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# Kramers low-damping escape rate for fine ferromagnetic particles by the uniform asymptotic expansion of the first-passage-time method

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**Abstract.** The calculation of the low-damping Kramers escape rate (in the context of magnetic relaxation of single-domain ferromagnetic particles i.e. superparamagnetism) for non-axially-symmetric potentials of the magneto-crystalline anisotropy (which is of importance in view of recent experiments on the superparamagnetic relaxation time of individual small ferromagnetic particles) is considered in detail (in view of the intricate mathematical manipulations which are required) using the uniform expansion of the transition rate method proposed by Matkowsky *et al* (1984 *J. Stat. Phys.* **35** 443) which has been adapted to spins by Klik and Gunther (1990 *J. Stat. Phys.* **60** 473). The results agree with those of Klik and Gunther (up to a factor of 2) and with later calculations of the escape rate using the original Kramers energy diffusion method.

## 1. Introduction

Recent successes [1, 2] 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 time of reversal of the magnetization (Néel time [3]) of an individual particle and in verifying [4] the behaviour of the reversal time as a function of the damping parameter predicted by the Néel–Brown [3] theory have stimulated renewed interest in the Kramers [5, 6] theory of escape of particles over potential barriers (flux over barrier method) due to the shuttling action of the Brownian motion. The Néel–Brown [3] theory is in effect an adaptation to spin relaxation of the Kramers theory so that the verification [4] of that theory in effect confirms the Kramers [5, 6] conception of a thermal relaxation process over a potential barrier.

The Kramers calculation was originally (in order to make rigorous the supposition of Néel [7] that the reversal time was governed by an Arrhenius process [7]) adapted to spin relaxation by Brown [8] who in his first calculation [8] confined himself to axially symmetric (functions of the latitude only) potentials of the magnetocrystalline anisotropy so that the calculation of the reversal time  $\tau$  in the context of the Kramers theory is governed by a one dimensional Fokker–Planck equation with the result that the  $\tau$  value obtained is *valid for all values of the damping parameter* [3]. As a consequence of this very particular result the analogy with the Kramers theory only becomes fully apparent when an attempt [3, 9, 10] is made to treat

*non-axially-symmetric potentials* of the magnetocrystalline anisotropy which are functions of both the latitude and longitude in which context all the particular cases of the escape rate as a function of the friction considered by Kramers will appear. In this context Brown [3, 9, 11] succeeded in giving a formula for the relaxation time for single-domain particles (spins) in the intermediate- to high-damping (IHD) limit (overdamped oscillator) which is the exact analogue of the Kramers IHD formula (his equation (25)) for particles [3]. The calculation is however very much more involved [11] than that for particles by virtue of the facts that it must be carried out in spherical polar co-ordinates, that the undamped motion is *rotational* rather than *librational* in origin [12] and that the inertia of the particle plays no role—the role of inertia being mimicked [3] by the gyromagnetic term in the equation of motion of the magnetisation (see Gilbert's equation [13]).

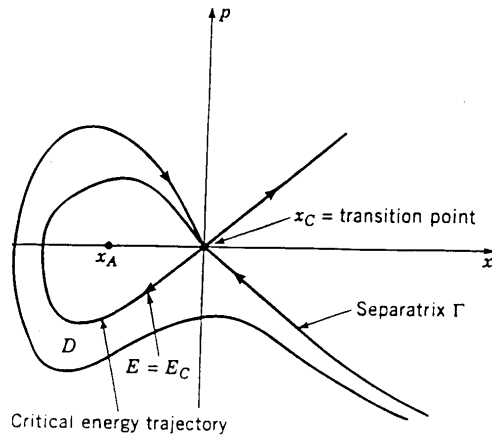
Brown [9] in his 1979 calculation for non-axially-symmetric potentials only considered the IHD case when adapting the Kramers theory to spin relaxation, while Kramers [5] also showed (by essentially treating the low-damping case as a perturbation of the zero-damping case and constructing a diffusion equation for the energy) how a simple formula (his equation (28)) for the inverse relaxation time (escape rate) could be obtained in the very low-damping limit where the condition that the damping times the barrier height is much less than unity holds (with of course the barrier height being very much greater than unity so as to maintain the concept of a lifetime). This defect was remedied by Klik and Gunther [14, 15] 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 analysis thus completed the extension of the ideas of Kramers to spin relaxation, as it was now possible to delineate a region of validity as a function of the friction of the various  $\tau$  formulae for spins just as in the corresponding Kramers formulae for Brownian particles [3, 5]. Subsequently, the low-damping formula has been rederived by Coffey [17] who used the energy diffusion method as slightly modified by Praestgaard and van Kampen [21] (i.e. the virial theorem [12] is invoked) and by Garanin *et al* [18] who (in a discussion of how non-axially-symmetric asymptotes tend to the axially symmetric asymptotes in the appropriate limits) used the Kramers method with a transformation to energy-phase variables as in Risken's book [20] equations (4.130)–(4.132).

The calculation of Klik and Gunther [14, 15] (since it involves an extension to spins of the uniform asymptotic method for the calculation of first passage times which Matkowsky *et al* [16] formulated for the original Kramers problem) involves complicated mathematical manipulations [3] of which essentially no details are given. Hence it is the purpose of this paper to show in detail how the low-damping Kramers escape rate may be derived from the first-passage-time method. The essence of the calculation is the fact that for a domain  $D$  the first passage time is approximately the time for a random walker to reach the boundary of the domain for the first time from a point  $x_0$  well embedded in the domain. Thus the mean first passage time is the average time for the random walker to reach the separatrix manifold between the bounded and unbounded motions for the first time [6].

Matkowsky *et al* [16] have proposed a method which they term the uniform asymptotic expansion of the transition rate which may be described as follows: They first remark that the Kramers escape rate  $\kappa$  is the reciprocal of the mean time to escape the well. This time is the sum of the mean time  $\tau_1(A)$  to reach the trajectory  $E = E_c$  (see figure 1) from the bottom of the well and the mean time to proceed from  $E = E_c$  to  $\Gamma$  (see figure 1) and then escape the well. The latter is twice the mean first passage time  $\tau_2(E_c)$  from  $E_c$  to  $\Gamma$ , since trajectories that reach  $E = E_c$  are equally likely to leave or to return to the well.

Hence a formula for  $\kappa$  is, according to Matkowsky *et al* [16], given by

$$\kappa_{unif} = \frac{1}{\tau_1(A) + 2\tau_2(E_c)}. \quad (1)$$



**Figure 1.** Sketch of the critical energy curve  $E = E_c$  and the separatrix  $\Gamma$  [16] in phase space. The critical energy  $E_c$  is the energy required by a particle to just escape from the well. When a particle reaches this energy it may escape or fall back with equal probability. The separatrix separates the bound and unbound motions. The separation of these curves (greatly exaggerated in the diagram) is infinitesimally small.

Matkowsky *et al* [16] show that for small friction, that is in the low-temperature limit,

$$\tau_1(A) = O\left(\frac{1}{\eta}\right)$$

while

$$\tau_2(E_c) = O(1)$$

so that  $\tau_1(A) \gg \tau_2(E_c)$  thus  $\kappa_{unif} \approx 1/\tau_1(A)$ .

Kramers [5] developed (by writing the Fokker–Planck equation in angle (fast) action (slow) variables and averaging out the fast angle (phase) variable) the formula

$$\kappa_1 = \frac{1}{\tau_1(A)} = \frac{\eta\beta I_c \omega_A}{2\pi} \exp(-\beta E_c) \quad (2)$$

with  $\beta = 1/kT$ , where the system is governed by the Langevin equation

$$\ddot{x} + \eta\dot{x} + \frac{\partial U}{\partial x} = \lambda(t)$$

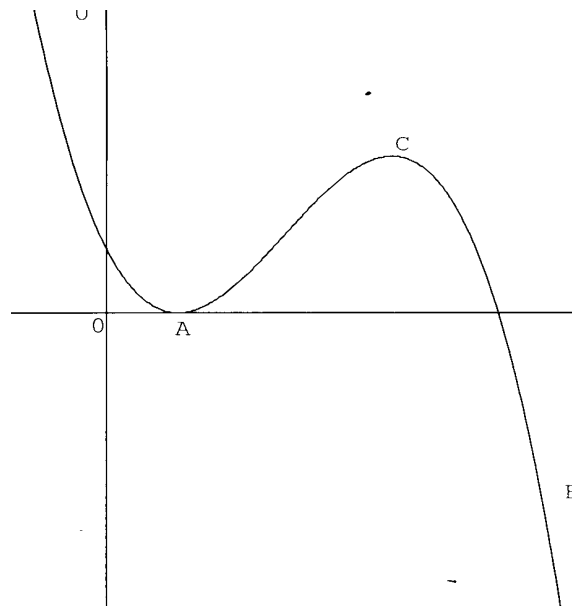
where  $\lambda(t)$  is the white noise term and for convenience we take the mass to be one, also:

$$\begin{aligned} \omega_A &= \sqrt{U''(x_A)} \\ I_c &= \oint_{E=E_c} \dot{x} dx \\ \dot{x} &= \sqrt{2[E_c - U(x)]} \end{aligned}$$

for low values of  $\eta \ll 1$ , while Matkowsky *et al* [16] have shown that the same formula (2) holds for low temperatures and arbitrary  $\eta$ . Matkowsky *et al* [16] and Kramers [5] developed these formulae for point particles with energy given by

$$E = \frac{p^2}{2m} + V(q)$$

where  $p$  is the momentum of the particle and  $q$  is its position and  $m$  is taken equal to unity. In all the calculations a single potential well is assumed (see figure 2) so that a particle once



**Figure 2.** A sketch of the type of well dealt with in the article. When a particle escapes from the well it never returns. A is the minimum of the potential function ( $U$ ). B is the region to which the particles escape. C is the top of the barrier over which the particles escape.

having reached the separatrix never returns which means  $\rho(\Gamma) = 0$  where  $\rho(\Gamma)$  is the density of particles at the separatrix. However, a similar analysis also holds for orientations of the magnetization vector for magnetic particles, the role of the inertia in mechanical problems being mimicked, as stated above, by the gyromagnetic term in Gilbert's equation [13]. Thus in this paper, we shall calculate  $\kappa_1$  by the method of Matkowsky *et al* giving all the details of the considerable mathematical manipulations which are involved.

## 2. The adjoint Fokker–Planck operator and differential equation for the mean first passage time

In order to calculate the mean first passage time, in general (we remark that, although we shall be concerned only with the high-barrier or weak-noise limit here, the concept of a first passage time holds, unlike that of an escape rate, irrespective of the height of any potential barrier that may be involved), it is first necessary to construct the adjoint Fokker–Planck equation (or backward Kolmogorov equation) from the Fokker–Planck (or forward Kolmogorov equation) for the distribution of magnetic moments on the surface of the unit sphere. Risken [20] gives the Fokker–Planck operator in  $n$  dimensions as

$$L_{FP}(\{x\}, t) = -\frac{\partial}{\partial x_i} D_i^{(1)}(\{x\}, t) + \frac{\partial^2}{\partial x_i \partial x_j} D_{ij}^{(2)}(\{x\}, t) \quad (3)$$

where  $\{x\} = x_1, x_2, \dots, x_n$  are the co-ordinates of a point in space at time  $t$  and  $D_i^{(1)}$ ,  $D_{ij}^{(2)}$  are the drift and diffusion coefficients respectively and the Einstein summation convention is used.

In terms of the spherical polar co-ordinates  $(\varphi, p)$  where  $p = \cos \theta$  [3, 14, 15] the operator in equation (3) operating on  $W(\varphi, p, t)$  becomes

$$L_{FP}W(p, \varphi, t) = \frac{\partial}{\partial p} \left[ \frac{\alpha\gamma}{M_s}(1-p^2)H_p + \frac{\gamma}{M_s}H_\varphi \right] W + \frac{\partial}{\partial p} \left[ \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2) \frac{\partial}{\partial p} \right] W \\ + \frac{\partial}{\partial \varphi} \left[ -\frac{\gamma}{M_s}H_p + \frac{\alpha\gamma}{M_s}(1-p^2)^{-1}H_\varphi \right] W + \frac{\partial}{\partial \varphi} \left[ \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2)^{-1} \frac{\partial}{\partial \varphi} \right] W \quad (4)$$

(again  $\beta = 1/kT$ ; see below for the other quantities).  $W(\varphi, p, t)$  is the concentration of particles whose magnetization vector has orientation  $(\varphi, p)$ .

Brown [8] actually derived the Fokker-Planck equation

$$\frac{\partial W}{\partial t} = L_{FP}W$$

from Gilbert's equation

$$\frac{d\mathbf{M}}{dt} = \gamma\mathbf{M} \times \left( -\frac{\partial V}{\partial \mathbf{M}} - \eta \frac{d\mathbf{M}}{dt} \right)$$

where  $V$  is the Gibbs free energy,  $\mathbf{M}$  is the magnetisation vector for a single particle whose magnitude is  $M_s$ ,  $\gamma$  is the gyromagnetic ratio,  $\eta$  is a phenomenological damping constant and

$$\frac{\partial V}{\partial \mathbf{M}} \equiv \frac{\partial V}{\partial M_x} \mathbf{i} + \frac{\partial V}{\partial M_y} \mathbf{j} + \frac{\partial V}{\partial M_z} \mathbf{k}.$$

If we define the friction  $\alpha$  by the equation

$$\alpha = \eta\gamma M_s$$

then an equivalent form for this equation is

$$-\frac{d\mathbf{M}}{dt} = \gamma \left( \mathbf{M} \times \frac{\partial V}{\partial \mathbf{M}} \right) + \frac{\alpha\gamma}{M_s} \left( \mathbf{M} \times \frac{\partial V}{\partial \mathbf{M}} \right) \times \mathbf{M}$$

whence Klik and Gunther [14] wrote down the Langevin equations for a single particle in spherical polar co-ordinates

$$\dot{p} = -\frac{\alpha\gamma}{M_s}(1-p^2)H_p - \frac{\gamma}{M_s}H_\varphi \\ \dot{\varphi} = \frac{\gamma}{M_s}H_p - \frac{\alpha\gamma}{M_s}(1-p^2)^{-1}H_\varphi$$

where  $H$  is the Hamiltonian function equal to the energy  $E$ .

Now

$$\frac{\partial}{\partial p} \left[ \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2) \frac{\partial W}{\partial p} \right] = \frac{\partial^2}{\partial p^2} \left[ \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2)W \right] + \frac{\partial}{\partial p} 2 \frac{1}{\beta} \frac{\alpha\gamma}{M_s} pW.$$

Substituting this into the equation for  $L_{FP}W$  gives:

$$L_{FP}W = \frac{\partial}{\partial p} \left[ \frac{\alpha\gamma}{M_s}(1-p^2)H_p + \frac{\gamma}{M_s}H_\varphi + 2 \frac{1}{\beta} \frac{\alpha\gamma}{M_s} p \right] W + \frac{\partial^2}{\partial p^2} \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2)W \\ + \frac{\partial}{\partial \varphi} \left[ -\frac{\gamma}{M_s}H_p + \frac{\alpha\gamma}{M_s}(1-p^2)^{-1}H_\varphi \right] W + \frac{\partial^2}{\partial \varphi^2} \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2)^{-1}W \quad (5)$$

which is of the form of equation (3) above with drift and diffusion coefficients:

$$D_p^{(1)} = -\frac{\alpha\gamma}{M_s}(1-p^2)H_p - \frac{\gamma}{M_s}H_\varphi - 2 \frac{1}{\beta} \frac{\alpha\gamma}{M_s} p \quad D_\varphi^{(1)} = \frac{\gamma}{M_s}H_p - \frac{\alpha\gamma}{M_s}(1-p^2)^{-1}H_\varphi \\ D_{pp}^{(2)} = \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2) \quad D_{\varphi\varphi}^{(2)} = \frac{1}{\beta} \frac{\alpha\gamma}{M_s}(1-p^2)^{-1} \quad D_{p\varphi}^{(2)} = D_{\varphi p}^{(2)} = 0.$$

Now the backward Kolmogorov equation is, according to Risken [20]

$$\frac{\partial}{\partial t'} P(\{x\}, t | \{x'\}, t') = -L_{FP}^+(\{x'\}, t') P(\{x\}, t | \{x'\}, t') \quad (6)$$

$$L_{FP}^+(\{x'\}, t') = D_i^{(1)}(\{x'\}, t') \frac{\partial}{\partial x'_i} + D_{ij}^{(2)}(\{x'\}, t') \frac{\partial^2}{\partial x'_i \partial x'_j} \quad (7)$$

whence the Fokker–Planck adjoint operator  $L_{FP}^+$  is given by:

$$L_{FP}^+ = D_p^{(1)} \frac{\partial}{\partial p'} + D_\varphi^{(1)} \frac{\partial}{\partial \varphi'} + D_{pp}^{(2)} \frac{\partial^2}{\partial p'^2} + D_{\varphi\varphi}^{(2)} \frac{\partial^2}{\partial \varphi'^2} \quad (8)$$

(since  $D_{p\varphi}^{(2)} = D_{\varphi p}^{(2)} = 0$ ), so that

$$\begin{aligned} L_{FP}^+ = & \left[ -\frac{\alpha\gamma}{M_s} (1 - p'^2) H_{p'} - \frac{\gamma}{M_s} H_{\varphi'} - 2 \frac{1}{\beta} \frac{\alpha\gamma}{M_s} p' \right] \frac{\partial}{\partial p'} \\ & + \left[ \frac{\gamma}{M_s} H_{p'} - \frac{\alpha\gamma}{M_s} (1 - p'^2)^{-1} H_{\varphi'} \right] \frac{\partial}{\partial \varphi'} \\ & + \frac{1}{\beta} \frac{\alpha\gamma}{M_s} (1 - p'^2) \frac{\partial}{\partial p'^2} + \frac{1}{\beta} \frac{\alpha\gamma}{M_s} (1 - p'^2)^{-1} \frac{\partial^2}{\partial \varphi'^2}. \end{aligned} \quad (9)$$

The partial differential equation for the mean first passage time is then in terms of the source polar co-ordinates  $(\varphi', p')$  as in Risken [20], chapter 8, equation 8.15(a)

$$L_{FP}^+(\{x'\}) \tau(\{x'\}) = -1 \quad (10)$$

which must be solved subject to the boundary conditions that  $\tau(\{x'\})$  must vanish at the saddle point  $\{x\}_m$  (which is an absorbing point or trap); furthermore, since the poles of the sphere are reflecting boundaries situated at  $p = \pm 1$ , the probability current must vanish at the poles.

The backward operator (which refers to the evolution of the system starting from the source point) is written in terms of the source spherical polar co-ordinates  $\{x'\}$  while the forward operator is written in terms of the field co-ordinates  $\{x\}$ . In general this equation may only be solved in closed form if the magnetic moment is a function of the angle  $\theta$  only, whence the first mean passage time may be written in terms of quadratures as described by Coffey [3]. The resulting formula for the mean first passage time is then valid for all values of the damping parameter  $\alpha$  (frequently called  $a$ ). In the general case, where the distribution function depends on both  $\theta$  and  $\varphi$ , the mean first passage time is not usually used (because of the difficulties involved in integrating partial differential equations when more than one space variable is involved); rather the smallest non-vanishing eigenvalue  $\lambda_1$  of the Fokker–Planck equation is calculated. The inverse of this in the high-barrier limit is then the normalized relaxation time, where the relaxation time itself is  $\tau \approx 2\tau_N/\lambda_1$ .

The above discussion pertains to the exact calculation of the mean first passage time. Here we are only interested in the mean first passage time for very weak damping (where  $\tau_2$  is neglected) so that we may use a method (based on a uniform asymptotic expansion of the mean first passage time) which has been developed by Matkowsky *et al* [16] and which is described below.

### 3. Formal expression for the mean first passage time from the uniform asymptotic method

Equation (10) now allows us, following Klik and Gunther [14, 15], to write down a formal expression for the mean first passage time  $\tau_1$  for spins in the high-barrier and very low-dissipation limit for non-axially-symmetric potentials, in a manner analogous to that used by Matkowsky *et al* to treat the Kramers very low-damping case for particles. Just as for

particles we will assume a single potential well (see figure 2) so that a spin having reached the separatrix never reverses. The extension to the actual bistable or multistable potentials characteristic of magnetic relaxation may be achieved by extending the arguments given in section D, equations 4.51 *et seq.* of Hänggi *et al* [6].

According to Matkowsky *et al* [16] in the context of particles and Klik and Gunther [14, 15] in the context of spins, the contour of critical energy,  $E = E_c$ , which passes through the saddle point, lies within the boundary layer near the separatrix,  $\Gamma$ , separating (taking the spin example) the clockwise and anti-clockwise spins. Thus the uniform asymptotic expansion method relies on the introduction of a domain,  $Q$ , such that  $E < E_c$ , so that the spin cannot reverse on the interior of  $Q$ , and  $E = E_c$  on the boundary,  $\partial(Q)$ . It is assumed that the boundary,  $\partial(Q)$ , is so close to the separatrix,  $\Gamma$ , that the passage time,  $\tau_2$ , from  $\partial(Q)$  to  $\Gamma$  may be ignored to the first order in temperature, i.e. the low-temperature, weak-noise limit, in comparison to the mean time,  $\tau(\varphi, p)$  (i.e.  $\tau_1$ ), to reach the boundary  $\partial(Q)$  starting from a point  $(\varphi, p)$  well embedded in  $Q$ . Thus, in equation (10), following the method of [14]–[16], we introduce an exponentially large quantity,  $\tau(Q)$ , independent (because the noise is assumed to be very weak) of the starting point  $(\varphi', p')$  in  $Q$ , with

$$\tau(\varphi', p') = \tau(Q)u_T(\varphi', p') \tag{11}$$

and  $\sup_Q\{u_T(\varphi', p')\} = 1$ .

Multiplying equation (10) across by  $e^{-\beta H}$  and integrating over  $Q$  ([20] p 182) then yields

$$\iint_Q e^{-\beta H} L_{FP}^+ \tau(\varphi', p') dp' d\varphi' = - \iint_Q e^{-\beta H} dp' d\varphi'. \tag{12}$$

Now using equations (11) and (12), we have:

$$- \iint_Q e^{-\beta H} dp' d\varphi'' = \tau(Q) \iint_Q e^{-\beta H} L_{FP}^+ u_T(\varphi', p') dp' d\varphi' \tag{13}$$

since  $\tau(Q)$  is constant on  $Q$ .

Thus

$$\tau(Q) = - \frac{\iint_Q e^{-\beta H} dp' d\varphi'}{\iint_Q e^{-\beta H} L_{FP}^+ u_T(\varphi', p') dp' d\varphi'}. \tag{14}$$

Equation (14) is the leading term in the uniform asymptotic expansion of the first passage time of Matkowsky *et al* [16] for the problem at hand. The next step in the calculation is to express the denominator of the right-hand side of equation (14), which is a surface integral over  $Q$ , as a line integral using Stokes' theorem. This calculation is rather intricate, so we present it in detail in appendix A and simply give the main steps in the calculation below:

#### 4. Expression of the denominator of equation (14) as a line integral using Stokes' theorem

The first step in this calculation is to write out the denominator in equation (14) explicitly as follows:

$$\begin{aligned} \iint_Q e^{-\beta H} L_{FP}^+ u_T dp' d\varphi' &= \iint_Q \left\{ e^{-\beta H} \left[ - \frac{\alpha\gamma}{M_s} (1 - p'^2) H_{p'} - \frac{\gamma}{M_s} H_{\varphi'} - 2p' \frac{1}{\beta} \frac{\alpha\gamma}{M_s} \right] \frac{\partial u_T}{\partial p'} \right. \\ &+ e^{-\beta H} \left[ \frac{\gamma}{M_s} H_{p'} - \frac{\alpha\gamma}{M_s} (1 - p'^2)^{-1} H_{\varphi'} \right] \frac{\partial u_T}{\partial \varphi'} \\ &\left. + e^{-\beta H} \left[ \frac{1}{\beta} \frac{\alpha\gamma}{M_s} (1 - p'^2) \frac{\partial^2 u_T}{\partial p'^2} + \frac{1}{\beta} \frac{\alpha\gamma}{M_s} (1 - p'^2)^{-1} \frac{\partial^2 u_T}{\partial \varphi'^2} \right] \right\} dp' d\varphi'. \tag{15} \end{aligned}$$



equation (14) may then be written with the aid of Stokes's theorem (details in appendix A) as

$$\tau(Q) = - \frac{\iint_Q e^{-\beta H} dp' d\varphi'}{\frac{1}{\beta} \frac{\alpha \gamma}{M_s} \oint_{\partial(Q)} e^{-\beta H} \left[ (1-p'^2) \frac{\partial u_T}{\partial p'} d\varphi' - (1-p'^2)^{-1} \frac{\partial u_T}{\partial \varphi'} dp' \right]} \quad (16)$$

which is an expression for the first mean passage time,  $\tau(Q)$ , in the limit of high barriers essentially in terms of the quantity  $u_T$ ;  $u_T$  must now be expressed in terms of known quantities. To do this, we need to construct a boundary layer approximation to  $u_T$  near  $E = E_c$  by introducing the stretching transformation:

$$\eta = \beta(E_c - E) = \beta(E_c - H). \quad (17)$$

The calculations for  $u_T$  in the boundary layer (using the dimensionless energy variable  $\eta$ ) are again rather involved; thus they are presented in detail in appendices B and C.

### 5. Final result for the mean first passage time using the stretching transformation

Since

$$u_T = 1 - e^{-\eta}$$

(see appendix C) we have

$$\frac{\partial u_T}{\partial p'} = e^{-\eta} \frac{\partial \eta}{\partial p'} = e^{-\eta} (-\beta H_{p'}) \quad \text{and} \quad \frac{\partial u_T}{\partial \varphi'} = e^{-\eta} \frac{\partial \eta}{\partial \varphi'} = e^{-\eta} (-\beta H_{\varphi'}).$$

So the denominator in equation (16) becomes:

$$\begin{aligned} & \frac{1}{\beta} \frac{\alpha \gamma}{M_s} \oint_{\partial(Q)} e^{-\beta H} e^{-\beta E_c} e^{\beta H} [-(1-p'^2)\beta H_{\varphi'} d\varphi' + (1-p'^2)^{-1}\beta H_{p'} dp'] \\ &= - \frac{\alpha \gamma}{M_s} e^{-\beta E_c} \oint_{\partial(Q)} [(1-p'^2)H_{p'} d\varphi' - (1-p'^2)^{-1}H_{\varphi'} dp'] \\ &= - \frac{\gamma}{M_s} \Delta E e^{-\beta E_c} \end{aligned} \quad (18)$$

where [14, 15].

$$\Delta E \equiv \alpha \oint_{\partial(Q)} [(1-p'^2)H_{p'} d\varphi' - (1-p'^2)^{-1}H_{\varphi'} dp']$$

and  $\alpha$  is the friction (see the Gilbert equation above).

$\Delta E$  [6] is the energy loss per cycle of the almost periodic motion at the saddle point which follows by taking the time average of the rate of change of angular momentum. Equation (18) represents the final simplification of the denominator.

The surface integral in the numerator in equation (16) may be approximately evaluated using the method of steepest descents as follows:

We expand  $H$  as a Taylor series about the minimum

$$H = E_0 + \frac{(p-p_0)^2}{2!} E_{pp}^0 + \frac{(\varphi-\varphi_0)^2}{2!} E_{\varphi\varphi}^0$$

where  $E_0$  is the value of the energy at the minimum,  $E_{pp}^0$ ,  $E_{\varphi\varphi}^0$  are the partial derivatives of the energy function evaluated at the minimum, and we have chosen a system of co-ordinates in which the second-order mixed partial derivatives vanish at the minimum [19].

We shall now assume that most of the particles stay in the well  $E < E_c$  and that the number at large distances from the minimum is negligible. So we may extend the double integral over  $Q$  to a double integral over the entire sphere without serious error. We further assume that

instead of integrating over  $p$  from  $-1$  to  $+1$  that we can integrate from  $-\infty$  to  $+\infty$ . We also assume that we can integrate over  $\varphi$  from  $-\infty$  to  $+\infty$  instead of  $0$  to  $2\pi$ .

So the numerator of the right-hand side of equation (16) becomes:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta E_0} e^{-\frac{1}{2}\beta(p'-p_0')^2 E_{pp}^0} e^{-\frac{1}{2}\beta(\varphi'-\varphi_0')^2 E_{\varphi\varphi}^0} dp' d\varphi' \approx e^{-\beta E_0} \frac{2\pi}{\beta \sqrt{E_{pp}^0 E_{\varphi\varphi}^0}} \quad (19)$$

and the final formula for the mean first passage time from the minimum to the critical energy curve in accordance with the equation

$$\kappa = \frac{1}{\tau_1(A)}$$

(combining equations (18) and (19)) is:

$$\tau(Q) = \frac{M_s}{\gamma} \frac{2\pi}{\beta \Delta E} \frac{1}{\sqrt{E_{pp}^0 E_{\varphi\varphi}^0}} e^{\beta(E_c - E_0)}$$

which on noting that the well angular frequency is given by

$$\omega_1 \equiv \frac{\gamma}{M_s} \sqrt{E_{pp}^0 E_{\varphi\varphi}^0}$$

becomes

$$\tau(Q) = \frac{2\pi}{\omega_1} \frac{1}{\beta \Delta E} e^{\beta(E_c - E_0)} \quad (20)$$

which differs from equation 4.5 of Klik and Gunther [14] by a factor of  $1/2$ , a correction which has been checked with and agreed to by Dr Klik (Klik I 1997 personal communication).

We remark that equation (20) has been derived under the assumption that all spins are absorbed at the boundary, i.e. having reached the separatrix they never return to their original orientation. In practise the potential in superparamagnetism will have several states of stability. For the purposes of illustration it is useful to consider a symmetric bistable potential which arises if a transverse field is applied to a system with simple uniaxial anisotropy. Here it may be shown that the Kramers escape rate is, in the low damping limit,

$$\kappa = \frac{\omega_1}{2\pi} \beta \Delta E e^{-\beta(E_c - E_0)}.$$

This equation takes account of crossings and recrossings of moments in a bistable potential. The escape rate from one of the wells is then

$$\kappa_{one\ well} = \frac{\omega_1}{4\pi} \beta \Delta E e^{-\beta(E_c - E_0)}$$

with corresponding relaxation time

$$\tau_e = \kappa^{-1} = \frac{4\pi}{\omega_1} \frac{1}{\beta \Delta E} e^{\beta(E_c - E_0)}.$$

$\tau$ , as calculated in this equation takes account of crossings and recrossings which occur with probability 0.5. The time to reach the separatrix, which is the quantity calculated in the present paper (where it is supposed that all particles that reach the separatrix never return), is

$$\tau = \frac{\tau_e}{2} = \frac{2\pi}{\omega_1} \frac{1}{\beta \Delta E} e^{\beta(E_c - E_0)}.$$

We have illustrated how the calculation for a single-well potential may be adapted to a symmetric bistable potential. The extension to an asymmetric bistable potential may be carried

out in the manner described in section D of Hänggi *et al* [6] alluded to above. The result, which is similar to that for particles, is

$$\kappa = \beta \frac{\Delta E_1 \Delta E_2}{\Delta E_1 + \Delta E_2} (\kappa_{A \rightarrow B}^{TS} + \kappa_{B \rightarrow A}^{TS})$$

where

$$\kappa_{A \rightarrow B}^{TS} = \frac{\omega_1}{2\pi} e^{-\beta(E_c - E_1)}$$

$$\kappa_{B \rightarrow A}^{TS} = \frac{\omega_2}{2\pi} e^{-\beta(E_c - E_2)}$$

$E_i$  is the value of the energy at the minimum in well number  $i$  and  $\Delta E_i$  is the energy loss per cycle at the saddle point for particles in well  $i$ .

## 6. Conclusion

In this paper in view of the extreme importance of accurate theoretical expressions for the superparamagnetic relaxation time for the purpose of interpretation of experimental results on individual small ferromagnetic particles [1, 2] we have given in detail the calculation of the low-damping Kramers escape rate using the uniform asymptotic expansion of the transition rate proposed by Matkowsky *et al* [16] and adapted to spins by Klik and Gunther [14]. The analysis in this paper provides the details of the complicated mathematical manipulations which are required in order to establish the low-damping formula for spins and which have not been given hitherto. The results of the present detailed analysis verify the calculations of Klik and Gunther and are in agreement with derivations of the low-damping formula using the entirely different energy diffusion method of Kramers as adapted to spins which have been independently carried out by Coffey using the method of Praestgaard and van Kampen [17] and by Garanin *et al* (to be published) using a method involving a change of variables to energy and phase.

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## Appendix A. Derivation of equation (16) from equation (14)

We expand the terms on the right-hand side of equation (15) as follows

$$-e^{-\beta H} \frac{\alpha \gamma}{M_s} (1 - p'^2) H_{p'} \frac{\partial u_T}{\partial p'} = \frac{\alpha \gamma}{M_s} kT (1 - p'^2) \frac{\partial e^{-\beta H}}{\partial p'} \frac{\partial u_T}{\partial p'} \quad (\text{A1})$$

$$-\frac{\gamma}{M_s} H_{\varphi'} e^{-\beta H} \frac{\partial u_T}{\partial p'} = \frac{1}{\beta} \frac{\gamma}{M_s} (-\beta H_{\varphi'} e^{-\beta H}) \frac{\partial u_T}{\partial p'} = \frac{1}{\beta} \frac{\gamma}{M_s} \frac{\partial e^{-\beta H}}{\partial \varphi'} \frac{\partial u_T}{\partial p'} \quad (\text{A2})$$

$$-2p' \frac{1}{\beta} \frac{\alpha \gamma}{M_s} e^{-\beta H} \frac{\partial u_T}{\partial p'} = + \frac{1}{\beta} \frac{\alpha \gamma}{M_s} \left\{ \frac{\partial}{\partial p'} (1 - p'^2) \right\} e^{-\beta H} \frac{\partial u_T}{\partial p'} \quad (\text{A3})$$

$$\frac{\gamma}{M_s} H_{p'} e^{-\beta H} \frac{\partial u_T}{\partial \varphi'} = - \frac{1}{\beta} \frac{\gamma}{M_s} (-\beta H_{p'} e^{-\beta H}) \frac{\partial u_T}{\partial \varphi'} = - \frac{1}{\beta} \frac{\gamma}{M_s} \frac{\partial e^{-\beta H}}{\partial p'} \frac{\partial u_T}{\partial \varphi'} \quad (\text{A4})$$

$$-e^{-\beta H} \frac{\alpha \gamma}{M_s} (1 - p'^2)^{-1} H_{\varphi'} \frac{\partial u_T}{\partial \varphi'} = \frac{1}{\beta} \frac{\alpha \gamma}{M_s} (1 - p'^2)^{-1} \frac{\partial e^{-\beta H}}{\partial \varphi'} \frac{\partial u_T}{\partial \varphi'}. \quad (\text{A5})$$

Referring to the first term in the final square bracket of the above double integral on the right-hand side of equation (15) as (A6), and to the second term as (A7),

$$\text{collecting together (A1) + (A3) + (A6) yields : } \frac{1}{\beta} \frac{\alpha\gamma}{M_s} \frac{\partial}{\partial p'} \left[ (1 - p^2) e^{-\beta H} \frac{\partial u_T}{\partial p'} \right]$$

$$\text{collecting together (A5) + (A7) yields : } \frac{1}{\beta} \frac{\alpha\gamma}{M_s} \frac{\partial}{\partial \varphi'} \left[ (1 - p^2)^{-1} e^{-\beta H} \frac{\partial u_T}{\partial \varphi'} \right]$$

$$\text{collecting together (A2) + (A4) yields : } \frac{1}{\beta} \frac{\gamma}{M_s} \left[ \frac{\partial e^{-\beta H}}{\partial \varphi'} \frac{\partial u_T}{\partial p'} - \frac{\partial e^{-\beta H}}{\partial p'} \frac{\partial u_T}{\partial \varphi'} \right].$$

So

$$\begin{aligned} \iint_Q e^{-\beta H} L_{FP}^+ u_T \, dp' \, d\varphi' &= \frac{1}{\beta} \frac{\alpha\gamma}{M_s} \iint_Q \left\{ \frac{\partial}{\partial p'} \left[ (1 - p^2) e^{-\beta H} \frac{\partial u_T}{\partial p'} \right] \right. \\ &\quad \left. + \frac{\partial}{\partial \varphi'} \left[ (1 - p^2)^{-1} e^{-\beta H} \frac{\partial u_T}{\partial \varphi'} \right] \right\} dp' \, d\varphi' \\ &\quad + \frac{1}{\beta} \frac{\gamma}{M_s} \iint_Q \left[ \frac{\partial e^{-\beta H}}{\partial \varphi'} \frac{\partial u_T}{\partial p'} - \frac{\partial e^{-\beta H}}{\partial p'} \frac{\partial u_T}{\partial \varphi'} \right] dp' \, d\varphi'. \end{aligned}$$

Now on applying Stokes' theorem in a plane [22, 23] (also known as Green's theorem in a plane) to the second integral on the right-hand side we find

$$\begin{aligned} \frac{1}{\beta} \frac{\gamma}{M_s} \iint_Q \left[ \frac{\partial e^{-\beta H}}{\partial \varphi'} \frac{\partial u_T}{\partial p'} - \frac{\partial e^{-\beta H}}{\partial p'} \frac{\partial u_T}{\partial \varphi'} \right] dp' \, d\varphi' \\ = \frac{1}{\beta} \frac{\gamma}{M_s} \oint_{\partial(Q)} e^{-\beta H} \left[ \frac{\partial u_T}{\partial \varphi'} d\varphi' + \frac{\partial u_T}{\partial p'} dp' \right] = \frac{1}{\beta} \frac{\gamma}{M_s} \oint_{\partial(Q)} e^{-\beta H} du_T \end{aligned}$$

and, since on  $\partial(Q)$  we have  $H = E_c = \text{constant}$ , we find

$$\frac{1}{\beta} \frac{\gamma}{M_s} \iint_Q \left[ \frac{\partial e^{-\beta H}}{\partial \varphi'} \frac{\partial u_T}{\partial p'} - \frac{\partial e^{-\beta H}}{\partial p'} \frac{\partial u_T}{\partial \varphi'} \right] dp' \, d\varphi' = \frac{1}{\beta} \frac{\gamma}{M_s} e^{-\beta E_c} \oint_{\partial(Q)} du_T = 0.$$

Again, applying the same theorem to the first integral on the right-hand side above we find

$$\begin{aligned} \frac{1}{\beta} \frac{\alpha\gamma}{M_s} \iint_Q \left\{ \frac{\partial}{\partial p'} \left[ (1 - p^2) e^{-\beta H} \frac{\partial u_T}{\partial p'} \right] + \frac{\partial}{\partial \varphi'} \left[ (1 - p^2)^{-1} e^{-\beta H} \frac{\partial u_T}{\partial \varphi'} \right] \right\} dp' \, d\varphi' \\ = \frac{1}{\beta} \frac{\alpha\gamma}{M_s} \oint_{\partial(Q)} \left[ (1 - p^2) e^{-\beta H} \frac{\partial u_T}{\partial p'} d\varphi' - (1 - p^2)^{-1} e^{-\beta H} \frac{\partial u_T}{\partial \varphi'} dp' \right] \end{aligned}$$

and the desired result (equation (16)) follows.

## Appendix B. Justification for the use of the boundary layer approximation for $u_T$

The Langevin equations in the low-temperature, zero-noise limit arise from Gilbert's equation [13] and are [14]:

$$\begin{aligned} \dot{p} &= -\frac{\alpha\gamma}{M_s} H_p (1 - p^2) - \frac{\gamma}{M_s} H_\varphi \\ \dot{\varphi} &= \frac{\gamma}{M_s} H_p - \frac{\alpha\gamma}{(1 - p^2)M_s} H_\varphi. \end{aligned} \tag{B1}$$

Now  $u_T$  [16] satisfies approximately the equation:

$$L_{FP}^+ u_T = 0$$

which yields (cf equation (9))

$$\left[ \frac{\alpha\gamma}{M_s}(1-p^2)H_p + \frac{\gamma}{M_s}H_\varphi + 2\frac{\alpha\gamma}{\beta M_s}p \right] \frac{\partial u_T}{\partial p} + \left[ -\frac{\gamma}{M_s}H_p + \frac{\alpha\gamma H_\varphi}{M_s(1-p^2)} \right] \frac{\partial u_T}{\partial \varphi} - \frac{\alpha\gamma}{\beta M_s}(1-p^2) \frac{\partial^2 u_T}{\partial p^2} - \frac{\alpha\gamma}{\beta M_s} \frac{1}{1-p^2} \frac{\partial^2 u_T}{\partial \varphi^2} = 0 \quad (\text{B2})$$

which in the low-temperature limit further reduces to

$$\left[ -\frac{\alpha\gamma}{M_s}(1-p^2)H_p - \frac{\gamma}{M_s}H_\varphi \right] \frac{\partial u_T}{\partial p} + \left[ \frac{\gamma}{M_s}H_p - \frac{\alpha\gamma}{M_s} \frac{H_\varphi}{1-p^2} \right] \frac{\partial u_T}{\partial \varphi} = 0 \quad (\text{B3})$$

and which, using (B1), yields:

$$\frac{\partial u_T}{\partial p} \dot{p} + \frac{\partial u_T}{\partial \varphi} \dot{\varphi} = 0.$$

Hence we have proved that

$$\frac{du_T}{dt} = 0 \quad (\text{B4})$$

where  $(\varphi(t), p(t))$  is any trajectory of equations (B1), so  $u_T$  is constant on any such trajectory. Now all such trajectories converge to the point A of stable equilibrium, and since  $u_T$  is continuous for  $E < E_c$

$$u_T(\varphi, p) = u_T(\text{A}) = \text{constant for } E < E_c. \quad (\text{B5})$$

We normalize this constant to 1.

Now  $u_T$  must also satisfy the boundary condition  $u_T = 0$  for  $E = E_c$  (cf the boundary condition after equation (10)). So  $u_T \equiv 1$  cannot be a valid solution near  $E = E_c$ .

This justifies the construction of a boundary layer approximation to  $u_T$  near  $E = E_c$  as carried out in appendix C below.

### Appendix C. Derivation and solution of the boundary layer equation

The partial derivatives of  $\eta$  are

$$\eta_p = -\beta H_p \quad \eta_{pp} = -\beta H_{pp} \quad \eta_\varphi = -\beta H_\varphi \quad \eta_{\varphi\varphi} = -\beta H_{\varphi\varphi}.$$

Also

$$\begin{aligned} \frac{\partial}{\partial p} &= \frac{\partial \eta}{\partial p} \frac{\partial}{\partial \eta} = -\beta H_p \frac{\partial}{\partial \eta} \\ \frac{\partial}{\partial \varphi} &= \frac{\partial \eta}{\partial \varphi} \frac{\partial}{\partial \eta} = -\beta H_\varphi \frac{\partial}{\partial \eta} \\ \frac{\partial^2}{\partial p^2} &= \frac{\partial}{\partial p} \left( \frac{\partial \eta}{\partial p} \frac{\partial}{\partial \eta} \right) = \frac{\partial^2 \eta}{\partial p^2} \frac{\partial}{\partial \eta} + \left( \frac{\partial \eta}{\partial p} \right)^2 \frac{\partial^2}{\partial \eta^2} = -\beta H_{pp} \frac{\partial}{\partial \eta} + \beta^2 H_p^2 \frac{\partial^2}{\partial \eta^2} \\ \frac{\partial^2}{\partial \varphi^2} &= \frac{\partial}{\partial \varphi} \left( \frac{\partial \eta}{\partial \varphi} \frac{\partial}{\partial \eta} \right) = \frac{\partial^2 \eta}{\partial \varphi^2} \frac{\partial}{\partial \eta} + \left( \frac{\partial \eta}{\partial \varphi} \right)^2 \frac{\partial^2}{\partial \eta^2} = -\beta H_{\varphi\varphi} \frac{\partial}{\partial \eta} + \beta^2 H_\varphi^2 \frac{\partial^2}{\partial \eta^2} \end{aligned}$$

so that the equation (B2) for  $u_T$  becomes:

$$\left[ \frac{\alpha\gamma}{M_s}(1-p^2)\beta H_p^2 + 2\frac{\alpha\gamma}{M_s}pH_p + \frac{\alpha\gamma}{M_s} \frac{\beta H_\varphi^2}{(1-p^2)} - \frac{\alpha\gamma}{M_s}(1-p^2)H_{pp} - \frac{\alpha\gamma}{M_s} \frac{H_{\varphi\varphi}}{1-p^2} \right] \frac{\partial u_T}{\partial \eta} + \left[ \frac{\alpha\gamma}{M_s}(1-p^2)\beta H_p^2 + \frac{\alpha\gamma}{M_s} \frac{\beta H_\varphi^2}{(1-p^2)} \right] \frac{\partial^2 u_T}{\partial \eta^2} = 0.$$

Dividing across by  $\beta$ , simplifying and ignoring terms of order  $\beta^{-1}$ , we have:

$$\left[ \frac{\alpha\gamma}{M_s} (1 - p^2) H_p^2 + \frac{\alpha\gamma}{M_s} \frac{H_\phi^2}{1 - p^2} \right] \left( \frac{\partial u_T}{\partial \eta} + \frac{\partial^2 u_T}{\partial \eta^2} \right) = 0$$

yielding the so-called boundary layer equation for  $u_T$

$$\frac{\partial^2 u_T}{\partial \eta^2} + \frac{\partial u_T}{\partial \eta} = 0$$

which must be solved subject to the boundary conditions:

$$\begin{aligned} u_T &= 0 \text{ when } \eta = 0 \\ u_T &\rightarrow 1 \text{ as } \eta \rightarrow \infty \end{aligned}$$

which has solution:

$$u_T = 1 - e^{-\eta}.$$

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