on the other hand, shows results when

$$a\beta(V_0 - V_2)$$

is of the order unity or slightly less.

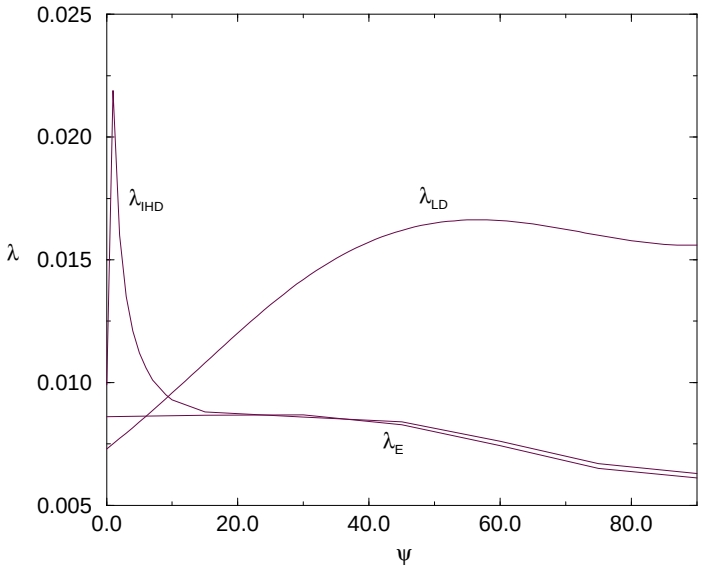

Figure 2. Smallest non-vanishing eigenvalue λ as a function of relative orientation ψ in degrees for $h = 0.1$, $a = 1$, $\sigma = 10$. Here the IHD asymptote, equation (18), provides a much better approximation than the LD formula, equation (25), since (table 4), $a\beta(V_0 - V_1) > 1$, $a\beta(V_0 - V_2) > 1$, with the exception of small values of ψ as discussed in the text.

Table 4. Barrier heights for $h = 0.1$, $a = 1.0$, $\sigma = 10$.

ψ	$\beta(V_0 - V_1)$	$\beta(V_0 - V_2)$	$a\beta(V_0 - V_2)$
0	12.1	8.1	8.1
15	11.5159	7.6535	7.6535
30	10.8340	7.3743	7.3743
45	10.1005	7.2792	7.2792
60	9.3667	7.3743	7.3743
75	8.6841	7.6537	7.6537
90	8.1	8.1	8.1

Table 5. Values of λ_E, λ_{LD} and λ_{IHD} for $h = 0.1$, $a = 0.2$, $\sigma = 10$.

ψ	λ_E	λ_{LD}	λ_{IHD}
0	0.008 60	0.0073	0.0099
15	0.009 54	0.0108	0.0125
30	0.001 14	0.0142	0.0142
45	0.012 56	0.0162	0.0153
60	0.012 33	0.0166	0.0147
75	0.011 34	0.0160	0.0134
90	0.010 81	0.0156	0.0127

Here it is apparent that the LD formula provides on average a closer approximation to the exact solution. The fact that both LD and IHD formulae yield a sensible approximation to λ_1 near the crossover region is substantially in accord with the discussion of Kramers [5]

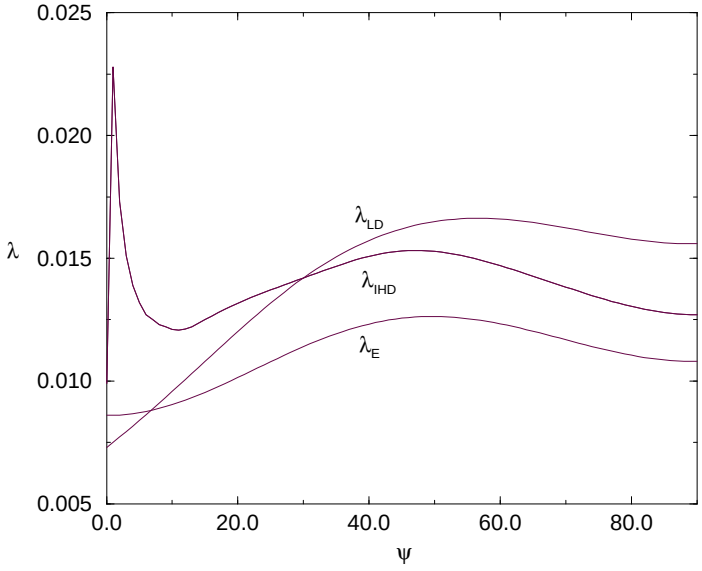

Figure 3. Smallest non-vanishing eigenvalue λ as a function of relative orientation ψ in degrees for $h = 0.1$, $a = 0.2$, $\sigma = 10$. Here both IHD and LD asymptotes provide a reasonable approximation to λ_E since on inspection of table 6 $a\beta(V_0 - V_1)$ is in the range 1 to 2 and the IHD formula is marginally better.

Table 6. Barrier heights for $h = 0.1$, $a = 0.2$, $\sigma = 10$.

ψ	$\beta(V_0 - V_1)$	$\beta(V_0 - V_2)$	$a\beta(V_0 - V_2)$
0	12.1	8.1	1.62
15	11.5159	7.6535	1.53
30	10.8340	7.3743	1.475
45	10.101	7.2792	1.4558
60	9.3667	7.3743	1.475
75	8.6841	7.6537	1.53
90	8.1	8.1	1.62

Table 7. Values of λ_E, λ_{LD} and λ_{IHD} for $h = 0.2$, $a = 0.2$, $\sigma = 10$.

ψ	λ_E	λ_{LD}	λ_{IHD}
0	0.038 34	0.0271	0.0456
15	0.057 77	0.0563	0.0754
30	0.093 28	0.0887	0.1160
45	0.1121	0.1063	0.1360
60	0.098 24	0.0991	0.1173
75	0.067 88	0.0777	0.0796
90	0.052 69	0.0663	0.0612

in p 299 of his paper. Although it is apparent from all these figures that both equations (18) and (25) yield acceptable approximations to λ_1 in the range of values of a in which each is applicable, a more refined estimate of λ_1 could be constructed by adapting the methods

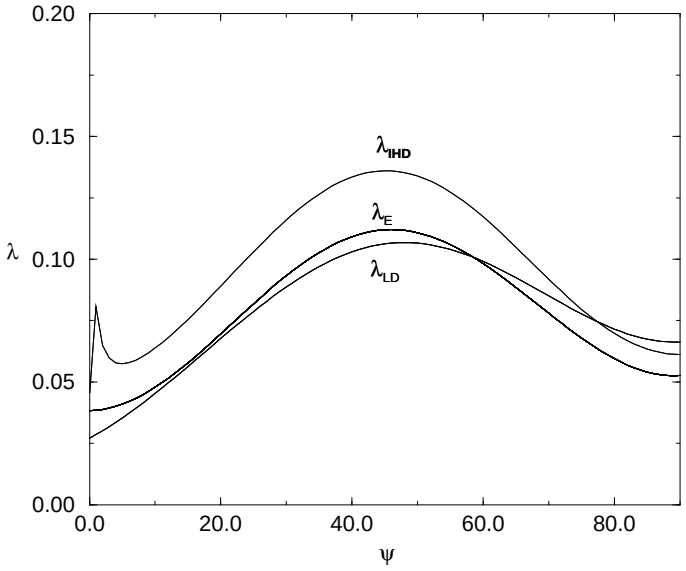

Figure 4. Smallest non-vanishing eigenvalue λ as a function of relative orientation ψ in degrees for $h = 0.2$, $a = 0.2$, $\sigma = 10$. Here the LD formula is marginally better as $a\beta(V_0 - V_2)$ is marginally less than unity as is apparent on inspection of table 8.

Table 8. Barrier heights for $h = 0.2$, $a = 0.2$, $\sigma = 10$.

ψ	$\beta(V_0 - V_1)$	$\beta(V_0 - V_2)$	$a\beta(V_0 - V_2)$
0	14.4	6.4	1.28
15	13.245	5.528	1.1056
30	11.883	4.991	0.9981
45	10.408	4.809	0.9619
60	8.9295	4.9906	0.9981
75	7.5595	5.5280	1.1050
90	6.4	6.4	1.28

of Matkowsky *et al* [19] or other techniques which attempt to provide asymptotic Kramers formulae which are valid for all ranges of the friction for the Klein–Kramers problem (for a review see Büttiker [25], Landauer [26] and Hänggi *et al* [23]). This is, however, likely to be more difficult to carry out than in the Klein–Kramers problem.

6. Validity of asymptotic formulae as a function of the field angle

A feature common to all the results we have presented so far is the departure of the asymptotes calculated from the IHD formula from the exact solution when the field angle is very small so that the problem becomes almost axially symmetric. This is particularly noticeable in the results presented in figure 5 and tables 9 and 10.

It is apparent from figure 5 that in the range 0–10° where one would expect that the departure from axial symmetry is small, that the non-axially symmetric asymptotes equations (18) and (25) depart significantly from the exact solution λ_E. Such asymptotic

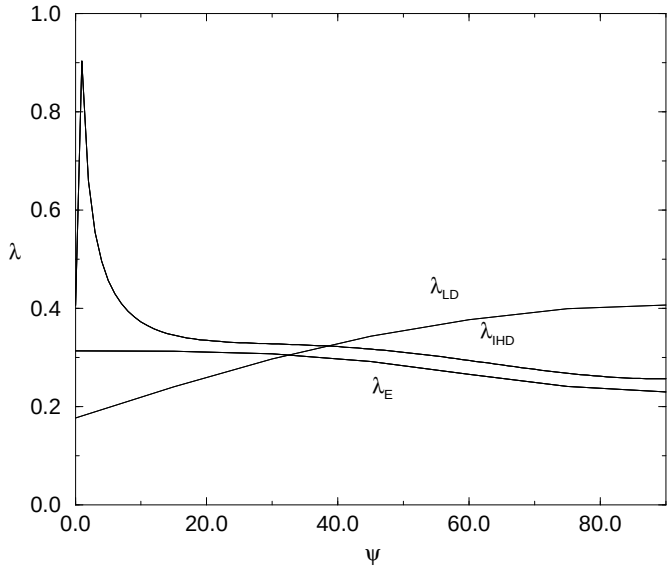

Figure 5. Smallest non-vanishing eigenvalue λ as a function of relative orientation ψ in degrees for $h = 0.2$, $a = 5.0$, $\sigma = 5$. Here the IHD formula is a much better approximation than the LD formula as is to be expected from table 10, except for small angles $\leqslant 10^\circ$ where spurious resonant effects occur as discussed in the text.

Table 9. Values of λ_E, λ_{LD} and λ_{IHD} for $h = 0.2$, $a = 5.0$, $\sigma = 5$.

ψ	λ_E	λ_{LD}	λ_{IHD}
0	0.3131	0.1763	0.4058
15	0.3125	0.2398	0.3452
30	0.3072	0.2970	0.3277
45	0.2914	0.3429	0.3170
60	0.2657	0.3770	0.2938
75	0.2406	0.3990	0.2678
90	0.2300	0.4068	0.2563

Table 10. Barrier heights for $h = 0.2$, $a = 05.0$, $\sigma = 5$.

ψ	$\beta(V_0 - V_1)$	$\beta(V_0 - V_2)$	$a\beta(V_0 - V_2)$
0	7.2	3.2	16
15	6.6223	2.7640	13.82
30	5.9415	2.4953	12.476
45	5.2042	2.4048	12.024
60	4.4648	2.4953	12.476
75	3.7797	2.7640	13.82
90	3.2	3.2	16

behaviour is in essence a consequence of the linearization of the FPE about the minima and the saddle points because for very small angles one is significantly outside the range of validity of the Taylor series expansion of the potential given by equation (16). Here

Table 11. Values of λ_E and λ_{IHD} for $h = 0.1$, $a = 10$, $\sigma = 10$.

ψ	λ_E	λ_{IHD}
0	0.0383	0.0456
1	0.0384	0.0742
2	0.0384	0.0560
3	0.0385	0.0487
4	0.0386	0.0449
5	0.0388	0.0427
6	0.0389	0.0413
7	0.0392	0.0406
8	0.0394	0.0402
9	0.0398	0.0400
10	0.0401	0.0401
11	0.0404	0.0403
12	0.0408	0.0407
13	0.0412	0.0411
14	0.0416	0.0416
15	0.0420	0.0422
16	0.0424	0.0428
17	0.0429	0.0434
18	0.0433	0.0440
19	0.0438	0.0447
20	0.0442	0.0454

it appears that the Brown axially symmetric solution, equations (11) and (13), provides a more accurate approximation to the exact solution λ_E for small angles as is borne out by the results shown in table 11. An interesting feature of figures 1 and 5 (tables 1, 2, 9 and 10) is that the asymptotic eigenvalue yielded by the IHD formula for small angles requires different explanations in each case.

In case 1, the gyroscopically modified well is shallow and the other is deep, hence we have rapid relaxation. In case 5, both wells are comparatively very deep; so that the gyroscopic term must artificially create a spurious resonance between the two deep wells. In each of the cases 1 and 5, we thus have artificial resonance for small ψ, for different reasons, however, essentially because the harmonic oscillator approximation for each cell is in general a poor one, for small ψ, particularly for case 5 (two deep wells) but also for case 1 (one deep well).

The axially symmetric formula equation (13) gives 0.0456 which is, in general, a better approximation than the IHD formula in the small angle region.

We finally remark that unlike the exact solution which is of course valid for all values of the angle ψ, it is impossible (again essentially due to the procedures involved in linearizing the FPE about the minima and the saddle points) to smoothly join the axially and non-axially symmetric asymptotic formulae, equation (11) and equations (18) and (25) as the latter arise from a two variable FPE while the former arises from a single space variable FPE which results from symmetry. This is in marked contrast to the Klein–Kramers problem [5] where the one variable equation arises from the strong damping of the momentum and so the IHD asymptote derived from the Klein–Kramers equation goes over smoothly into the very high-damping asymptote. This mathematical constraint appears to be of little practical consequence, however, as is apparent by inspection of table 11 that in the region 0–4° of smallest departure from axial symmetry, the axially symmetric asymptote appears to give a reasonable approximation to λ_E.

7. Conclusions and experimental parameter values

The derivation of reliable approximate expressions for the relaxation time τ of the magnetic moment of fine particles for non-axially symmetric potentials which we have presented is very important for the modelling of experiments. For example, in the most common experiment used for characterizing fine particle assemblies, which is zero-field cooled magnetization (M_{ZFC}) measurements, the temperature T_m of the maximum of M_{ZFC} is directly related to the blocking temperature T_B. T_B is obtained from a transcendental equation involving [2] τ. An analytical expression for T_B is useful for determining T_m and its variation with experimental parameters and can be derived only if an analytical expression for τ is available.

We have seen that an asymptotic expression for τ can be derived by suitably adapting the original Kramers approach [5, 26] to the calculation of escape rates to non-axially symmetric problems in superparamagnetism. This was achieved by Brown [7, 17] essentially by calculating the flow of representative points across a saddle point of the potential. His general non-axially symmetric IHD result, equation (18), is in essence a particular practical example of the results of Langer [22, 23, 26] for the multireaction coordinate Kramers problem.

In using Brown's results however, certain conditions must be fulfilled. First, for the shallower of the two minima

$$E = \beta[V_0 - V_2] \gg 1. \tag{36}$$

Second, two expressions, equations (18) and (25), can be derived according to the value of $E(a)$ with

$$E(a) = a\beta[V_0 - V_2]. \tag{37}$$

We have seen that the first expression, equation (18), corresponds to the high- or intermediate-damping limit (IHD), that is for $E(a) \gg 1$ and the second to the low-damping limit (LD), that is for $E(a) \ll 1$. However, despite the reasonable results of figures 3 and 4, we do not have a formula which is rigorously valid in the crossover region $E(a) \approx 1$ where the damping roughly lies between the very low-damping and aperiodic regimes. Before we discuss this point at all however, it is important to ascertain if $E(a) \approx 1$ corresponds to an actual case from an experimental point of view or if it is only a theoretical question! In view of these considerations we remark that experiments can mainly investigate the relaxation of the magnetic moment $\boldsymbol{m}$ of the particle when the relaxation time τ is of the order of magnitude of the measuring time τ_m. If $\tau \gg \tau_m$, $\boldsymbol{m}$ appears to be blocked and the measured properties correspond to the static properties of the particles. If $\tau \ll \tau_m$, on the other hand, the average of the properties over the measuring time is measured and so the properties do not depend on τ. Taking into account the values of the various parameters included in the τ expression, the order of magnitude of E varies from 5 (in the case of Mössbauer spectroscopy where the measuring time is very small $\tau_m \approx 10^{-8}$ s to 30 (quasi-static measurements where the measuring time is very large $\tau_m \approx 10^2$ s). This means that the high-barrier condition, equation (36), is always fulfilled so that the factor which determines the choice of formulae is always the a value.

Very few data have been published on a values for fine particles. For γFe_2O_3 particles in a polymer, a ranges between 0.05 and 1 depending on the interparticle interaction strength [27] for interacting $Fe_2\gamma Fe$ particles in an alumina matrix [28] $a \approx 1$. On the other hand for bulk materials, $a \approx 0.01$ for Fe. Furthermore, lower values of a are observed for particular compounds such as yttrium garnet as well as higher values depending on the

compound. We remark nevertheless that, in fine particles, a is a phenomenological constant in the Gilbert equation relative to the whole particle including the defects inherent in the particle surface. Thus, one may expect that the smaller the particle is, the more pronounced will be the increase of a with respect to its bulk value. Therefore, one may reasonably expect that for big particles or particles with few defects a ranges between 0.01 and 1, while for smaller particles or particles with many defects, a ranges between 0.05 and 5. As a consequence, we can see that the three cases are possible from an experimental point of view, viz $E(a) \gg 1$ mainly for quasi-static measurements, $E(a) \ll 1$ mainly for short τ_m such as arise in Mössbauer spectroscopy and $E(a) \approx 1$ for all experiments in which a is small. The fact that $E(a) \approx 1$ is likely to be of experimental significance indicates that the present treatment should be extended (using one of the methods which have been devised [19, 23, 25] to yield a formula for the escape rate in the Klein–Kramers problem which is valid for all values of the friction), to yield a formula for the relaxation time which is valid for all values of a.

In conclusion, we remark that the very low-damping Kramers formula equation (25) for magnetic relaxation has recently been rederived [29] in a very simple fashion using the original Kramers energy diffusion method. The undamped motion is considered as the rotation of a gyro in a uniform field (so that the harmonic oscillator equation applies) rather than the librational motion in a well, as in the original Kramers problem. We also remark that equations (18) and (25) yield fair approximations [30] to the experimental angular variation of the prefactor of Co and BaFeCoTiO particles as well as providing a good description of the behaviour of the prefactor in the non-axially symmetric problem of magnetic relaxation in a cubic anisotropy potential [31].

Acknowledgments

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Note added in proof. Finally the IHD formula (equation (18)), although discussed in the context of aperiodic to overdamped behaviour, will also provide a reasonable approximation to the inverse relaxation time even in the underdamped case as long as [32] the criterion of applicability embodied in the equation (27) is fulfilled.

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