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Langer's Method for the Calculation of Escape Rates and its Application to Systems of Ferromagnets

Gerard Duff

Thesis for the Award of Ph.D

Dublin Institute of Technology

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Supervised by

Dr. David M^{c}Carthy M.Sc, Ph.D.

Abstract

This work is a study of the application of a theory proposed by J. S. Langer (J.S. Langer, Statistical Theory of the Decay of Metastable States, Annals of Physics 54, 258-275 (1969)) for the calculation of the decay rate (relaxation rate) of a metastable state. The theory is set in the context of statistical mechanics, where the dynamics of a system with a large number of degrees of freedom (order 10^{23}) are reduced to N degrees of freedom, where N is small, when a steady state or equilibrium position is maintained by the entire system. In this thesis N equals 1 or 2 degrees of freedom for a single particle and N equals 4 degrees of freedom for two particles with interaction. In particular, we are interested in the mathematical details of the theory when applied to a Single Domain Ferromagnetic Particle in the Intermediate to High Damping limit, which represents one type of statistical mechanical system for which Langer's theory is applicable. We show by example, that the choice of coordinate system in which the ferromagnetic particle's energy function is written, i.e. with $2N$ conjugate spherical polar coordinates, has a direct bearing on the successful application of the theory. We elucidate the mathematical details of the application of Langer's theory to systems of non-interacting particles in the presence of zero and non-zero eigenvalues, with examples therein. Finally, we rigorously apply the theory to a system of interacting ferromagnetic particles.

Declaration

I certify that this thesis which I now submit for examination for the award of Ph.D is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

This thesis was prepared according to the regulations for postgraduate study by research of the Dublin Institute of Technology and has not been submitted in whole or in part for an award of any other Institute or University.

The work reported on in this thesis conforms to the principles and requirements of the Institutes guidlines for ethics in research. The Institute has permission to keep, to lend or to copy this thesis in whole or in part, on condition that any such use of the material be duly acknowledged.

Signature : ..... Date: .....

Gerard Duff

Acknowledgments

I am very much indebted and wish to acknowledge the contribution to the delivering of this thesis made my supervisor Dr. David M^{c}Carthy. Apparently, the role of the researcher is *not* to try to fit a square peg into a round hole. Thanks are due, not only for consistent technical supervision, but also for keeping my mind on the task we set at the start, almost five years ago. This is not just because it was such a long period of time, part of which Dave was quite seriously ill, but rather because the topic of my proposed thesis had to be chopped and changed on a regular basis right from the start. Thankfully, I think we managed to produce a thesis of our own which is unique and a useful contribution to the subject. Thanks to my advisory supervisor, Prof. Daphne Gilbert for her support and encouragement.

Thanks to my family, especially my father without whose support I could not have stayed in school this long.

To all the staff at DIT for reminding me that good science is about diligence and lifestyle.

And last but not least to Sheelagh, thanks for being kind and quirky.

For my two teachers:

Bernadette E. Duff (1940-1989)

and

Michael J. Tuite (1946-2006)

Contents

Chapter 1

Introduction

1.1 Motivation for this work

Since the pioneering work of Néel [1] and Stoner and Wohlwarth [2] at the end of the 1940's, magnetic particles have been the subject of considerable interest to scientists and engineers alike, as the study of their properties has proved to be scientifically and technologically very challenging [3, 4, 5]. In particular it was recognised that a tiny particle, of micrometer size and lower, with a specific orientation of the particle's magnetic moment, has a remnant magnetization [6, 7]. This marked the beginning of the manufacture of huge permanent magnets and also of great strides in the magnetic recording industry. However, despite intense activity during the last few decades, the difficulties in making nanoparticles of good enough quality has slowed the advancement of this field [8].

As a consequence, for 50 years, engineering and science concentrated on the application of these particles above and then near the micrometer scale [8]. In the last decade, this has no longer been the case because of the emergence of new manufacturing techniques which have led to the possibility of making small objects with the required structural and chemical qualities [8, 9, 10]. This is leading to a new understanding of the magnetic behaviour of nanometer scale particles, which is now very important for the development of new fundamental theories of magnetism and in modeling new magnetic materials for permanent magnets or high density recording devices [11].

Fig. (1.1) (taken from [8]) presents a scale of size ranging from macroscopic down to nanoscopic sizes. The unit of this scale (Ref. Fig.1.1) is the number of magnetic moments in a magnetic system. At macroscopic sizes, a magnetic system is described by magnetic domains which are separated by domain walls, known as Bloch walls [12]. Magnetization *reversal* occurs when thermal energy is absorbed by the particle which sets off a kind of reaction, referred to as a nucleation process [13, 14, 15], within the particle and results in a change of direction of its magnetisation. As well as the effects of temperature, the shape, size and surface of the magnetic system and the influence of external fields to which the system may be exposed, will ultimately determine whether the system's magnetic moment changes direction.

Single-domain nanoparticles are arrangements of matter which we may assume are ellipsoidal and have macroscopic dimensions typically of the order 5 to 10

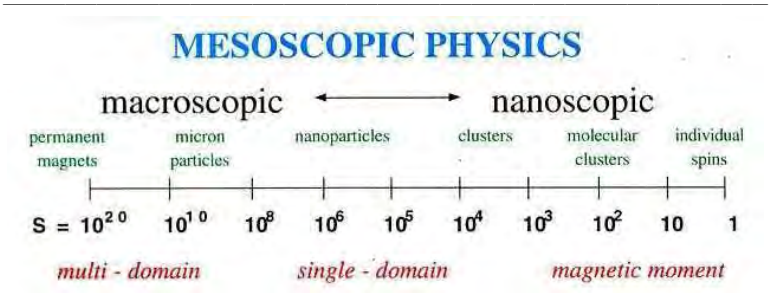

Figure 1.1: Shape and width of domain walls depend on the material of the ferromagnet [8]. Reversal of the magnetic moment may be accessed via propagation and annihilation of domain walls ($10^8 < S \leq 10^{20}$), via uniform rotation ($10^3 < S \leq 10^8$), and quantum tunneling ($1 < S \leq 10^3$) [8]. N.B. **S** is the number of spins or magnetic vectors in the magnetic system which is approximately equal to the number of atoms or molecules in that system [8].

nanometers [16]. They contain approximately $10^4 - 10^5$ individual atoms or molecules, each of which has a magnetic moment [3, 8, 17]. They are sufficiently small that they may be regarded as particles consisting of a single domain having a north and south pole. The particles are usually composed of metals, such as iron, chromium, cobalt, nickel, palladium, and alloys of these [18, 19, 20]. Their size places them above molecules and nanoclusters, but below so-called micron-particles and permanent magnets in the hierarchy of magnetic matter. Reversal of the particles magnetisation vector may be due to thermal fluctuations, referred to as Néel-Brown relaxation [21, 22, 23], or the reversal may be primarily due to the particles (weak) magnetic

anisotropy, referred to as the Stoner-Wohlwarth model [24, 25, 26]. Also, interactions between neighbouring atoms [27, 28] and the presence of external magnetic fields [29, 30, 31] can contribute to the reversal process.

Smaller particles are magnetically more unstable than larger particles [32], this fact can be attributed to the fact that surface effects are more pronounced in smaller particles, since, as their size decreases, their surface to volume ratio increases. So, the *size* of a particle itself, that is, the volume it occupies, has a bearing on (i) the ease with which it may be magnetised (coercivity) [33] (ii) its ability, or otherwise, to maintain that magnetisation (anisoptropy) [34] and (iii) the mechanism by which the reaction proceeds, that is, uniform (coherent) or nonuniform (incoherent) magnetisation reversal [35]. References [33, 34, 35] emphasise that the size and atomic structure of some single-domain particles means they are regarded as being suitable for use in information storage devices since they exhibit long-range stability of the thermally assisted magnetization reversal and thereby that of the information stored in recording media. The storage density may be increased by a factor of 10 by using very small, highly coercive anisotropic particles [36].

So, from one point of view, rather than being a problem, thermally assisted magnetic relaxation may turn out to be a useful phenomenon. The experimental evidence for thermally assisted relaxation is well known [37] and these thermal fluctuations have been detected and are measurable [38, 39] using electron microscopic techniques such as Mössbauer [40, 41] and Lorentz [42, 43, 44] spectroscopies and

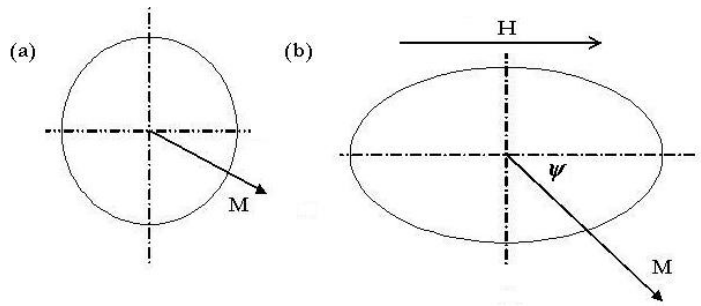

Figure 1.2: A magnetic particle's anisotropy or otherwise may be due to (i) its underlying crystal structure and (ii) its shape. Tiny particles possess a very high degree of *shape anisotropy*. The diagram (a) shows an isotropic particle, i.e. the particle has no preferred direction of magnetisation. A single domain particle is uniformly magnetized with magnetisation along an easy axis (major axis of the ellipsoid) [6]. The diagram (b) is of an anisotropic particle, i.e. one with a preferred direction of magnetisation **M** at an angle ψ from the easy axis (the major axis of the ellipsoid) of magnetisation. The external magnetic field **H** is parallel to the easy axis. For our purposes ($\psi = 0$), so the easy axis, the magnetic vector and the external field are parallel.

also superconducting quantum interference devices ($\mu-$SQUID) [36] based on the Josephson junction [45]. Magnetisation reversal measurements have been detected in biological systems [46], they are used in medicine [47] as a diagnostic tool [48] and a means of cure, and have found applications in chemistry and in electronics [32]. One of the more recent applications is that of high density Magnetic Random Access Memory (MRAM) elements [11, 49]. MRAM is a type of random access memory

based on magnetoresistance and developed for use in the computer industry. It is hoped that MRAM will eventually replace conventional RAM [50]. The small scale of single-domain ferromagnetic particles indicates that they should assist miniturei-sation of the components which go into modern computers. Unlike conventional RAM, MRAM is non-volatile as it does not require a voltage source to maintain it, which is also of interest to computer manufacturers. Therefore, knowledge of the thermally assisted magnetization reversal of small particles is of great importance to the scientific community.

1.1.1 Magnetisation Reversal

With decreasing particle size, different rotation mechanisms dominate the thermally activated magnetization reversal in ferromagnetic particles [10, 35]. For sufficiently small system size, the magnetic moments rotate coherently [10], that is, all moments align themselves simultaneously, which can also be referred to as uniform rotation or uniform relaxation [24, 51]. At this size and scale, surface effects become considerable and affect the magnetization relaxation [27, 28, 52].

The model of uniform rotation (coherent relaxation) of magnetization introduced by Stoner and Wohlfarth [2] and Néel [1, 53, 54] was further developed by Bean and Livingston [56, 57], and Brown [22, 23]. The so-called Néel-Brown model is the simplest classical model describing magnetization reversal. It may be further simplified by considering an assembly of non-interacting particles having energy of

magnetic anisotropy in one direction only, that is, uniaxial anisotropy [32, 38]. The original study by Stoner and Wohlfarth [2] also assumed uniaxial shape anisotropy. Thiaville [55] has generalized the Stoner-Wohlfarth model for an arbitrary effective anisotropy which includes magnetocrystalline anisotropy and surface anisotropy.

The Néel model considers a particle of an ideal magnetic material where exchange energy holds all magnetic moment vectors tightly parallel to each other so the magnetization magnitude and the exchange energy are constant and play no role in the energy minimization. Consequently, there is *competition* only between the anisotropy energy of the particle and the effect of the applied field [8]. As the particle size is increased, the magnetic moments can rotate by a mechanism other than coherent relaxation [8], which for simplicity we will refer to as incoherent relaxation.

1.1.2 Focus of the Thesis

We are primarily concerned with the correct application of a theory, developed by J.S. Langer (1969) [13], for the calculation of the rate of decay of a metastable state in the intermediate to high damping (IHD) limit. The single domain ferromagnet, described above, is a physical *system* containing a metastable state [13, 15, 32]. The metastable state may decay, that is, the particle may relax by escaping from that state to a state of lesser energy and greater stability if it receives enough thermal energy from it's surroundings. The system is in contact with a heat bath which is a source of the required thermal energy.

Although such a magnetic system has no internal dynamics of it's own [13], a single domain particle of sufficiently small size can undergo a type of *Brownian rotation* so that the stable magnetic behaviour characteristic of a ferromagnet *would be destroyed* [1, 12, 32]. The decay process or relaxation process may then be referred as a *homogenous nucleation* [13, 15] as the reversal of the bulk magnetic vector is *initiated* at a small region within the bounds of the system itself. In the absence of the heat bath the system's configuration remains fixed [13]. The system may therefore, be regarded as a canonical ensemble [58] and obey's the laws of statistical mechanics [59, 60, 61, 62].

The systems (i.e. single domain ferromagnets) we shall analyse within Langer's theory, have certain properties which make them of particular interest. Single domain ferromagnetic particles possess a *non-additive* energy function or Hamiltonian (H) [15, 63], where H is a function of a particle's position only. That is, the particle's energy is expressed as a potential energy function in *configuration space*. This is in contrast to the model of Brownian motion for mechanical particles which is a sum of potential energy and kinetic energy expressed in, for example, phase space. Such a phase space energy function may be referred to as an *additive* Hamiltonian [15, 63] of the form

$$H = H(p, q) = T(p) + V(q) \tag{1.1}$$

where p are the generalized momenta, q are the generalised position coordinates, so T and V are the kinetic and potential energies respectively.

Magnetic particles, in contrast, have Hamiltonians composed of potential energy contributions *only*, i.e.,

$$H = H(q) = V(q). \tag{1.2}$$

The particle's motion can, nevertheless, be described in terms of $2N$ canonical variables just as would be expected from a system possessing an additive Hamiltonian [15]. This is because, a particle's momentum p, or rather velocity $\dot{q}$, can be expressed in terms of its position coordinates q [64]. This fact allows for the employment of, in particular, the Boltzmann distribution in the calculation of particle population numbers [15].

Also, Langer's theory, as a multi-dimensional theory, lends itself to the analysis of bi-axial or non-axially symmetric potential energy functions [51] as well as axially symmetric (uniaxial) potential energy functions [23, 65, 66]. Although it is not without its limitations as it does not apply to the low damping regime [67, 68] and requires knowledge of the entire energy landscape, the theory is nevertheless useful and can be compared to other relaxation calculation methods [69, 70, 71, 72, 73, 74, 75].

So, we look at the strengths of the theory as it is an extension to many dimensions of Kramers' one dimensional model [76] in phase space (p, x). We also point out how, due care and diligence must be exercised when applying the theory so that the appropriate coordinate system is chosen at the outset. This is because, when necessary adjustments (substitutions) are made to the energy function, vital

ingredients must remain, that is, technically necessary criteria must remain intact, in order that the present application of Langer's theory be valid and mathematically correct. We emphasise this point for two reasons:

1. since the Hessian matrices in the Taylor series expansions about the saddle point and metastable state are not covariant under a non-linear transformation, and,

2. the energy landscape must possess, at least, a metastable well and a stable well separated by a saddle point *after* the necessary non-linear transformation.

A major aim of this thesis therefore is to apply rigourously Langer's theory to a topical and technologically interesting problem [10, 24, 51, 77, 78]. Specifically, we aim to include surface effects in the calculation of the relaxation time of the particle magnetization [27, 28].

1.2 A Brief History of Relaxation Time

Anyone who has ever dropped an aspirin into a glass of water and watched as it dissolved, or had a slow puncture in an inflated bicycle tyre, or watched a camera-flash go off has had first-hand experience of an equation of the type,

$$\Gamma = A \exp\left\{-\frac{\Delta E}{kT}\right\}. \tag{1.3}$$

This is a decaying exponential, and is characteristic of many physical phenomena. A is a unitless constant, k is Boltzmann's constant and T is the temperature in

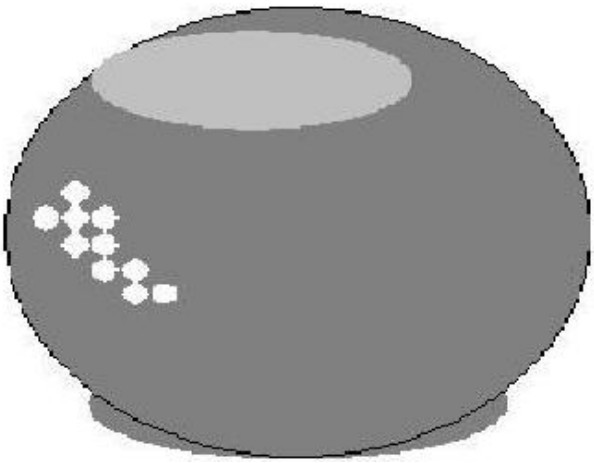

Figure 1.3: Surface effects: The above diagram is a 3-dimensional impression of a bulk (many domain) particle. The white circles represent individual magnetic moments on the particles surface. As the particle size decreases, the particle may be considered as having a single domain but the surface to volume ratio increases. This has a considerable influence on the mechanism by which reversal of the magnetic moment comes about.

degrees Kelvin. ΔE is the activation energy, i.e. the energy required for the system under consideration to undergo a physical or chemical change. For example, ΔE maybe the energy in a chemical bond, or the potential energy of a trapped gas (e.g. characterized by the pressure exerted by a fixed volume of gas per unit area on the wall of its container), or the energy stored in a capacitor.

In the context of chemical reactions, Equation (1.3) is known as the Arrhenius equation, named after the Swedish chemist Svante August Arrhenius $(1859 - 1927)$. The equation was first proposed by the Dutch chemist J. H. van 't Hoff in 1884 [79].

But, in 1889 Arrhenius explained the fact that *chemical reactions* require heat energy to proceed by formulating the concept of activation energy, an energy threshold or barrier that must be overcome before two molecules will react. This became known as Transition State Theory (TST) as the barrier represents an intermediate, highly volatile, transition state between two states of relative stability. The TST version of the Arrhenius Equation is,

$$\Gamma = \Gamma_{TS} = \frac{\omega_A}{2\pi} \exp\left\{-\frac{\Delta E}{kT}\right\} \tag{1.4}$$

(where the subscript TS refers to transition state). The formula has the form of an *attempt frequency* $\frac{\omega_A}{2\pi}$, where ω_A is the angular frequency, times a Boltzmann factor $\exp\left\{-\frac{\Delta E}{kT}\right\}$, which weighs the escape from the well. The attempt frequency, ω_A, is the angular frequency of a particle performing oscillatory motion at the bottom of a well. The barrier arises from the potential function of some external force, which may be electrical, magnetic, gravitational etc. The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate, Γ, at which a reaction evolves (otherwise known as the Escape Rate). The formula does not give a complete description however, as it does not account for interactions with an external energy source or heat bath. Over the succeeding years, many theories and methodologies emerged to calculate Γ for many phenomena. We will outline one such theory in the next section. These theories to which we refer, are based on the more modern ideas governing random variables [80, 81, 82], probability theory and stochastic processes [83, 84, 85]. They are referred to now under the umbrella

term Escape Rate Theory.

In simple terms, Escape Rate Theory is primarily concerned with the calculation of the activation energy E and the prefactor A in Equation (1.3) [13, 14, 32, 86]. In fact, it has been shown [87] that, even when the decay is exponential, the prefactor A, can vary dramatically with changes in the system parameters. Indeed, this seems to be the case for the systems of interacting and non-interacting ferromagnetic particles considered in this thesis.

1.2.1 Early Brownian Motion: learning to crawl

Almost all young students of science will be familiar with the term "Brownian Motion". The definition is part of most introductory courses in science. Personally, I can remember it from preparations for my first state examination. "Brownian Motion is the random movement of tiny particles in a gas or liquid." At the time, reciting that definition to myself over and over, gave me cause to think about my own personal experience and observation. Brownian motion is readily observable, and was first described in a meticulous series of observations by the botanist Robert Brown in 1828 [88]. That Jan Ingen-Housz [1730-1799)], a Dutch-born biologist famous for showing that light was required in photosynthesis, observed and described Brownian motion even earlier, in 1785, is another illustration of *Stiglers Law of Eponymy* [82, 89, 90] which states that no discovery is named after its original discoverer. Ingen-Housz described the irregular movement of coal dust on the surface

of alcohol and therefore has a claim as discoverer of what came to be known as Brownian motion.

When looking through a microscope at grains of pollen suspended in water, Brown noticed that a group of grains always disperses and that individual grains move around continuously and irregularly. Brown originally thought that he had discovered the irreducible elements of a vitality common to all life forms [15, 32]. However, upon systematically observing these irregular motions in pollen from live and dead plants, in pieces of other parts of plants, in pieces of animal tissue, in fossilized wood, in ground window glass, various metals, granite, volcanic ash, siliceous crystals, and even in a fragment of the Sphinx, he gave up the hypothesis that this motion was in some way a manifestation of life. We now know, as postulated by Einstein [91] that Brownian motion is a consequence of the atomic theory of matter. When a particle is suspended in any fluid media, for example air or water, the atoms or molecules composing the fluid hit the particle from different directions in unequal numbers during any given interval. While the human eye cannot distinguish the effect of individual molecular impacts, it can observe the net motion caused by many impacts over a period of time.

1.2.2 Theoretical Brownian Motion: first steps

A rigourous mathematical treatment of Brownian motion was recognised as an important research topic by physicists of the early 20th century, and was theoretically

explained by Einstein in 1905, [91, 92, 93, 94] in terms of a large (Brownian) particle such as a pollen grain suspended in a colloidal suspension. The Brownian particle executes a discrete time random walk in the diffusion limit of a very large number of microscopic steps with the same variance, each taking, on average, the same microscopic time. Mathematically, it is a consequence of the central limit theorem of probability theory, the only random variable being the direction of the walker [15, 32, 63].

Einstein, from this, was able to write down a probability density diffusion equation in configuration space governing the time evolution of the concentration of the Brownian particles. Hence, he was able to calculate the mean square displacement of a Brownian particle regarded as a sphere in terms of the viscous drag (given by Stokes law) imposed by the surroundings, the absolute temperature and the time between successive observations of the displacement of the particle. Einstein envisaged the motion in physical terms as an inescapable consequence of the second law of thermodynamics and as incontrovertible evidence for the existence of atoms, as later (1908) verified experimentally by Perrin [15, 95]. Perrin used Einstein's formula in order to determine Avogadro's number and obtained satisfactory agreement with the accepted value. Einstein's theory, which ignores the inertia of the particle, and its subsequent extensions, which are outlined in the list below, effectively enables the construction of a classical theory of dissipative phenomena [78].

Now following [32] we list the most significant extensions to Transition State

Theory that are of physical interest.

- Smoluchowski (1906) [96], who treated the noninertial Brownian motion in an external potential, such as that due to gravity. Einstein [91] independently proposed a theory of Brownian motions at roughly the same time.

- Langevin (1908) [97, 98], who proceeded from the Newtonian equation of motion of the particle augmented by stochastic terms imposed by the surroundings, essentially considered the position and momentum of the particle as random variables. He rederived Einstein's results (in the non-inertial limit) and must therefore be regarded as the founder of the stochastic differential equations [78].

- Debye (1913), following Einstein's original theory of specific heat, Debye considered the atoms as oscillating independently about their equilibrium positions and applied classical statistics to these oscillators. In the words of Coffey et al [78], Debye considered the non-inertial rotational Brownian motion of a rigid rotator in the presence of an applied alternating electric field for the purpose of explaining dielectric relaxation of polar molecules at high frequencies.

- Ornstein (1917), who included the inertia of the Brownian particle in the formula for the mean square displacement.

- Klein (1921), who gave a probability density diffusion equation (Klein-Kramers equation) for the evolution of the joint probability density function of the

positions and momenta of an assembly of Brownian particles in phase space in the presence of an external potential, so that inertial effects could be included exactly.

- Kramers (1940) [32, 76], who treated noise-activated escape over a potential barrier due to the Brownian motion.

- Doob (1942) [32, 99], who showed that the proper interpretation of the Langevin equation was as an integral equation leading inter alia to the Itô and Stratonovich interpretations of that equation [42]).

- Brinkman (1956) [100], who formulated the Klein-Kramers equation in the presence of an arbitrary potential as a partial differential recurrence relation in configuration space.

- Risken [101] who developed effective matrix continued fraction algorithms for the exact solution of Brinkman's recurrence relation using matrix methods based on a Heisenberg-like formulation of the solution of the problem.

1.3 Relaxation Times: Methods of Calculation

1.3.1 Introduction

The last century has seen an evolution in the application of the theoretical Brownian motion [102]. The theory of Einstein, based on the Smoluchowski equation, and that

of Langevin, based on Newtonian mechanics, have been formulated as differential equations and as integral equations [15, 32, 101, 103]. The evolution, in the context of magnetic and dielectric relaxation [104, 105, 106, 107], has been accompanied by the development of various methods, both numerical and analytical methods [108, 109, 110, 111], for the solution of those differential and integral equations [112, 113]. Some of the methods have been compared by Coffey [30, 114] and by Cregg et al. [115] for the classical theoretical and experimental predictions of *superparamagnetic* relaxation, see Fig.(1.3.1) below, and by Topaler et al. in the quantum framework [116]. As with almost all assumption based theories, the methods are valid for specific damping regimes or values of the equation parameters only [117, 118, 119]. Also the type of energy function, axially symmetric or otherwise, often dictates the use of a particular numerical method or whether an analytical method can be applied [115].

Theorists have sought formulae to bridge the gap between the various damping regimes. Melni'kov and Meshkov [120] have presented a remedy for Kramers' [76] so called turnover problem, the region between low damping [121] and intermediate to high damping. In the context of magnetic particles, M^{c}Carthy [122], Déjardin et al. [123] and Coffey et al. [124, 125] have presented interpolation formula dealing with the so-called Kramers' turnover problem for multidimensional magnetic vectors. The results are in good agreement with the work of Melni'kov and Meshkov for mechanical particles. In fact, the interpolation formulae (crossover formulae) in

[122], across all ranges of damping, were found orginally by Coffey et al. [124, 125] thus solving the Kramers' turnover problem for magnetic particles. Déjardin et al. [123] considered the interpolation of uniaxial and biaxial potential energy functions. Coffey et al. [118, 119, 126] found by numerical methods an exact solution of Brown's differential equation for uniaxial anisotropy and an arbitrary applied field direction. They also derived an asymptotic general solution for the case of large energy barriers in comparison to the thermal energy kT. This asymptotic solution is of particular interest for single domain particle measurements, as they behave as superparamagnets. The results of Coffey et al. [30] are in good agreement with the work of Vouille et al. [49]. Aharoni [127] also gave numerical solutions to Brown's problem which concluded that Brown's assumption of coherent relaxation is not necessarily true for very small magnetic particles.

1.3.2 The Klein-Kramers equation: Application to Reaction Rate Theory

The classical theory of Brownian motion [128] arises via the Langevin equation and the corresponding evolution equation (as a particular form of the Boltzmann equation) for the single particle distribution function in phase space. This type of equation is known as a Fokker-Planck equation (Fokker (1914); Planck (1917) [129]) and is obtained when the collisions of a Brownian particle such as a pollen grain with its surroundings are frequent but weak [78]. The Fokker-Planck equation

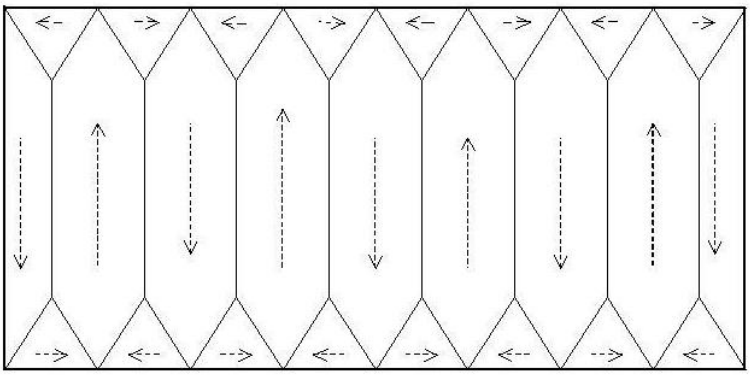

Figure 1.4: Representation of a bulk magnet; If the particle is large enough, domain walls are present and the orientation of each magnetic moment is not uniform, rather it is random. When exposed to a magnetic field of sufficient strength, *almost all* of the magnetic moments align themselves in the bulk magnet, this is referred to as superparamagnetism. If a particle is small enough, the domain walls are not present, referred to as a single domain ferromagnet, and the particle *has the characteristic* of a superparamagnet.

for the phase space (x, p) probability distribution function $f(x, p, t)$ of a Brownian particle of mass m ($m = 1$ in Kramers' paper [76]) moving in an external potential $V(x)$ is known as the Klein-Kramers equation,

$$\frac{\partial f}{\partial t} + \frac{p}{m}\frac{\partial f}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial f}{\partial p} = \frac{\zeta}{m}\frac{\partial}{\partial p}\left(fp + mkT\frac{\partial f}{\partial p}\right) \tag{1.5}$$

where k is Boltzmann's constant, T is the temperature and ζ is a dissipation (damping) parameter. The Klein-Kramers equation may be solved by transforming it, via appropriate orthogonal expansions of the phase space variables, into a set of differ-

ential recurrence relations for the decay functions of the system [78, 130]. These may be represented as matrix continued fractions in the frequency domain [15, 101, 103]. The continued fraction representation has led to many exact solutions, as outlined in Refs. [15, 101, 103].

The same representation may also be obtained directly from the Langevin equation

$$\dot{x}(t) = \frac{p(t)}{m} \quad ; \quad \dot{p}(t) = -\frac{d}{dx}V\left(x(t)\right) - \frac{\zeta}{m}p(t) + \Xi(t) \tag{1.6}$$

by averaging that equation over its realizations in phase space [15]. The Langevin equation is the Newtonian equation of motion of the particle augmented by a systematic frictional force $p(t)$ proportional to the velocity of the particle, superimposed on which is a rapidly fluctuating random force $\Xi(t)$, with both forces representing the effect of the heat bath on the particle. The rapid variation of $\Xi(t)$ can be expressed by,

$$\overline{\Xi(t)\Xi(t')} = 2\zeta kT\delta\left(t - t'\right) \tag{1.7}$$

where the overbar indicates statistical averaging, δ is the Dirac delta function, t and t' are two values of the time and $2\zeta kT$, the spectral density [32], is a centered Gaussian random variable which must obey Isserilis's theorem [131, 133, 132, 134], namely, for $2n$ $\Xi(t)$'s

$$\overline{\Xi\left(t_1\right)\Xi\left(t_2\right)\Xi\left(t_3\right)\ldots\Xi\left(t_{2n}\right)} = \sum \prod_{k_i<k_j} \overline{\Xi\left(t_{k_i}\right)\Xi\left(t_{k_j}\right)} \tag{1.8}$$

and it is assumed that

$$\overline{\Xi(t)} = 0. \tag{1.9}$$

1.3.3 Brief Discussion of Damping Regimes

Kramers [76] considered two main damping regimes. These were Very Low Damping (VLD) and Intermediate to High Damping (IHD). An outline of Kramers' calculations follows this short discussion. Kramers' VLD or energy controlled diffusion regime [78], supposes that the energy trajectories of the Brownian particle in the well closely approximate the undamped periodic motion in the well, i.e., the energy of a particle is almost conserved [78]. The trajectories are almost closed ellipses except for a particular trajectory with energy corresponding to the saddle point energy associated with the transition state. Particles on this particular trajectory, known as the separatrix [32] between the bounded motion in the well and the unbounded motion outside, may, through the action of thermal fluctuations, either escape the well or else may be returned to the depths of the well, with equal probability P, i.e. ($P = 0.5$) for either eventuality. The VLD regime is then defined by the condition that the energy loss per cycle of the almost periodic motion of a particle having the saddle-point energy is much *less than* the thermal energy kT [15].

Unlike in TST, the escape rate, which is now directly proportional to the friction, vanishes in the absence of coupling to the heat bath so reconciling reaction rate theory with the fluctuation-dissipation theorem [78]. Kramers obtained his solution

for the VLD escape rate by first writing the Klein-Kramers equation in energy/phase variables. He then eliminated the fast phase variable by averaging along the energy trajectories, so obtaining a one-dimensional diffusion equation in the slowly diffusing energy variable, which can be solved for the escape rate. In his derivation, the coupling between the conservative and diffusion terms in the Klein-Kramers equation is effectively ignored because the motion is supposed to be almost conservative.

The VHD regime is a limiting case of the IHD regime considered in this thesis. In the VHD regime it is supposed that the damping is so large that the Maxwell-Boltzmann distribution has been quickly attained in the well to a high degree of accuracy. Thus, Kramers was able to derive the Smoluchowski equation which is an *approximate* partial differential equation (diffusion equation) for the evolution of the distribution function in configuration space only. This mechanical particle model is in contrast to the model of magnetic vector rotation described by a single space variable FPE, which is an *exact* equation [125]. Near the barrier top, the distribution function deviates from the Maxwell-Boltzmann distribution due to the slow leaking of particles across the barrier and the potential may be approximated by an inverted parabola. The resulting formula may be used to derive the IHD result which is of the form of the TST result.

Kramers was, however, unable to find asymptotic solutions valid in the so called *Kramers' turnover* (crossover in [122, 125]) region, where the energy loss per cycle of a particle having the saddle point energy is of the order of the thermal energy.

Here, there is coupling between the conservative and dissipative terms in the Klein-Kramers equation, so that the conservative term may no longer be ignored as was done in his solution for the very low damping regime. In the words of Coffey et al. [78], the conservative term vanishes when averaged over the fast variable in the VLD case by the principle of the conservation of density in phase.

As stated previously, the Kramers' turnover problem was solved nearly 50 years later by Mel'nikov and Meshkov [120]. They gave an integral formula bridging the very low and intermediate damping asymptotic solutions simultaneously, establishing a range of validity for the TST solution. Their solution [120, 123, 125] for the energy distribution function, which was obtained by the Wiener-Hopf method, was based on the Green function of an energy/action diffusion representation of the Klein-Kramers equation in the Kramers turnover region. Mel'nikov and Meshkov obtained an integral called the *depopulation factor*, which, when multiplied by the intermediate damping result, yielded a formula that reduced to the VLD formula as the friction coefficient tends to zero, so solving the Kramers turnover problem.

Furthermore, Mel'nikov [112, 113] (see also Meshkov and Mel'nikov [120]) established, in the context of Kramers' Brownian motion model of noise assisted escape, that the TST escape rate is accurate provided the ratio of the thermal energy to the barrier height ΔE is less than the ratio of the friction coefficient ζ to the saddle angular frequency ω_C, with that ratio in turn much less than unity, thus defining the various damping regimes. The intermediate damping result is a particular case

of the IHD formula provided the (barrier height to friction) ratio condition is satisfied. In fact, that result constitutes the absolute lower limit of validity of the IHD solution as a function of friction [78]. Thus, they postulate that a formula valid in all damping regimes may be given by simply multiplying the general IHD result by their bridging integral. See [15] for a discussion of the range of validity of Kramers' formulae.

Comprehensive reviews of applications and developments of Kramers reaction rate theory have been given by Hänggi et al. [135] Mel'nikov [112], Coffey et al. [123, 125] and Pollak and Talkner [136]. These review articles provide a detailed theoretical description of reaction rate theory, a variety of examples of its application and relevant references.

1.3.4 Langer's Method

Another approach to the classical nucleation problem, and the one which is central to this thesis is Langer's theory [14, 137] (referred to in [78] as Langer's imaginary part of the free energy method), which springs from purely thermodynamic equilibrium concepts [138]. The calculation is a generalisation of Becker and Döring's calculation [139, 140] of the rate of condensation of a supersaturated vapour. The basic mathematical technique for this generalization had been described earlier by Landauer and Swanson [141]. Langer [13] formulated the multidimensional (IHD) Kramers' escape rate, which in his treatment is the classical nucleation rate gov-

erning the early stage of a first-order phase transition [142, 143, 144]. As explained earlier, the calculation is more general than that of Kramers' as the Hamiltonian is not necessarily separable and additive [78]. Consequently, Langer's approach is very useful in thermally activated magnetic relaxation of single domain ferromagnetic particles, as noted by Kachkachi [27] and Klik and Gunther [145, 146]. In the context of magnetic relaxation, Langer's formula was derived independently by Brown [23] and has been used by Braun [24, 51] and Kachkachi [27, 28] for the calculation of relaxation times in various magnetic reversal problems in the intermediate to high damping limit.

In Langer's treatment, the energy of the system is first examined to find points (states) of stability and metastability. These states occur near the positions of local minima of the energy function. In passing from one minimum of E to a neighbouring one, the system point is most likely to pass across the lowest intervening saddle point of the function E. It was argued by Langer in [137], and restated in [14], that the correct analytical definition of a metastable state requires its free energy to be a complex number and that the imaginary part of that free energy be proportional to the escape rate. This quantity is part of the prefactor in the multidimensional TST formula for the escape rate [78, 138] and is expressed in terms of the Hessians of the energy function evaluated at the saddle point and the metastable point. The saddle point Hessian possesses at least one negative eigenvalue which is characteristic of a saddle point and indicates motion away from that point [13]. We remark that the

Hessians of the energy function are not covariant under nonlinear transformations of the coordinate system in which the energy function is expressed. Therefore, we require that the coordinate system be chosen at the outset and that the necessary transformations be made *before* embarking on the calculation of the energy Hessians. The rest of the prefactor is expressed as the (unstable) positive eigenvalue characterizing the unstable barrier crossing mode of the set of noiseless Langevin equations of the system linearised about the saddle point. The result is identical to that yielded by multidimensional TST [15]. Thus, to calculate the escape rate, all that is necessary is knowledge of the energy landscape of a system, which is in itself, however, can be a very difficult problem.

1.3.5 The Quantum Treatment of Metastable Decay Rates

One shortcoming, or rather limitation [13] of Langer's theory is that it is purely classical and not quantum mechanical. The quantum theory of the decay rate of a metastable state [147] has been formulated from the string-particle model [78] using normal mode analysis [135, 148, 149, 150, 151]. The theory is a reformulation of classical statistical mechanics [152, 153, 154], in which the motion of the particle is coupled to the degrees of freedom of the heat bath. So it is equivalent to a multidimensional Transition State Theory (TST) rate in which the dissipative motion is modelled in the complete phase space of the system [78].

The resulting decay rate at a finite temperature, based in part on TST, is not

valid for very low values of the friction coefficient ζ. It is valid in the Intermediate-to-High Damping (IHD) Kramers' rate. In the very high damping (VHD) limit, $\zeta >> 1$, the same calculation [15] predicts that the escape rate is inversely proportional to the damping parameter ζ. (The reader is referred to Fig. 1.13.2 of [15] for a schematic representation of the various asymptotic escape rate regimes). The Kramers' turnover problem, based and the quantum Langevin equation [155], has been tackled from a quantum tunnelling persective in [156, 157]. This forms the basis of a subject of much interest, is that, the study of the macroscopic Brownian motion and the interface between the classical and the quantum theories [78, 147, 158].

1.4 A Brief Outline of Kramers' (1940) Calculations

1.4.1 Assumptions made by Kramers'

1. The particles are initally trapped near A (which is a source of probability) see Fig (1.5).

2. The barrier heights are very large compared with kT (Kramers takes k to be 1).

3. In the well, the number of particles with energy between E and $E+dE$, is proportional to $e^{-E/kT}dE$, that is a Maxwell-Boltzmann distribution is attained

in the well.

4. Quantum effects are negligible.

5. The escape of particles over the barrier is very slow so that the disturbance to the Maxwell Boltzmann distribution is almost negligible at all times.

6. Once a particle escapes over the barrier it practically never returns

7. A typical particle of the reacting system may be modelled by the theory of the Brownian motion, including the inertia of the particles.

The barrier height should be of the order of $5kT$, or greater, in order that the Boltzmann distribution may be set up and maintained in the well to a high enough degree of accuracy. Kramers' goal was to calculate the prefactor μ in,

$$\Gamma = \mu \frac{\omega_A}{2\pi} \exp\left\{\frac{-\Delta E}{kt}\right\} \tag{1.10}$$

from a microscopic model of the chemical reaction. The fact that a microscopic model of the reaction system (viz., an assembly of Brownian particles in a potential well) is taken account of in the calculation of the prefactor μ means that the prefactor is closely associated both with the stochastic differential equation underlying the Brownian motion process, which is the Langevin equation for the evolution of the random variables (position and momentum) describing the process, and the associated probability density diffusion equation describing the time evolution of the density of the realisations of these random variables in phase space. This is a

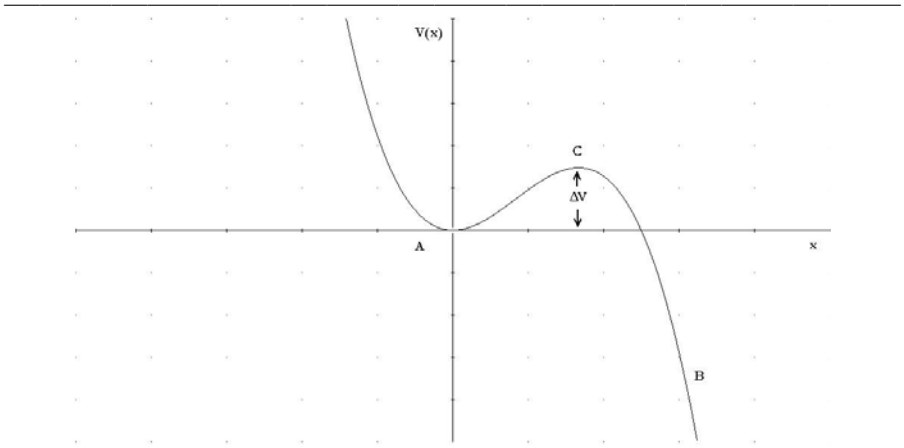

Figure 1.5: Single well potential function as the simplest example of escape over a barrier. Particles are initially trapped in the well near the point A by a high potential barrier at the point C. Particles at A may gain sufficient thermal energy to escape the well over the barrier at C, from which they never return. The barrier at C is assumed to be large enough so the the rate of escape of particles is very small.

(Klein-Kramers) Fokker-Planck equation, which like the Boltzmann equation is a closed equation for the single particle or single system distribution function. We will use as our staring point, the Klein-Kramers equation and derived in [15],

$$\frac{\partial \rho}{\partial t} + \frac{p}{m}\frac{\partial \rho}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial \rho}{\partial p} = \frac{\zeta}{m}\frac{\partial}{\partial p}\left(\rho p + mkT\frac{\partial \rho}{\partial p}\right) \tag{1.11}$$

where ζ is a constant, the drag factor in [32]. By supposing that

$$\frac{\partial \rho}{\partial t} \approx 0 \tag{1.12}$$

in the Klein-Kramers equation, Equation (1.11), i.e. the steady state situation,

Kramers discovered two asymptotic formulae for the escape rate out of a will for a system governed by the Langevin equation. The first is the intermediate-to-high (IHD) formula

$$\Gamma = \frac{\omega_A}{2\pi}\left[\left(1+\frac{\eta^2}{4\omega_C^2}\right)^{\frac{1}{2}} - \frac{\eta}{2\omega_C}\right] e^{-\frac{\Delta V}{kT}} \tag{1.13}$$

where $\eta = \zeta/m$. In the IHD formula, the corresponding μ in the TST result in the prefactor of Equation (1.10) is the positive eigenvalue, characteristic of the unstable direction away from the saddle point, of the Langevin equations, Equation (1.6). The Langevin equations, in the IHD limit, may be linearized about the saddle point by approximating $V(x,p)$ by its Taylor series about the saddle point truncated at the quadratic term. This corresponds in the Klein-Kramers equation to having coefficients which are linear in the momentum and displacement and such an equation is called a linearised Klein-Kramers equation[15]. Equation (1.13) formally holds [125] when the energy loss per unit cycle of the motion of a particle in the well with energy equal to the barrier energy $E_C = \Delta V$, is very much greater than kT. The energy loss per cycle of the motion of a barrier crossing particle is $\eta I(E_C)$, where E_C is the energy contour through the saddle point of the potential and I is the action [125] evaluated at $E = E_C$. This criterion effectively follows from the Kramers very low damping result (see [15]).

The IHD asymptotic formula, which is of primary interest to this thesis, is derived by supposing that,

1. the barrier is so high and the dissipative coupling to the bath so strong that

a Maxwell-Boltzmann distribution always holds to a high degree of accuracy at the bottom of the well and

2. the Langevin equation may be linearised in the region very close to the summit of the potential well, meaning all the coefficients in the corresponding Klein-Kramers equation are linear in the positions and velocities.

If these simplifications can be made, then the Klein-Kramers equation, although it remains an equation in two phase variables (x, p), may be integrated by introducing an independent variable which is a linear combination of x and p, namely $u = p - ax'$ where a is a constant, $x' = x - x_C$ and x_C is the value of the position coordinate at the saddle point. So, the Klein-Kramers equation may be written as an ordinary differential equation in a single variable.

1.4.2 Very Low Damping (VLD) limit

In this case the coupling to the heat bath is very weak, and the assumption that the Maxwell-Boltzmann distribution is valid to a high degree of accuracy in the well is not valid. Hence, Kramers' [32, 76] devised a different treatment for the calculation of the escape rate for values of the friction for so called crossover [32, 122], that is, when $\eta I(E_C) << kT$ where I is the so called action integral taken around the curve of constant energy which passes through the saddle point.

$$I \equiv \oint_{E=E_C} p dx \tag{1.14}$$

where E_C is the energy at the saddle point barrier. Using Equation (1.5) with $\zeta/m = \eta$, we follow the language and logic of Kramers [76]. As usual, a stationary state of diffusion, i.e. $\partial\rho/\partial t = 0$, with current density q corresponds to

$$q = -\eta I\rho + kTI\frac{\partial\rho}{\partial E} \tag{1.15}$$

or,

$$q = -\eta kTIe^{-E/kT}\frac{\partial}{\partial E}\left[\rho e^{E/kT}\right] \tag{1.16}$$

since the continuity equation in I space is

$$\frac{\partial\rho}{\partial t} = -\frac{\partial q}{\partial I}. \tag{1.17}$$

Integrating with respect to E between two points A (at the bottom of the well) and B (some point over and far away from the barrier) along the E coordinate yields,

$$q = \frac{\eta kT\left[\rho e^{E/kT}\right]_A^B}{\int_A^B \frac{1}{I}e^{E/kT}\,dE.} \tag{1.18}$$

Since a Boltzmann distribution is set up in the well, except for a very small neighbourhood around the barrier, the density $\rho = \rho_0 e^{-E/(kT)}$ is almost constant along the line of almost constant energy AB . So, Equation (1.18) may be written

$$q = \eta kT\frac{\left(\rho e^{E/kT}\right)_{\tilde{A}} - \left(\rho e^{E/kT}\right)_C}{\int_{\tilde{A}}^B \frac{1}{I}e^{E/kT}\,dE} \tag{1.19}$$

where $\tilde{A}$ means 'near A'. We must avoid integrating from the point A itself because at this point $E = I = 0$ and the integral would diverge. 'Near A' means a point

with an energy value of the order of the thermal energy kT [15], that is, a point in phase space where the energy is nonzero and the density of states ρ is of the order of the density at A. So,

$$q = \eta kT \rho_A \left[\int_{kT}^{\Delta V} I^{-1} e^{E/(kT)} \, dE \right]^{-1}. \tag{1.20}$$

This integral may be approximated by assuming that it is mainly due to energy values of the order of magnitude kT, so that we may take I to have the value I_C, hence

$$\int_{kT}^{\Delta V} I^{-1} e^{E/(kT)} \, dE \approx \frac{1}{I_C} e^{\Delta V/(kT)} \int_{kT}^{\Delta V} e^{-(\Delta V - E)/(kT)} \, dE \tag{1.21}$$

Now, let $\Theta \equiv \Delta V - E$, so $dE = -d\Theta$. Now take the high barrier limit by integrating over E from $-\infty$ (very near A) to ΔV so that the above integral governing the current q now becomes

$$\int_{kT}^{\Delta V} I^{-1} e^{E/(kT)} \, dE \approx -\frac{1}{I_C} e^{\Delta V/(kT)} \int_{\infty}^{0} e^{-\Theta/(kT)} \, d\Theta = \frac{kT}{I_C} e^{\Delta V/(kT)} \tag{1.22}$$

so the current is

$$q \approx \eta \rho_A I_C e^{-\Delta V/(kT)}. \tag{1.23}$$

The number of particles trapped in the well near A is

$$n_A = \rho_A 2\pi kT/\omega_A, \tag{1.24}$$

and so, the escape rate is given by,

$$\Gamma = \frac{q}{n_A} = \eta \frac{I(E_C)}{kT} \frac{\omega_A}{2\pi} e^{-E_C/(kT)} \tag{1.25}$$

where $E_C = \Delta V$, since the well is at the origin (Fig. 1.4.1), and

$$I\left(E_C\right) = \oint_{E_C} p dx \tag{1.26}$$

is the action of the almost periodic motion on the saddle point energy contour [15]. As discussed in [15] this result holds when η is small compared with ω_A.

Kramers roughly approximates the action of the almost periodic motion at the saddle point by,

$$I_C = 2\pi E_C/\omega_A \tag{1.27}$$

so Equation (1.25) can be written

$$\Gamma = \eta \frac{\Delta V}{kT} e^{-\Delta V/(kT)} \tag{1.28}$$

which can also be written in the form,

$$\Gamma = \frac{\Delta E}{kT} \frac{\omega_A}{2\pi} e^{-\Delta V/(kT)} \tag{1.29}$$

where,

$$\Delta E = \eta I\left(E_C\right) << kT \tag{1.30}$$

is the energy loss per cycle per cycle at the saddle point [32].

1.4.3 Applications of Kramers' Theory

Kramers (1940) [76] based his calculations from the standpoint of non-equilibrium statistical mechanics and also building on the stochastic methods of Langevin [97],

was able to describe much of what is known today of escape rate theory [32, 83, 88]. A full description of Kramers work, the subsequent improvements on it, and the development of escape rate theory, including that for mechanical particles (Brownian motion) can be found in [135] and [32].

From the molecular theory of gases to the movement of electrons in the conduction bands of metals and more recently to define the properties of fullerene (so-called carbon nanotubes, $\mathbf{C}_{60}$) and to develop queuing theory. So today, the theory of Brownian motion is part of the repertoire of most theorists. A full description of Kramers work, the subsequent improvements on it, and the development of escape rate theory, including that for mechanical particles (Brownian motion) can be found in [135] and [32]. The following list [32, 102] indicates the broad range of applicability of the theory of Brownian Motion (or escape rate theory) [32].

1. The current-voltage characteristic of the Josephson tunnelling junction [32].

2. Dielectic and Kerr-effect relaxation of an assembly of dipolar molecules, including inertial effects and dipole-dipole interactions [32, 159, 160].

3. The mobility of superionic conductors.

4. Linewidths in nuclear magnetic resonance.

5. Incoherent scattering of slow neutrons.

6. Cycle slips in second-order phase-locked loops [32].

7. Quantum noise in ring laser gyroscopes [161, 162].

8. Thermalisation of neutrons in a heavy gas moderator [163, 164, 165].

9. The photoelectromotive force in semiconductors.

10. Escape of particles over potential barriers [76, 122].

11. The analytical evaluation of the line shape of single mode semiconductor lasers [166, 167].

12. Motion of single domain charge-density wave-systems [168].

13. Light scattering from macromolecules.

14. Magnetic relaxation of single domain ferromagnetic particles [137].

15. Ferrofluids [169, 170] and plasmas [171, 172].

16. Queueing theory [175].

17. The statistical physics of spin glass [173, 174]

This thesis is primarily concerned with items 10 and 14 in the above list. All of these phenomena in one way or another depend on the nucleation and growth of some characteristic disturbance within a metastable system, for example, condensation of a saturated vapour is initiated by the formation of a sufficiently large droplet of the liquid [13, 78]. If this droplet is big enough it will be more likely

to grow than to dissipate and will bring about condensation of the entire sample. Kramers [76] used as his model of a chemical reaction, a classical particle moving in a one-dimensional potential. The particle is embedded in a heat bath, the source of thermal energy. This is essentially a model of Brownian motion. The heat bath is in perpetual thermal equilibrium at temperature T and it represents all the remaining degrees of freedom of the system [15]. In Kramers' model, the particle coordinate x represents the reaction coordinate, the distance between two fragments of a dissociated molecule. The value of this coordinate at $x = x_A$, the first minimum of the potential, represents the reaction state. The value $x = x_C$, at the saddle point, represents the transition state.

1.4.4 Escape rate in the IHD limit

We write down the Klein-Kramers equation, and follow the summary of Kramers' theory in [15]

$$\frac{\partial \rho}{\partial t} = \frac{\partial V}{\partial x}\frac{\partial \rho}{\partial p} - \frac{p}{m}\frac{\partial \rho}{\partial x} + \eta \frac{\partial}{\partial p}\left(\rho p + mkT\frac{\partial \rho}{\partial p}\right) \tag{1.31}$$

where,

$$V = -\omega_C^2 \left(x - x_C\right)^2 / 2 \tag{1.32}$$

is the Taylor series expansion of $V(x)$ about the saddle point x_C, with $V(x_C) = 0$ taken as the top of the barrier. Considering the process to be quasi-stationary, i.e. very slow diffusion over the barrier, $\frac{\partial \rho}{\partial t} \approx 0$, made possible by the condition

$\Delta V >> kT$, where the barrier height ΔV is given by $V(x_C) - V(x_A)$, the Equation (1.31) reduces to the stationary equation,

$$\omega_C^2 x' \frac{\partial \rho}{\partial p} + p \frac{\partial \rho}{\partial x'} - \eta \frac{\partial}{\partial p} \left(\rho p + kT \frac{\partial \rho}{\partial p} \right) = 0 \tag{1.33}$$

where $x' = x - x_C$ and we have taken $m = 1$. Now, we make the substitution

$$\rho \equiv \zeta \left(x', p \right) \; e^{-(p^2 - \omega_C^2 x'^2)/(2kT)} \tag{1.34}$$

and Equation (1.33) becomes,

$$\omega_C^2 x' \frac{\partial \zeta}{\partial p} + p \frac{\partial \zeta}{\partial x'} + \eta p \frac{\partial \zeta}{\partial p} - \beta kT \frac{\partial^2 \zeta}{\partial p^2} = 0. \tag{1.35}$$

Here $\zeta \left(x', p \right)$, referred to a crossover function [15, 125], is a rapidly varying function which takes on the value zero in the well ($x = x_A = 0$), and 1 over the barrier ($x = x_c$). This leads to the boundary conditions thus; when

$$x = 0, \quad \zeta = 1 \tag{1.36}$$

which is the condition in the well, and as

$$x \to \infty, \quad \zeta \to 0 \tag{1.37}$$

is the condition over the barrier. By inspection we see that, in general, $\zeta =$ constant is a solution of Equation (1.33). This yields a Maxwell Boltzmann distribution. Another solution can be obtained [15, 125] if we assume that the crossover function satisfies the condition

$$\zeta = \zeta(u), \tag{1.38}$$

where $u \equiv p - ax'$ and a is a constant. Substituting Equation (1.38) into Equation (1.33) leads to

$$\left(\omega_C^2 x' - (a-\eta)\, p\right) \frac{\partial \zeta}{\partial u} - \eta k T \frac{\partial^2 \zeta}{\partial u^2} = 0 \tag{1.39}$$

Equation (1.39) can be written as in a single variable u if

$$(a-\eta)\left[p - \frac{\omega_C^2}{(a-\eta)}\right] = \lambda u \tag{1.40}$$

where $\lambda = a - \eta$ is a scaling factor which forces,

$$\omega_C^2 = a\,(a-\eta)\,, \tag{1.41}$$

that is,

$$a = \frac{\eta}{2} \pm \sqrt{\omega_C^2 + \frac{\eta^2}{4}}. \tag{1.42}$$

Equation (1.39) is an ordinary differential equation in u;

$$\eta k T \zeta'' + (a-\eta)\, u \zeta' = 0 \tag{1.43}$$

which has as its solution,

$$\zeta = C' \int_u e^{-\frac{(a-\eta)u'^2}{2\eta k T}} du', \tag{1.44}$$

where C' is a constant of integration. We take the positive square root in Equation (1.42) to get,

$$\lambda_+ = a - \eta = -\frac{\eta}{2} + \sqrt{\omega_C^2 + \frac{\eta^2}{4}}, \tag{1.45}$$

which is positive so the solution for ζ, Equation (1.44), represents a diffusion of particles over the barrier at C. The quantity λ_+ then corresponds to the unique positive eigenvalue of the Langevin equations (Equation 1.6) linearised about C with the white noise term omitted and characterises the unstable barrier crossing mode. Now we apply the boundary conditions (Equations 1.36 and 1.37) to find the limits of integration in Equation (1.44), in u-space these transform as,

$$\zeta \to 0 \quad as \quad u \to -\infty, \tag{1.46}$$

to the right of the barrier in Fig. 1.4.1 and extending the upper limit, that is to the left of the barrier, in the depths of the well, we may extend the upper limit of the integration in Equation (1.44) to $+\infty$ to get,

$$\zeta = C' \sqrt{\frac{2\pi\eta kT}{(a-\eta)}} \tag{1.47}$$

since,

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \tag{1.48}$$

where α is a positive constant. Now the escape rate Γ is

$$\Gamma = \frac{q}{n_A} \tag{1.49}$$

where q is the number of particles passing over the barrier top in unit time and n_A is the number of particles in the well and is given by the integral

$$n_A = \int \int \rho\,(x,p)\ dx\ dp \tag{1.50}$$

where $\rho(x,p)$ is the density of states in phase space. Near the bottom of the well, $x \approx x_A = 0$ in line with Kramers convention, the potential $V(x)$ is approximated by

$$V(x) = -\Delta V + \omega_A^2 x^2/2 \tag{1.51}$$

where $\Delta V = V_{saddle} - V_{min}$ and $V_{saddle} = 0$ as per Fig. 1.5, again in lines with Kramers convention, so,

$$n_A = C' \sqrt{\frac{2\pi\eta kT}{a-\eta}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{p^2+\omega^2 x^2}{2kT}} dp\, dx \tag{1.52}$$

$$n_A = C' \frac{2\pi kT}{\omega_A} \sqrt{\frac{2\pi\eta kT}{a-\eta}} e^{\frac{\Delta V}{kT}}. \tag{1.53}$$

The value of q is obtained [15, 125] by evaluating the integral

$$q = \int_{-\infty}^{\infty} \rho p\, dp \tag{1.54}$$

i.e.

$$q = C' \int_{-\infty}^{\infty} p e^{\frac{p^2}{2\eta kT}} \int_{-\infty}^{p} e^{\frac{(a-\eta)p'^2}{2\eta kT}}\, dp' dp. \tag{1.55}$$

We evaluate this integral by the method of integration by parts. Thus,

$$q = C' \left(-kT \exp\left\{ -\frac{p^2}{2kT} \right\} \int_{-\infty}^{p} \exp\left\{ -\frac{a-\eta}{2\eta kT} s'^2 \right\}\, ds' \,]_{p=-\infty}^{\infty} + kT \int_{-\infty}^{\infty} \exp\left\{ -\frac{p^2}{2kT} \right\} \exp\left\{ \frac{a-\eta}{2\eta kT} p^2 \right\}\, dp \right) \tag{1.56}$$

$$= C' kT \int_{-\infty}^{\infty} \exp\left\{ -\left(\frac{\eta}{2\eta kT} + \frac{a-\eta}{2\eta kT} \right) p^2 \right\} dp \tag{1.57}$$

$$= C'kt \int_{-\infty}^{\infty} \exp\left\{-\frac{a}{2\eta kT}p^2\right\}\, dp \tag{1.58}$$

$$= C'kT\sqrt{\frac{2\pi\eta kT}{a}} \tag{1.59}$$

$$q = C'kT\sqrt{2\pi\eta kT/a}. \tag{1.60}$$

So, putting the Equations (1.49),(1.53) and (1.60) together we have,

$$\Gamma = \frac{\omega_A}{2\pi}\sqrt{1-\eta/a}e^{-\frac{\Delta V}{kT}} \tag{1.61}$$

and substituting the value of a in Equation (1.42) into Equation (1.61) to get,

$$\Gamma = \frac{\omega_A}{2\pi\omega_C}\left(\sqrt{\eta^2/4+\omega_C^2}-\eta/2\right)e^{-\Delta V/kT}. \tag{1.62}$$

This result applies in the IHD limit only as it relies [15, 125] of the assumption that the friction is large enough to ensure that the particles approaching the barrier from the depths of the well are in thermal equilibrium. If the friction coefficient becomes too small, this condition is violated and the IHD solution is no longer valid because the space interval in which the non-equilibrium behaviour prevails exceeds that where an inverted parabola approximation to the potential is valid.

Kramers theory may be verified numerically for large potential barrier heights by calculating the smallest non-zero eigenvalue of the Klein-Kramers equation [125]. This procedure is possible because of the exponential nature of the escape rate, so that, in effect, the smallest eigenvalue of the Fokker-Planck equation is very much smaller than all the higher order eigenvalues, which are associated with the fast

motion in the well. Thus the Kramers escape rate is approximately given by the smallest non-zero eigenvalue if the barrier height is sufficiently large, $> 5kT$. This method has been extensively used to verify the Kramers theory, in particular the application of the theory to magnetic relaxation of single domain ferromagnetic particles.

1.4.5 Range of Validity of Kramers' Formulae

In the limit $\eta \to 0$ the IHD escape rate approaches the TST result [176], Equation (1.63)

$$\Gamma = \Gamma_{TS} = \frac{\omega_A}{2\pi} \exp\left\{-\frac{\Delta E}{kT}\right\} \tag{1.63}$$

It is explained in [15] that the taking of that limit is inconsistent with the derivation of the IHD result, Equation (1.62). This is because [15], in the limit of vanishing friction, the variation of x is not the same as the variation of u. So, the correct formula to use in that limit is the one we have derived for very low damping, Equation (1.25), i.e.,

$$\Gamma = \frac{q}{n_A} = \frac{\eta}{kT} I(E_C) \frac{\omega_A}{2\pi} e^{-E_C/(kT)} \tag{1.64}$$

where,

$$\eta I\left(E_C\right) << kT. \tag{1.65}$$

The barrier height ΔV appears in the prefactor as well as the exponent, so in the VLD limit, Equation (1.64), is useful for obtaining a criterion in terms of the barrier

height for the ranges of friction in which the VLD and IHD Kramers formulae are valid. Kramers was unable to extend the VLD result to values of η which were not small compared with $2\omega_A$, that is the region were the particle undergoes aperiodic damping, referred to as the *crossover region* between the VLD and the IHD. Coffey et al. [15] define the crossover region as

$$\alpha \frac{\Delta V}{kT} \approx 1 \tag{1.66}$$

where $\alpha = \frac{2\pi\eta}{\omega_A}$ is a dimensionless friction parameter.

1.4.6 A Note on the Kramers' Turnover Problem

> "The classical Kramers turnover problem may be considered as solved despite some open questions remaining [136]."

The classical formula of Mel'nikov and Meshkov [120] provides an accurate approximation to the exact rate for all values of damping, including the VHD, VLD, and the Kramers turnover regions and has been repeatedly verified theoretically (see, e.g., Ref. [177, 178, 179, 180], and [71, 181, 182]). Furthermore, Coffey et al. [125] have extended the Mel'nikov method to the magnetization relaxation of single-domain ferromagnetic particles. The calculation of the longest relaxation time for various magnetocrystalline anisotropies has been accomplished in Ref. [65, 183, 184, 185]. According to [78], in spite of very good overall agreement between numerical results and the universal turnover formula, a marked difference of the order of 20%

between numerical and analytical results in the VLD region at moderate barriers exists [177, 178, 179, 180, 182]. In order to improve the accuracy of the universal turnover formula in this region, Mel'nikov [186, 187] suggested a systematic way of accounting for finite-barrier corrections. If such a correction is included, the accuracy of the universal formula is considerably improved (see, e.g., Ref. [70]). We shall now briefly summarize the extension of the Kramers theory to many dimensions due to Langer [13].

1.4.7 A Note on the Applicability of Langer's Theory

The theoretical approach to the nucleation phenomenon developed by Langer [13, 14] is a generalisation of the earlier works of Landauer and Swanson [141], and Cahn and Hilliard [188]. In Langer's work [13, 14], the prefactor A of Equation 1.3 is shown to be a product of the dynamical prefactor κ and the statistical prefactor Ω_0, and both prefactors are determined explicitly in the theory. The dynamical prefactor is related to the growth rate of the critical cluster, and the statistical prefactor is a measure of the phase space volume available for the nucleation. Since the beginning of 1970's, Langer's theory has been applied to describe first order phase transition in various systems including the vapor condensation [189, 190], nucleation in binary fluids [129], solidification of the melt [142], and hadronisation of the quark-gluon plasma [143, 172], produced in heavy-ion collisions.

Langer's theory, as presented here, is applicable only when the reaction rate

is slow, as it requires the system to be in a state of equilibrium or very close to equilibrium at all times. It is applicable only with the damping is sufficient to allow a Maxwell-Boltzmann distribution to built up and to a high degree of accuracy, maintained in the well except to within the region very near to the saddle point barrier. But it wasn't until H.B. Braun's 1994 paper [51], that Langer's theory was used in the context of the relaxation of a magnetic particle in a uniform external magnetic field. Subsequently, in 2001, Coffey, Garanin and McCarthy [125] showed that Kramers' [76] famous expression for the Escape Rate of mechanical particles in a harmonic oscillator potential with $N = 1$ in the Intermediate to High Damping (IHD) limit followed as a special case of Langer's formula [13]. The same paper [125] goes on to derive an IHD formula for magnetic spins with two degrees of freedom. This thesis borrows on the calculation for magnetic spins in [125], improves upon it by allowing for the existence of zero eigenvalues in the Energy Hessian matrix, and applies the results to three different models for a single domain ferromagnetic particle.

1.5 The Layout of this Thesis

In Chapter 2, we describe Langer's Theory and the assumptions therein for the process of magnetic relaxation for a single domain ferromagnet in the intermediate to high damping limit. In Chapter 3, we highlight problems and pitfalls associated

with applying the theory in our calculations, in particular the existence of zero eigenvalues in the Hessian matrix for the energy function of the magnetic particle, and we give the mathematical details of a calculation which leads to a modified version of Langer's formula for the escape rate. Also in Chapter 3, we emphasize how the choice of coordinate system, spherical polar coordinates $(1, \theta, \phi)$, impacts on the subsequent calculation of the prefactor A in the Escape Rate, due to the fact that the Hessian Matrices, which occur in the approximation of the energy E, are not covariant under nonlinear coordinate transformations. Such a transformation is required for our model for a single domain ferromagnetic particle to fit into Langer's formula for the escape rate, Γ. So, as a consequence of the non-covariance of the Hessian matrix, a coordinate system is setup *a priori* and that coordinate system is used throughout the calculations which lead to an expression for Γ.

In Chapter 4, we analyse the energy function for a system of two interacting ferromagnetic particles in a parallel external field with four degrees of freedom. We find that the energy landscape or energy profile (the maxima, minima and saddle points) varies depending on the values of the parameters h, $h \in [0, 1)$ and j, $j \in (0, \infty)$, the reduced external field and the interaction coefficient respectively. We interpret the results of the analysis on the energy function and set about applying Langer's theory to the system. We give an expression for the Escape Rate for values of the interaction coefficient j, when $j > 2$. We also give the total escape rate when $j \in (1, 2)$, which is the sum of three escape rates. Our analysis is not

exhaustive however because, as we can show, the energy profile becomes complicated by a system of fourth order polynomials when $j \in (0, 1]$, which is solvable, but the solutions are complicated in the extreme. Finally, in Chapter 5 we propose some material which could be the subject of further study. Amongst other questions, we present the quartic equations mentioned above, the solutions to which may lead to an expression for the escape rate when $j \in (0, 1]$.

Chapter 2

Langer's Method in the IHD limit with Non-zero Eigenvalues

2.1 Introduction

The theory and method employed by J.S. Langer [13][14] for the calculation of the Escape Rate is set in the context of statistical mechanics. In the two papers cited above, Langer proposes a theory for the decay of a metastable state, a problem which he says "is an old one, (yet) one of the more important outstanding problems in statistical mechanics." In particular, central to the working of the theory is the (classical) Maxwell-Boltzmann distribution function and the equipartition theorem, which is often discussed in books on the subject of Statistical Mechanics and Thermodynamics [58][59][60], and has been described as the pinnacle of Statistical

Mechanics [152] since everything else in the subject is either a climb up to, or a slide down from that pinnacle. We embark on one possible slide down. The Maxwell-Boltzmann distribution function for the density of states $\rho(\boldsymbol{\eta})$ is,

$$\rho(\{\eta_i\}) = \frac{1}{Z}\exp\{-\beta E(\{\boldsymbol{\eta}\})\} \tag{2.1}$$

where, $\beta = \frac{1}{k_B T}$ and k_B is the Boltzmann constant. T is the absolute temperature. E is the total energy. $\boldsymbol{\eta} = \eta_i$, $i = 1, 2, \ldots, N$ are usually taken to be functions of the coordinates, they may or may not be the actual coordinates themselves and η_i, $i = N+1, N+2, \ldots, 2N$ are the conjugate momenta repectively. The density of states $\rho = \rho\{\eta\}$ is a function the finite set of variables $\boldsymbol{\eta}$ where,

$$\{\eta\} = \eta_1, \eta_2, \ldots \eta_N, \eta_{N+1} \ldots \eta_{2N} \tag{2.2}$$

In this thesis, the first N are functions of the spacial coordinates x, y and z, and the second N are the corresponding time derivatives. Frequently, we will take the $\{\eta\}$ to be the unit sphere coordinates $(1, \theta, \phi)$, see Fig 2.1, where

$$\begin{aligned} x &= \sin\theta\cos\phi \\ y &= \sin\theta\sin\phi \\ z &= \cos\theta \end{aligned} \tag{2.3}$$

Even when E depends solely on the coordinates, as opposed to both the coordinates and the momenta, the equipartition theorem holds, as discussed on page 23 of [32]. The right-hand side of Equation (2.1) is the density of states for all states

η_i, $i = 1, 2, \ldots, 2N$. On normalising the density of states in Equation (2.1),

$$\int_{-\infty}^{\infty} \rho\left(\{\eta_i\}\right) d\eta = 1 \tag{2.4}$$

where $d\eta = d\eta_1 d\eta_2 \ldots d\eta_{2N}$ the partition function may be written,

$$Z = \int_{\infty}^{\infty} \cdots \int_{\infty}^{\infty} \exp\left\{-\beta E\left(\{\eta\}\right)\right\} \; d\eta_1 \cdots d\eta_{2N}. \tag{2.5}$$

Combining Equations (2.1), (2.3) and (2.4) yields,

$$\int_{-\infty}^{\infty} \rho\left(\{\eta\}\right) d\eta = \frac{1}{Z} \int_0^{2\pi} \int_0^{\pi} \exp\left\{-\beta E\left(\theta, \phi\right)\right\} \sin\theta d\theta d\phi = 1 \tag{2.6}$$

when $N = 2$. In order to apply Langer's method we make the substitution $p = \cos\theta$ in Equation (2.6) to get

$$\int_{-\infty}^{\infty} \rho\left(\{\eta\}\right) d\eta = \frac{1}{Z} \int_0^{2\pi} \int_{-1}^{1} \exp\left\{-\beta E\left(p, \phi\right)\right\} \; dp \; d\phi. \tag{2.7}$$

The systems under consideration, such as the rotation of the magnetic vector of a single domain ferromagnetic particle, may have a number of degrees of freedom of the order 10^{23} and the problems associated with such systems are therefore, in practice, intractable. Kramers' and Langer's theories treat the collection of particles as an *ensemble* and so certain assumptions are made in that context. In this sense, statistical averaging is employed and is just one of the assumptions of the theory. The theory is concerned with the phenomenon of so called "metastable state" decay. A metastable state may be defined as a state of relative stability. That is, a metastable state is a state that is unstable, but the instability is so small as to be negligible to

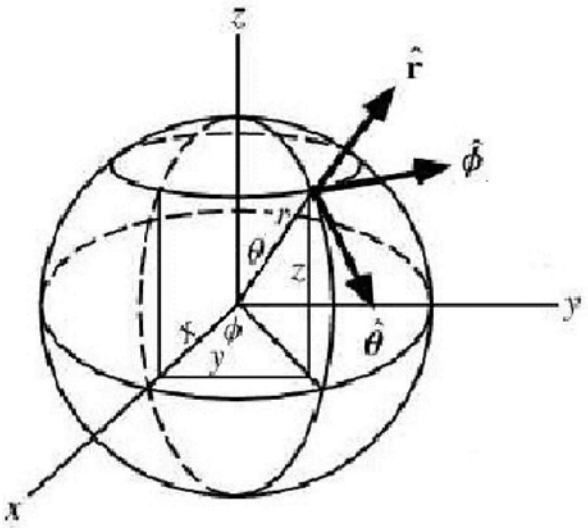

Figure 2.1: Spherical Polar Co-ordinate System: This is the coordinate system used in the application of Langer's method to systems of single domain ferromagnets. It can be simplified by making r =*const*=1. This reduces the number of variables to 2 without loss of generality, since we are interested in the direction of the particle's magnetic moment only and not it's magnitude, which we assume is constant.

a high degree of accuracy. The decay of the metastable state is a type of diffusion process but since the metastable state itself is relatively stable the diffusion process is very slow.

The internal dynamics of the system follow the Gilbert equation,

$$\frac{\partial \mathbf{M}}{\partial t} = \gamma \left(\frac{\partial E}{\partial \mathbf{M}} + \alpha\gamma \frac{\partial E}{\partial \mathbf{M}} \times \mathbf{M} + \mathbf{\Xi} \right) \times \mathbf{M} \tag{2.8}$$

where, $\mathbf{M}$ is the magnetic vector, E is the energy, α and γ are positive constants

and $\boldsymbol{\Xi}$ is the random force. The random force $\boldsymbol{\Xi}$ satisfies the equations [125]

$$\begin{aligned} \overline{\Xi_i(t)} &= 0 \\ \overline{\Xi_i(t)\Xi_j(t')} &= \tfrac{2\alpha k_B T}{v}\delta_{ij}\delta(t-t') \end{aligned} \tag{2.9}$$

where the overbar denotes statistical averaging, v is the particle volume, δ_{ij} is the kronecker delta, and $\delta(t)$ is the Dirac delta function.

In Langer's theory a local minimum is the metastable state, and a minimum of lower energy is the "stable" state. There will be some leakage from the stable state back to the metastable state, but for simplicity we take this to be so small as to be negligible. So, the number of magnetic vectors in each of the minima is more or less constant. That is to say, the stable states are, to a close approximation, in equilibrium in terms of their populations, which follow a Maxwell-Boltzmann distribution. This is an important consideration for the successful application of the theory as it ensures that the process is *almost* stationary. This almost stationary situation is achieved in practice by making the barrier height sufficiently large. The stable states are separated from one another by one or more local maxima, in one-dimension, or by a saddle point or points in two or more dimensions. The saddle points are regarded as energy barriers and there should be only one direction, say η_1 in which the particles may escape the well as this is characteristic of a nucleating process [13]. So, in order for the magnetic vector to change its direction by π radians, that is, to fully switch its direction, it must escape from a well (metastable state) and cross over a potential barrier. If there is more than one barrier the particle will

traverse the lower or lowest of these, provided the difference in heights is large. If there is more than one barrier of the same low energy, the total escape rate will be the sum of the escape rates over each barrier. In order to overcome the barrier(s) the magnetic vector has to receive energy from an external source. The required energy source is present in the heat of the surroundings which acts as a heat bath.

The calculation of the escape rate may be summarised as follows; First, choose a *suitable* coordinate system. Write down the Hamiltonian (total energy function) E in the chosen coordinate system. By taking the first (partial) derivative of E with respect to each of the variables of E, identify the turning points of E. Next, identify the nature of each of the turning points, that is whether they are a maximum or a minimum or a saddle point. Then identify the metastable and stable states by calculating the difference in energy between these states and the saddle point or points. The difference in energy between the saddle point (top of the barrier) and the metastable state is less than that of the barrier and the stable state as in Fig.1.1. Then, based on the following assumptions, calculate the number of particles (magnetic vectors) in the metastable well (N_A) and the current of particles over the barrier q. The escape rate Γ is,

$$\Gamma = \frac{q}{N_A} \tag{2.10}$$

2.2 Assumptions in Langer's Model

Langer makes the following assumptions about systems for which the theory applies;

1. The entire system may be treated as an ensemble and its random field satisfies Equations (2.9).

2. The time development of the entire system obeys a second order differential equation (the Fokker-Planck equation).

3. The energy function E may be approximated by a Taylor series expansion truncated at the second order term.

4. In the metastable well $\rho(\{\eta\}) = \rho_{eq}(\{\eta\})$ to a high degree of accuracy except in a small region near the barrier top.

5. At the barrier we assume that $\rho(\{\eta\})$ can be written as $\rho(\{\eta\}) = \zeta(\{\eta\})\rho_{eq}(\{\eta\})$.

6. Beyond the barrier (point C in Fig.1.1) $\rho(\{\eta\}) = 0$.

where $\rho_{eq}(\{\eta\})$ is the density of states at equilbrium and ζ is a so-called crossover function [76].

When the system is in equilibrium

$$\rho = \rho_{eq} \tag{2.11}$$

where,

$$\rho_{eq}(\{\eta\}) = \frac{1}{Z} \exp\left\{-\beta E(\{\eta\})\right\}. \tag{2.12}$$

It is assumed that ζ can be written as a function of a single variable u [125], where u is a linear combination of the $\{\eta\}$

$$u = \sum_{i=1}^{2N} U_i(\eta_i - \tilde{\eta_i^s}) \tag{2.13}$$

where $\tilde{\eta_i^s}$ is the coordinate of the saddle point and a stationary point of E, and the U_i are constants which in practice can be chosen to suit the conditions of the problem. Also, it can be shown [125] that ζ has the form of the error function,

$$\zeta\left(\{\eta\}\right) = \zeta(u) = \frac{1}{\sqrt{2\pi kT}} \int_u^\infty \exp\left\{-\frac{\beta z^2}{2}\right\} dz. \tag{2.14}$$

2.3 Langer's Theory and Method

Langer [13] considers a system possessing N degrees of freedom and described by a set of $2N$ classical variables $\eta_i, i = 1, 2, 3 \ldots 2N$. The first N elements of $\{\eta\}$, $\{\eta_1, \eta_2 \ldots\ldots \eta_N\}$ being functions of the coordinates and η_{i+N} being the conjugate momentum to η_i.

Let $\rho(\{\eta\}, t)$ be the probability density of states for the $2N$ states as a function of time and the set of state variables $\{\eta\}$. Then the system evolves according to the second order partial differential equation,

$$\frac{\partial \rho(\{\eta\}, t)}{\partial t} = \sum_{i=1}^{2N} \sum_{j=1}^{2N} \frac{\partial}{\partial \eta_i} M_{ij} \left[\frac{\partial E}{\partial \eta_j} + kT \frac{\partial}{\partial \eta_j}\right] \rho(\{\eta\}, t). \tag{2.15}$$

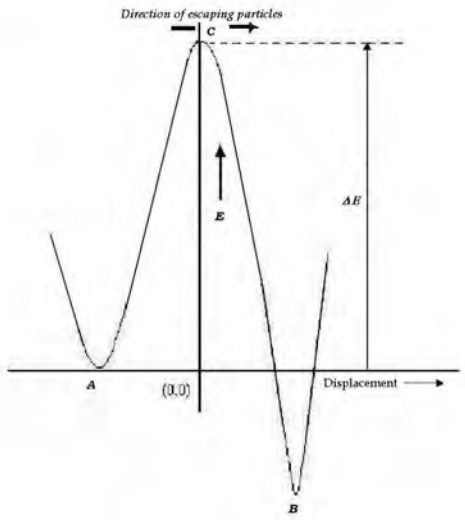

Figure 2.2: Typical Energy profile for systems which may be considered in Langer's theory have a barrier separating two wells. ΔE is the energy required to escape the well at A and traverse the barrier at C. The particle again comes to rest in the lower energy well at B.

Equation (2.15) is known as a Fokker-Planck equation (FPE) [32].

M_{ij} is a real N-square matrix referred to as the transport matrix, for simplicity it is taken to be constant. $\mathbf{M}$ has a symmetric part referred to as the diffusion matrix $\mathbf{D}$,

$$\mathbf{D} = \frac{1}{2}(\mathbf{M} + \mathbf{M}^t), \tag{2.16}$$

and an anti-symmetric part $\mathbf{A}$, referred to as the transport matrix,

$$\mathbf{A} = \frac{1}{2}(\mathbf{M} - \mathbf{M}^t). \tag{2.17}$$

That is,

$$\mathbf{M} = \mathbf{A} + \mathbf{D}. \tag{2.18}$$

(This is slightly different to the way Langer defines the matrix $\mathbf{M}$ but here we follow the definition in [125] so the negative eigenvalue κ in [13] is the positive eigenvalue λ_+ in [125]). The internal dynamics of the system follow Hamiltons equations,

$$\dot{\eta}_i = -\sum A_{ij} \frac{\partial E}{\partial \eta_j}. \tag{2.19}$$

If A_{ij} identically zero, the motion is conservative and D_{ij} satisfies [135]

$$\dot{E} = -\sum_{i,j} \frac{\partial E}{\partial \eta_i} D_{ij} \frac{\partial E}{\partial \eta_j} \leq 0. \tag{2.20}$$

In reference [13], Langer refers to the following two scenarios; if the interaction with the heat bath is much more rapid than the internal dynamics of the system, the diffusion process is dominant and the matrix A_{ij} can be neglected from Equation (2.18), and if the fluctuation rate is very slow, as is the case here, the matrix D_{ij} may be neglected in Equation (2.18) as the system is approaching equilibrium. Also, an important assumption in Langer's theory [13][14] is that we may assume $E(\{\eta_i\})$ $i = 1, 2 \ldots 2N$ the total energy of the system, may be approximated by its Taylor series expansion about the barrier top and also the metastable minimum viz.,

$$E(\eta) \approx E^{(0)} + \frac{1}{2} \left[\sum_{i,j} \frac{\partial^2 E}{\partial \eta_i \partial \eta_j} \bigg|_{\{\tilde{\eta}\}} (\eta_i - \tilde{\eta_i})(\eta_j - \tilde{\eta_j}) \right] \tag{2.21}$$

where $\{\tilde{\eta}\}$ are the coordinates of the metastable minimum or saddle point. $E^{(0)}$ is the *zeroth order energy* at a turning point, that is, $E^{(0)}$ is the energy evaluated at

the turning point of interest. The FPE may be linearised at the saddle point by substituting Equation (2.21) into Equation (2.15) to get

$$\frac{\partial \rho}{\partial t} = \sum_{i,j}^{2N} M_{ij} \frac{\partial}{\partial \eta_j} \left[\sum_{i,j} \frac{e_{ij}}{2} \frac{\partial (\eta_i - \tilde{\eta_i^s})(\eta_j - \tilde{\eta_j^s})}{\partial \eta_i} + kT \frac{\partial}{\partial \eta_j} \right] \rho(\{\eta\}) \tag{2.22}$$

where, $\left\{\tilde{\eta_i^s}\right\}$ is the i^{th} coordinate of the saddle point. And the coefficients e_{ij} are the second order partial derivatives of E evaluated at $\left\{\tilde{\eta_i^s}\right\}$. After performing the partial differentiation Equation (2.22) becomes,

$$\frac{\partial \rho}{\partial t} = \sum_{i,j}^{2N} M_{ij} \frac{\partial}{\partial \eta_i} \left[\sum_{k} e_{jk} (\eta_k - \tilde{\eta_k}) + kT \frac{\partial}{\partial \eta_j} \right] \rho(\{\eta\}). \tag{2.23}$$

The FPE and may be interpreted as a continuity equation in η space,

$$\frac{\partial \rho(\{\eta\}, t)}{\partial t} = - \sum_{i} \frac{\partial J_i}{\partial \eta_i} \tag{2.24}$$

where the $2N$-dimensional probability current density is

$$J_i(\{\eta\}, t) = - \sum_{j=1}^{2N} M_{ij} \left[\frac{\partial E}{\partial \eta_j} + kT \frac{\partial}{\partial \eta_j} \right] \rho(\{\eta\}, t). \tag{2.25}$$

At or near equilibrium,

$$\frac{\partial \rho(\{\eta\}, t)}{\partial t} \approx 0. \tag{2.26}$$

We have two possible solutions to Equation (2.24)

$$J_i(\{\eta\}, t) = \mathbf{0} \tag{2.27}$$

which is the situation in the well, or

$$J_i(\{\eta\}, t) = \boldsymbol{k} \tag{2.28}$$

where $\boldsymbol{k}$ is a nonzero constant vector, which is the situation at the barrier.

The last term in Equation (2.21) may be written in matrix notation as

$$\left(\bar{\eta_1}, \bar{\eta_2}, \cdots, \bar{\eta_{2N}} \right) \begin{pmatrix} E_{\eta_1\eta_1} & E_{\eta_1\eta_2} & \cdots & E_{\eta_1\eta_{2N}} \\ \vdots & & & \vdots \\ E_{\eta_{2N}\eta_1} & E_{\eta_{2N}\eta_2} & \cdots & E_{\eta_{2N}\eta_{2N}} \end{pmatrix} \begin{pmatrix} \bar{\eta_1} \\ \bar{\eta_2} \\ \vdots \\ \bar{\eta_{2N}} \end{pmatrix} \tag{2.29}$$

where $\bar{\eta_i} = \eta_i - \tilde{\eta_i^s}$ $i = 1, \ldots, 2N$. The matrix $\left(E_{\eta_i\eta_j}\right)_{j=1\ i=1}^{2N\ 2N}$ is made up of the second order partial derivatives of E. That is, $\mathbf{E}$ is the Hessian matrix. Here the Hessian matrix is evaluated at $\{\tilde{\eta}\}$, where $\{\tilde{\eta}\}$ is either $\left\{\tilde{\eta^s}\right\}$ or $\left\{\tilde{\eta^A}\right\}$. We will denote the Hessian matrix at the barrier saddle point $\left\{\tilde{\eta^s}\right\}$ by $\mathbf{E}^s$ and at the well minimum $\left\{\tilde{\eta^A}\right\}$ by $\mathbf{E}^A$. Calculation of the escape rate involves finding Hessians, i.e. the determinants of $\mathbf{E}^A$ and $\mathbf{E}^s$. If one or both determinants is zero, calculation of the escape rate is facilitated by the matrices $\mathbf{E}^s$ and $\mathbf{E}^A$ being diagonalised to find their eigenvalues $\lambda_i, i = 1, 2, ..., 2N$. The diagonalisation may be accomplished via an orthogonal transformation of the $\bar{\eta}_i$ coordinates, thus

$$\eta_j - \tilde{\eta}_j \equiv \sum_j S_{ij} x_j. \tag{2.30}$$

where, the column vector, $\mathbf{x} = (x_j)$ is linear combination of the $\{\eta\}$ by the introduction of the diagonalisation matrix S_{ij} which has the property,

$$(S_{ij})^{-1} = (S_{ij})^t \tag{2.31}$$

So,

$$\sum_{i,j}\left[\delta_{i,j}\sum_{k,l}S^{-1}_{ik}E_{\eta_k\eta_l}S_{lj}\right]=\lambda_l \tag{2.32}$$

where $\delta_{i,j}$ is the kronecker delta. The matrix $S_{ij}=\mathbf{S}$ diagonalises the Hessian matrix $\left(E_{\eta_i\eta_j}\right)$ and the columns of S_{ij} are the eigenvectors $\mathbf{x}$, or a constant times the eigenvectors $\mathbf{x}$ which makes,

$$\det\mathbf{S}=1 \tag{2.33}$$

We will follow the notation of [125] in as far as is possible. We remark that Langer's assertion that there should be one and only one negative eigenvalue in the saddle point Hessian is not necessarily true for the magnetic particles with interaction considered in this thesis. The saddle point's negative eigenvalues indicate flow away from the saddle point towards the stable state and the corresponding eigenvectors indicate the direction of the flow. In our calculations we find that there maybe more than one negative eigenvalue at the saddle point, however, the eigenvalues are equal, indicating equal likelihood of flow in those directions.

In the case of a zero eigenvalue occurring in the diagonalised Hessian matrix, the formula for Langer's Escape Rate in [125] breaks down and requires a modification. This problem is commented upon by Langer and he accounts for it in his formula for the escape rate with the factor $\mathcal{V}$ [13], where $\mathcal{V}$ is the volume of the sub-space corresponding to the zero eigenvalue. In his paper [13], Langer refers to this as the particle volume. He goes on to comment that the zeros, if any, are model dependent

and (by) "dealing with the resulting integrals separately" the problem can be fixed up. The problem of zero eigenvalues in the Hessian matrix will be dealt with in the next chapter.

2.4 Calculation of the Escape Rate

The escape rate Γ is [125]

$$\Gamma = \frac{q}{N_A} \tag{2.34}$$

where N_A is the population in the metastable well and q is the current or flux over the barrier (see Fig. 1.1).

$$q = \sum_i \int_{u=0} J_i \left(\{\eta\}\right) d\eta. \tag{2.35}$$

We wish to solve Equation (2.23) when the system is in a steady state (equilibrium position), i.e.

$$\frac{\partial \rho}{\partial t} = 0. \tag{2.36}$$

After a lengthy calculation (see Appendix B) we can write q as,

$$q = \frac{\lambda_+}{2\pi} \left| \det \left[\frac{\mathbf{E}^s}{2\pi kT} \right] \right|^{-\frac{1}{2}} Z^{-1} \exp\left\{-\beta E_c\right\}. \tag{2.37}$$

Note that the calculation in Appendix B is merely a modification of the calculation in reference [125] (page 600) to cater for more than one negative direction indicating motion away from the saddle point to a lower energy position. This is necessary for

certain values of the coefficients j and h in the interacting particle problem which is the subject of Chapter 4. We note that Langer states there should be one and only one negative direction at the saddle point if the process is to be a (so-called) nucleating one. However, we see in Chapter 4, there are two negative and equal directions, indicating two possible directions of motion, each of equal probability. From [125] (and reproduced here in Appendix C) we have the expression for N_A, the population in the well

$$N_A = \left\{ \det \left[(2\pi k_B T)^{-1} \mathbf{E}^A \right] \right\}^{-\frac{1}{2}} Z^{-1}. \tag{2.38}$$

So,

$$\Gamma = \frac{\lambda_+}{2\pi} \left[\frac{\det \left\{ (2\pi k_B T)^{-1} \mathbf{E}^A \right\}}{|\det \left\{ (2\pi k_B T)^{-1} \mathbf{E}^s \right\}|} \right]^{1/2} \exp \left\{ -\beta E_c \right\} \tag{2.39}$$

$$\Gamma = \frac{\lambda_+}{2\pi} \left[\frac{\det \mathbf{E}^A}{|\det \mathbf{E}^s|} \right]^{1/2} e^{-\beta \Delta E} \tag{2.40}$$

where, ΔE is the barrier height and λ_+ is the positive eigenvalue in the Landau-Lifshitz equations, (cf. Appendix A).

As in [27][28] and using Equation (2.5) the Escape Rate may be written in terms of the partition functions as,

$$\Gamma = \frac{\lambda_+}{2\pi} \frac{Z_m}{Z_s} \tag{2.41}$$

where Z_s is the partition function with Energy $E = E_s$ expanded about the barrier saddle point, and Z_m is the partition function with Energy $E = E_m$ expanded about the metastable minimum.

2.4.1 Kramers' formula as a special case of Langer's formula

As a partial justification of Langer's method, we shall use the method to derive the IHD result of Kramers. To recover the Kramers formula, Equation (1.62), by Langer's method, we take $N = 1$, thus the state variables are the position and momentum, so that,

$$\eta_1 = x \quad ; \quad \eta_2 = p \tag{2.42}$$

So, the noiseless Langevin equations are,

$$\frac{dx}{dt} = \frac{p}{m} \quad ; \quad \frac{dp}{dt} = -\frac{\zeta}{m}p - \frac{dV}{dx} \tag{2.43}$$

where, V denotes the potential energy and ζ is the dissipation (friction) coefficient. Now in this case the energy is additive, i.e.

$$E = \frac{p^2}{2m} \pm V(x) \tag{2.44}$$

where the $\pm$ sign is included to emphasise the fact that we have to make the assumption that the potential is an inverted parabola near the saddle point (with potential $-V(x)$) so the energy profile conforms to the situation in Fig. (1.4.1). The Hamilton equations for the problem are,

$$\frac{\partial E}{\partial p} = \frac{p}{m} \quad ; \quad \frac{\partial E}{\partial x} = \frac{\partial V}{\partial x}, \tag{2.45}$$

and,

$$\dot{\eta}_1 = \frac{p}{m} = \frac{\partial E}{\partial p} = \frac{\partial E}{\partial p} \; ; \; \dot{\eta}_2 = -\zeta\frac{p}{m} - \frac{dV}{dx} = -\zeta\frac{\partial E}{\partial \eta_2} - \frac{\partial E}{\partial \eta_1}. \tag{2.46}$$

Hence, the equations of motion in terms of the state variables (η_1, η_2) of the general case of Langer's method above, as,

$$\begin{pmatrix} \dot{\eta}_1 \\ \\ \dot{\eta}_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ \\ -1 & -\zeta \end{pmatrix} \begin{pmatrix} \frac{\partial E}{\partial \eta_1} \\ \\ \frac{\partial E}{\partial \eta_2} \end{pmatrix}. \tag{2.47}$$

and so the transport matrix (M_{ij}) is the negative of the matrix in Equation (2.47), namely,

$$\mathbf{M} = M_{ij} = \begin{pmatrix} 0 & -1 \\ \\ 1 & \zeta \end{pmatrix}, \tag{2.48}$$

whence,

$$\tilde{\mathbf{M}} \equiv -\mathbf{M}^t = \begin{pmatrix} 0 & -1 \\ \\ 1 & -\zeta \end{pmatrix}. \tag{2.49}$$

Here we can take the saddle point as the origin so

$$\overset{S}{\eta_1} = 0. \tag{2.50}$$

The momentum of a particle just escaping over the saddle point is almost zero, so,

$$\overset{S}{\eta_2} \approx 0 \tag{2.51}$$

The Taylor series approximation of the energy function about the saddle point is

$$E = E_C - \frac{1}{2} \sum_{i,j} e_{ij} \left(\eta_i - \eta_i^S\right) \left(\eta_j - \eta_j^S\right) \tag{2.52}$$

which, if we regard the momentum as a constant, is essentially an inverted parabola at the saddle point, which can be seen clearly if we write,

$$E = \frac{p^2}{2m} - \frac{1}{2} m \omega_C^2 x^2, \tag{2.53}$$

or

$$E = \frac{1}{2m}\left(\eta_2 - \eta_2^S\right)^2 - \frac{1}{2}m\omega_C^2\left(\eta_1 - \eta_1^S\right)^2 \tag{2.54}$$

puts the equation in the required form with $E_C = 0$,

$$e_{11} = m\omega_C^2,\ e_{12} = e_{21} = 0\ e_{22} = -\frac{1}{m} \tag{2.55}$$

are the elements of the saddle point Hessian matrix, i.e.,

$$\mathbf{E}^S = \begin{pmatrix} m\omega_C^2 & 0 \\ 0 & -\frac{1}{m} \end{pmatrix} \tag{2.56}$$

Similarly, the energy in the well about the minimum point is approximated as

$$E = E_A + \frac{1}{2}\sum_{i,j} e_{ij}\left(\eta_i - \eta_i^A\right)\left(\eta_j - \eta_j^A\right) \tag{2.57}$$

so the energy Hessian matrix is

$$\mathbf{E}^A = \begin{pmatrix} m\omega_A^2 & 0 \\ 0 & \frac{1}{m} \end{pmatrix} \tag{2.58}$$

The Hessians are

$$\det\left\{\frac{\mathbf{E}^S}{2\pi kT}\right\} = -\frac{\omega_C^2}{2\pi kT}\ \ ;\ \ \det\left\{\frac{\mathbf{E}^\mathbf{A}}{2\pi kT}\right\} = \frac{\omega_A^2}{2\pi kT} \tag{2.59}$$

So,

$$\sqrt{\frac{\det\left\{\frac{\mathbf{E}^\mathbf{A}}{2\pi kT}\right\}}{\left|\det\left\{\frac{\mathbf{E}^S}{2\pi kT}\right\}\right|}} = \frac{\omega_A}{\omega_C} \tag{2.60}$$

Now we determine λ_+. We have the linearised noiseless Langevin equation

$$\begin{pmatrix} \dot{\eta}_1 \\ \\ \dot{\eta}_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ \\ -1 & -\zeta \end{pmatrix} \begin{pmatrix} \frac{\partial E^S}{\partial \eta_1} \\ \\ \frac{\partial E^S}{\partial \eta_2} \end{pmatrix}. \tag{2.61}$$

Now, linearise these equations by substituting Equation (2.54)

$$\begin{pmatrix} \dot{\eta}_1 \\ \\ \dot{\eta}_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ \\ -1 & -\zeta \end{pmatrix} \begin{pmatrix} -m\omega_C^2\eta_1 \\ \\ \frac{1}{m}\eta_2 \end{pmatrix}, \tag{2.62}$$

which can be written as

$$\begin{pmatrix} \dot{\eta}_1 \\ \\ \dot{\eta}_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ \\ -1 & -\zeta \end{pmatrix} \begin{pmatrix} -m\omega_C^2 & 0 \\ \\ 0 & \frac{1}{m} \end{pmatrix} \begin{pmatrix} \eta_1 \\ \\ \eta_2 \end{pmatrix} \tag{2.63}$$

$$\begin{pmatrix} \dot{\eta}_1 \\ \\ \dot{\eta}_2 \end{pmatrix} = \begin{pmatrix} 0 & \frac{1}{m} \\ \\ m\omega_C^2 & -\frac{\zeta}{m} \end{pmatrix} \begin{pmatrix} \eta_1 \\ \\ \eta_2 \end{pmatrix} \tag{2.64}$$

or, with $\mathbf{A}$ denoting the transition matrix

$$\dot{\boldsymbol{\eta}} = \boldsymbol{A}\boldsymbol{\eta} \tag{2.65}$$

with eigenvalue problem,

$$\det\left(\mathbf{A} - \lambda\mathbf{I}\right) = 0 \tag{2.66}$$

$$\lambda\left(\lambda + \kappa\right) - \omega_C^2 = 0, \tag{2.67}$$

where $\kappa = \frac{\zeta}{m}$ (β in [15])

$$\lambda_\pm = \pm\sqrt{\omega_C^2 + \frac{\kappa^2}{4}} - \frac{\kappa}{2} \tag{2.68}$$

We pick the positive root so that the solution (which is now always positive) corresponds to the unstable barrier crossing mode, hence

$$\lambda_+ = \sqrt{\omega_C^2 + \frac{\kappa^2}{4}} - \frac{\kappa}{2} \tag{2.69}$$

So the escape rate is,

$$\Gamma = \frac{\lambda_+ \omega_A}{2\pi\omega_C} e^{-\Delta V(kT)} = \frac{\omega_A}{2\pi} \left[\sqrt{1 + \frac{\kappa^2}{4\omega_C^2}} - \frac{\kappa}{2\omega_C} \right] e^{-\Delta V(kT)}. \tag{2.70}$$

Equation (2.70) is Kramers' IHD Equation (1.62) with $\kappa = \eta$.

2.5 Hessian Matrices and Coordinate Systems

In Subsection 1.4.3, we saw that the original IHD treatment of Kramers dealt with a mechanical system of one degree of freedom specified by the coordinate x with additive Hamiltonian $H = p^2/2m + V(x)$. Thus, the motion is separable and described by a two dimensional phase space with state variables (x, p). However, this may not always be the case. That is, the motion of the magnetic moment in a single domain ferromagnetic particle is governed by a Hamiltonian which is non-additive and is simply the magnetocrystalline anisotropy energy of the particle.

So, we find it necessary to emphasize a point that lacks emphasis in Langer's work. The coordinate system $\{\eta\}$ is chosen *a priori* by Langer, and all work is carried out in this coordinate system. If we were to use different coordinate systems at the minimum and at the saddle point, we would need the Hessian to be coordinate invariant [i.e. the Hessian would need to be a covariant tensor].

This section demonstrates by counter-example that the Hessian is not coordinate invariant under a *non-linear* transformation of the coordinate system or part of the coordinate system. The Hessian matrix is formed by the coefficients of the η_i variables in the second order term of the Taylor series expansion, i.e. the matrix $E_{\eta_i \eta_j}$ in Equation (2.29). Obviously, these coefficients will be different for different energy functions. What is not obvious is that the coefficients are dependent on the coordinate system in which the energy function is expressed. For this reason one coordinate system must be chosen at the outset and used throughout the calculation of the escape rate, Γ. To demonstrate this we consider a function f

$$\left\{ f : \Re^2 \rightarrow \Re \mid (x, y) \rightarrow x^2 + y^2 - 2x + 1 \right\}. \tag{2.71}$$

f has a turning point at $(x, y) = (1, 0)$. The Taylor series expansion of f about $(1, 0)$ is

$$f(x, y) \approx f(x, y)|_{(1,0)} + \frac{1}{2} \left[\left. \frac{\partial^2 f}{\partial x^2} \right|_{(1,0)} (x-1)^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{(1,0)} (y-0)^2 \right] \tag{2.72}$$

$$f(x, y) \approx \frac{1}{2} \left[2(x-1)^2 + 2y^2 \right]. \tag{2.73}$$

Written in terms of matrix notation we have

$$f(x, y) = \frac{1}{2} (x-1, y) \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \begin{pmatrix} x-1 \\ y \end{pmatrix} \tag{2.74}$$

where

$$\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \tag{2.75}$$

is the Hessian matrix. Now,

$$\Delta = 4 \tag{2.76}$$

where Δ denotes the Hessian. Now consider the *non-linear* transformation

$$x = u^2 \quad ; \quad y = v^2 \tag{2.77}$$

which gives rise to a function $g(u, v)$ such that

$$g = u^4 + v^4 - 2u^2 + 1. \tag{2.78}$$

The Hessian matrix for g is,

$$\begin{pmatrix} 12u^2 - 4 & 0 \\ 0 & 12v \end{pmatrix} \tag{2.79}$$

and,

$$\Delta = 12\left(12u^2 - 4\right)v^2 \tag{2.80}$$

and clearly, in general

$$12\left(12u^2 - 4\right)v^2 \neq 4 \tag{2.81}$$

Conclusion

We have seen that Hessians are not coordinate invariant under *non-linear* transformations. And therefore we must adhere strictly to the one coordinate system in all calculations for the Escape Rate.

Chapter 3

Zero Eigenvalues in Langer's Method

3.1 Introduction

Langer's method provides a powerful method for the calculation of the escape rate, for amongst others, systems of magnetic particles. However, the correct application of the method requires that the most appropriate coordinate system geometry be chosen in which to analyse the statics and dynamics of the system under consideration. Now, according to Langer [14],

> "The evaluation (of the escape rate) is perfectly feasible; the only reason that it has not been written out explicitly here is that the precise integrations required are model dependent. In particular, some of the

$\lambda's$ (eigenvalues) always will turn out to be zero because of symmetry properties of the system, and the associated integrals must be handled separately."

In other words, the occurrence of zero eigenvalues depends on the geometry of the model, which is chosen at the outset. The eigenvalues in question occur in the energy Hessian matrix which is part of the energy approximation of Equation (2.21). Therefore, they will appear in the exponent of Equation (2.7). Perhaps we should clear up the details of how one might handle these integrals involving zero eigenvalues. We assume the energy barrier is a high one, i.e. $\Delta E >> k_B T$. Researchers [87] have estimated that models similar to that in [22] and therefore comparable to the parallel field model given here, are valid when ΔE is of the order $40 k_B T$.

3.2 The Zero Eigenvalue Problem

The problem arises when one or more of the eigenvalues of the Hessian of the energy function approximation is zero. This can arise from two distinct cases.

1. The energy function is not a function of one of the variables, e.g. spherical symmetry, cylindrical symmetry etc.

2. The Hessian determinant turns out to be zero at either the saddle point or the metastable minimum.

These two cases require slightly different treatment.

3.2.1 Two Cases of Vanishing Eigenvalues

Case 1

We examine the integration over the variable η_i say where $E \neq E(\eta_i)$ in the evaluation of q (the current of particles) and N_A (the population in the well) in [125] where E is the energy function. Usually, in the case of a variable where the corresponding eigenvalue is non-zero, we have an integral of the type

$$\int \exp\left\{-\left|\mu_i\right| \eta_i^2\right\} d\eta_i \qquad \mu_i \neq 0 \tag{3.1}$$

and we can integrate over η_i from $-\infty$ *to* $+\infty$ if necessary i.e. depending on the domain of the η_i. However if $\mu_i = 0$ we have an integral of the type

$$\int d\eta_i \tag{3.2}$$

which is an entirely different type of integral. Nonetheless, this integral will appear in the numerator *and* the denominator of Langer's method and will cancel, subject of course to a limiting process being carried out in the domain of η_i where necessary or appropriate. The Escape Rate then, in the case of the energy not depending on exactly k of the variables is

$$\Gamma = \frac{\lambda_+}{2\pi} \left[\frac{\det{}' \left(\frac{\mathbf{E}^A}{2\pi k_B T} \right)}{\left| \det{}' \frac{\mathbf{E}^s}{2\pi k_B T} \right|} \right]^{1/2} \exp\left\{-\beta \Delta E\right\} \tag{3.3}$$

where ΔE is the barrier height and $\det{}'$ means omitting the k rows and columns corresponding to the zero eigenvalues in taking the determinant of the Hessian matrix.

Case 2

Case 2 looks at he situation where the zero eigenvalue occurs at either the saddle point or the metastable minimum. In this case we can only deal with the case where the set of values of η_i is finite. We deal in this thesis with the case where the zero eigenvalues occur at the saddle point, extension to the case where they occur at the metastable minimum is obvious.

Consider the integration over η_i. In Langer's method we get the term

$$\int_{\eta_i} d\eta_i \int_{-\infty}^{+\infty} \exp\left\{ikU_i\left(\eta_i - \eta_i^s\right)\right\} dk = \int_{\eta_i}\int_{-\infty}^{+\infty} \exp\left\{ikU_i\left(\eta_i - \eta_i^s\right)\right\} dk d\eta_i \ . \quad (3.4)$$

Now we can pick $U_i = 0$ so the term $\left\{ikU_i\left(\eta_i - \eta_i^s\right)\right\}$ contributes zero to the exponent $\exp\left\{ikU_i\left(\eta_i - \eta_i^s\right)\right\}$ and can be ignored. So we have

$$\int_{\eta_i} d\eta_i \ . \quad (3.5)$$

If the domain of η_i is finite we get a finite value for this integral which simply contributes to the final pre-factor in the expression for the escape rate.

So we must modify the factor

$$\sqrt{\frac{\det\left(\frac{\mathbf{E}^A}{2\pi k_B T}\right)}{\left|\det\left(\frac{\mathbf{E}^s}{2\pi k_B T}\right)\right|}} \quad (3.6)$$

in Equation (2.39). If we have a non-zero eigenvalue say μ_1 the multiplicative factor in the exponent is

$$\exp\left\{-\frac{\mu_1}{2k_B T}\eta_1^2\right\} \quad (3.7)$$

which, when integrated we get $\sqrt{\frac{2\pi kT}{\mu_1}}$. However if the eigenvalue μ_1 is zero, as before, we get an integral

$$\int d\eta_1 = \eta_f - \eta_i \tag{3.8}$$

where η_f and η_i are the bounding values of the coordinate η_1. (For example, the azimuthal angle ϕ ranges from 0 to 2π, so the definite integral is $\int_0^{2\pi} d\phi = 2\pi$.)

If we have k zero eigenvalues from among $2N$ eigenvalues, we will have a factor

$$\sqrt{\frac{(2\pi kT)^{2N-k}}{\mu_{n_1}\mu_{n_2}\cdots\mu_{n_{2N-k}}}} \tag{3.9}$$

where

$$\mu_{n_1}, \mu_{n_2}\cdots\mu_{n_{2N-k}} \tag{3.10}$$

are the absolute values of the nonzero eigenvalues. Now, we see that in a case where we have k such zero eigenvalues, we will have a factor

$$\int d\eta_{l_1} \int d\eta_{l_2} \ldots \int d\eta_{l_k} \tag{3.11}$$

in the integration. We refer to this as v, the volume of the k-dimensional subspace corresponding to the variables $\eta_{l_1}, \ldots, \eta_{l_i}, \ldots, \eta_{l_k}$ where η_{l_i} is the i^{th} such variable corresponding to a zero eigenvalue of E^s. So the factor in Equation (3.6) becomes,

$$v \prod_{l=1}^{2N-k} \sqrt{\frac{2\pi k_B T}{\mu_{n_l}}} \tag{3.12}$$

or

$$v\sqrt{\frac{(2\pi k_B T)^{2N-k}}{\prod_{l=1}^{2N-k}\mu_{n_l}}}. \tag{3.13}$$

We will show later, in Chapter 4 that the variable corresponding to the zero eigenvalue of E^s in the interacting particle case is $\frac{p_1+p_2}{\sqrt{2}}$ with subspace volume 2, where $p = \cos\theta$ and θ is the polar angle of the spherical polar coordinate system in Fig. 2.1. So, in the case of k zero eigenvalues at the saddle point we find the escape rate is,

$$\Gamma = \frac{\lambda_+}{2\pi} v \sqrt{\det\left(\frac{\mathbf{E}^A}{2\pi k_B T}\right)} \sqrt{\frac{(2\pi k_B T)^{2N-k}}{\prod_{l=1}^{2N-k} \mu_{n_l}}} e^{-\beta \Delta E}. \tag{3.14}$$

3.3 Coordinate Systems in Langer's Method

One very useful coordinate system in problems exhibiting spherical symmetry is that of spherical polar coordinates $(1, \theta, \phi)$ as in Fig.1.3 where,

$$\begin{aligned} x &= \sin\theta\cos\phi \\ y &= \sin\theta\sin\phi \\ z &= \cos\theta. \end{aligned} \tag{3.15}$$

This choice can lead to integrals of the type

$$\int_0^\pi \exp\left\{-c_1\theta^2\right\} \sin\theta \; d\theta \tag{3.16}$$

as in Equation (2.6). We now must make a suitable substitution such that the above integral may be transformed into an integral of the type in Equation (3.1), thus making it suitable for use in Langer's method. One possible substitution is

$$p = \cos\theta \tag{3.17}$$

where $p \in [-1, 1]$, since $\theta \in [0, \pi]$.

It is necessary to point out that Langer's Theory requires that we include the conjugate momenta in the list of variables. In the case of spherical polar coordinates, (p, ϕ) where $p = \cos\theta$, it can be shown [125] that p and ϕ can act as each others conjugate momentum, as in Hamilton's equations viz.,

$$\begin{aligned} \dot{\phi} &= \frac{\gamma}{M_s}\frac{\partial E}{\partial p}, \\ \dot{p} &= -\frac{\gamma}{M_s}\frac{\partial E}{\partial \phi} \end{aligned} \tag{3.18}$$

where, γ and M_s are constants. See Appendix A for the derivation of the equations as they apply to the single domain ferromagnetic particles considered in this thesis.

Hence, while it is not necessary to *use* conjugate momenta for p and ϕ explicitly, it is necessary to *include* both p and ϕ in the list of variables, even if one of them is absent from the list of variables on which the energy depends, necessitating the application of Case 1 in Subsection 3.2.1 above.

3.3.1 A Problem with Langer's Method

This concerns the application of Langer's theory to a single particle in a parallel external magnetic field and the need for the substitution $p = \cos\theta$ in the energy function in spherical polar coordinates. Consider the energy function for a single particle in a parallel external field,

$$E(\theta) = -K(\cos^2\theta + 2h\cos\theta) \tag{3.19}$$

where the z-axis is the easy axis of magnetisation, $K > 0$ and $h \in [0, 1)$. This is similar to the function considered in (the often cited) [23][22].

To find the turning points, we let

$$\frac{dE}{d\theta} = 0 \tag{3.20}$$

and find $E(\theta)$ has a metastable minimum at $\theta = \pi$ a stable minimum at $\theta = 0$ and a maximum at $\cos\theta = -h$. Now, substituting $p = \cos\theta$ we have

$$E(p) = -K(p^2 + 2hp). \tag{3.21}$$

Now, Equation (3.21) has one turning point, a maximum at $p = -h$. In other words, we have lost the roots of

$$\frac{d\theta}{dp} = 0 \tag{3.22}$$

in

$$\frac{dE}{dp} = \frac{dE}{d\theta}\frac{d\theta}{dp} = 0. \tag{3.23}$$

This means that the minima, which are solutions of the equation

$$\frac{d\theta}{dp} = \sin\theta = 0 \tag{3.24}$$

are not in a form that can be used in Langer's method, and so potentials of the type in Equation (3.21) are not suitable or cannot be considered within Langer's theory.

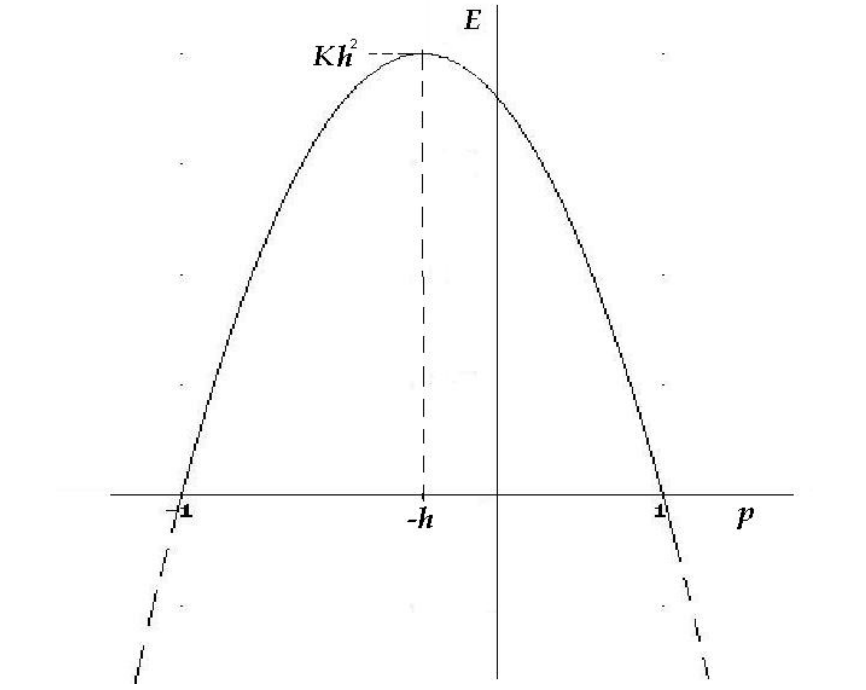

Figure 3.1: The substitution $p = \cos\theta$ in certain energy functions can result in a concave downwards quadratic potential in 'p' space which has no well or metastable state as defined in Langer's theory.

3.4 Example Illustrating Case 1: The Quartic Potential

3.4.1 Introduction

A typical generalised quartic equation or fourth order polynomial will possess three turning points. In this section we have constructed such a quartic in powers of p,

$p = \cos\theta$, to have a maximum at $p = -h$, a metastable state at $p = -1$ and a stable state at $p = 1$ (since $h \in [0, 1)$). This example is used here as a demonstration of Case 1 above, when the total energy is a function of one variable only.

3.4.2 The Quartic Potential

Consider the potential energy function,

$$E(\theta) = K\left[\frac{1}{4}\cos^4\theta + \frac{h}{3}\cos^3\theta - \frac{1}{2}\cos^2\theta - h\cos\theta + a_c\right] \tag{3.25}$$

where $0 \leq h < 1$, $K > 0$, and a_c is a constant, since only the derivatives of $E(\theta)$ are important, without loss of generality we can take $a_c = 0$.

Let $p = \cos\theta$,

$$E(p) = K\left(\frac{1}{4}p^4 + \frac{h}{3}p^3 - \frac{1}{2}p^2 - hp\right). \tag{3.26}$$

Now,

$$\frac{dE}{dp} = K\left(p^3 + hp^2 - p - h\right) = K(p + h)(p^2 - 1). \tag{3.27}$$

The turning points are the zeros of the RHS of Equation (3.27). The second derivative of E is,

$$\frac{d^2E}{dp^2} = K\left(3p^2 + 2hp - 1\right). \tag{3.28}$$

Now, the second derivative test shows,

$$\left.\frac{d^2E}{dp^2}\right|_{p=-h} = K\left(h^2 - 1\right) = -K\left(1 - h^2\right) < 0 \tag{3.29}$$

so, $p = -h$ is a maximum with energy $E(-h) = \frac{K}{2}h^2\left(1 - \frac{1}{6}h^2\right)$. Similarly, $p = -1$ is a metastable minimum with energy $E(-1) = -K\left(\frac{1}{4} - \frac{2}{3}h\right)$, and $p = 1$ is a minimum with energy $E(1) = -K\left(\frac{1}{4} + \frac{2}{3}h\right)$. The energy difference between the well and the barrier is ΔE,

$$\Delta E = \frac{K}{12}\left(3 - 8h + 6h^2 - h^4\right). \tag{3.30}$$

The Hessian at the barrier is $\mathbf{E}^s$,

$$\mathbf{E}^s = \begin{pmatrix} -K\left(1 - h^2\right) & 0 \\ 0 & 0 \end{pmatrix}. \tag{3.31}$$

Removing the zero eigenvalue (indicated by the prime), we have,

$$|\det{}'\mathbf{E}^s| = K\left(1 - h^2\right). \tag{3.32}$$

The energy approximation at the maximum $p = -h$ is

$$E = E^s \approx \frac{K}{2}h^2(1 - \frac{1}{6}h^2) - \frac{K}{2}(1 - h^2)p^2. \tag{3.33}$$

The Hessian at the metastable well is $\mathbf{E}^A$,

$$\mathbf{E}^A = \begin{pmatrix} K\left(1 - h\right) & 0 \\ 0 & 0 \end{pmatrix} \tag{3.34}$$

Again, removing the zero eigenvalue, we have,

$$\det{}'\mathbf{E}^A = K\left(1 - h\right). \tag{3.35}$$

Using Equation (3.3) the escape rate is,

$$\Gamma = \frac{\lambda_+}{2\pi}\left[\frac{\left(\frac{K(1-h)}{2\pi k_B T}\right)}{\left(\frac{K(1-h^2)}{2\pi k_B T}\right)}\right]^{1/2} \exp\left\{-\beta\Delta E\right\}. \tag{3.36}$$

The positive eigenvalue λ_+ is obtained from the equations of motion, the Landau-Lifshitz equations [c.f. Appendix A with $E = E^s$, a=α, $p = -h$ and $\phi = 0$], which are,

$$\begin{aligned} \dot{p} &= -\alpha K\left(1-h^2\right)^2(p+h) \\ \dot{\phi} &= bK\left(1-h^2\right)(p+h) \end{aligned} \tag{3.37}$$

which we write in matrix form to get,

$$\begin{pmatrix} \dot{p} \\ \dot{\phi} \end{pmatrix} = \begin{pmatrix} -\alpha K\left(1-h^2\right)^2 & 0 \\ bK\left(1-h^2\right) & 0 \end{pmatrix} \begin{pmatrix} p+h \\ \phi \end{pmatrix}. \tag{3.38}$$

So, the transition matrix is,

$$\begin{pmatrix} -\alpha K\left(1-h^2\right)^2 & 0 \\ bK\left(1-h^2\right) & 0 \end{pmatrix} \tag{3.39}$$

and its eigenvalues are $\lambda_- = 0$ and $\lambda_+ = \alpha K(1-h^2)^2$. So the escape rate Γ is,

$$\Gamma = \frac{\alpha K(1-h^2)^2}{2\pi}\frac{1}{\sqrt{1+h}}\exp\left\{-\beta\Delta E\right\} \tag{3.40}$$

3.5 Example Illustrating Case 2: Single Particle in a Parallel External Field

3.5.1 Introduction

In this section we consider the energy function for a single domain ferromagnet in a parallel external field. The energy function is written as a function of two variables $E = E(p, \phi)$. The choice of the x-axis as the easy axis of magnetisation avoids the problem of lost roots encountered in Subsection 3.3.1 above. In this example, which demonstrates Case 2 above, a zero eigenvalue appears in the Energy Hessian for the saddle point over the 'p' variable.

3.5.2 Parallel External Field Energy Function

Consider the equation,

$$E(\theta, \phi) = -K\left[\sin^2\theta\cos^2\phi + 2h\sin\theta\cos\phi\right] \tag{3.41}$$

where we have chosen $x = \sin\theta\cos\phi$ to be the easy axis of magnetisation. Let $p = \cos\theta$ and the equation for the potential energy becomes,

$$E(p, \phi) = -K\left[\left(1-p^2\right)\cos^2\phi + 2h\sqrt{1-p^2}\cos\phi\right]. \tag{3.42}$$

The partial derivatives of E are

$$\frac{\partial E}{\partial p} = 2K\left[p\cos^2\phi + \frac{hp}{\sqrt{1-p^2}}\cos\phi\right] \tag{3.43}$$

and

$$\frac{\partial E}{\partial \phi} = 2K\left[(1-p^2)\cos\phi\sin\phi + h\sqrt{1-p^2}\sin\phi\right]. \tag{3.44}$$

3.5.3 Turning Points of E in the case of a Parallel Field

Again, the turning points of E occur when the partial derivatives are simultaneously zero. So, when $\frac{\partial E}{\partial p} = 0$ we get,

$$\phi = \frac{\pi}{2}, \frac{3\pi}{2}, \qquad p = 0, \qquad \sqrt{1-p^2}\cos\phi = -h \tag{3.45}$$

where the solution $\sqrt{1-p^2}\cos\phi = -h$ [i.e. $x = -h$] is a plane which intersects the sphere in Fig. 2.1. The result of this intersection is a circle of equipotential, referred to in [27] as a saddle circle. This circle does not present a (mathematical) problem however, as we view the magnetic vector as a rigid rotor which remains in one plane as it changes direction. We choose this plane to be $p = 0$, or $\cos\theta = \pi/2$ as in [30], [i.e. the xy plane].

When $\frac{\partial E}{\partial \phi} = 0$ we get

$$\phi = 0, \pi, \qquad p = 0, \qquad \sqrt{1-p^2}\cos\phi = -h \tag{3.46}$$

which leads to the turning points (p, ϕ)

$$\{(0,0), (0,\pi), (0, \cos\phi = -h)\}. \tag{3.47}$$

The nature of these points is determined using the second derivative test for a function of two variables, see Ref. [197]. And we see that the motion from A to B

via C as in Fig. 1.1 is

$$A = (0, \pi) \rightarrow C = (0, \cos\phi = -h) \rightarrow B = (0, 0) \tag{3.48}$$

where $(0, \pi)$ is a metastable minimum with energy $-K(1-2h)$, $(0, \cos\phi = -h)$ is a saddle point on the saddle circle with energy Kh^2, and $(0, 0)$ is a stable minimum of energy $-K(1+2h)$. The second order partial derivatives (below) become infinite for stationary points involving $p = \pm 1$ and so are ruled out of the following analysis. The second order partial derivatives of E are,

$$\frac{\partial^2 E}{\partial p^2} = 2K\left[\cos^2\phi + \frac{h\cos\phi}{(1-p^2)^{3/2}}\right] \tag{3.49}$$

$$\frac{\partial^2 E}{\partial \phi^2} = 2K\left[(1-p^2)(\cos^2\phi - \sin^2\phi) + h\sqrt{1-p^2}\cos\phi\right] \tag{3.50}$$

$$\frac{\partial^2 E}{\partial p \partial \phi} = -2K\left[2p\cos\phi\sin\phi + \frac{hp}{\sqrt{1-p^2}}\sin\phi\right] \tag{3.51}$$

The energy approximation at the metastable minimum is

$$E_m \approx E_m^{(0)} + K(1-h)p^2 + K(1-h)\Phi_m^2 \tag{3.52}$$

where $\Phi_m = \phi - \pi$, and $E_m^{(0)} = -K(1-2h)$. The energy Hessian matrix at the metastable state is,

$$\mathbf{E}^A = \begin{pmatrix} K(1-h) & 0 \\ 0 & K(1-h) \end{pmatrix} \tag{3.53}$$

and

$$\det \mathbf{E}^A = K^2(1-h)^2 \tag{3.54}$$

Point	∂E_{pp}	$\partial E_{\phi\phi}$	**Type**	**Energy**
$(0, 0)$	$2K(1+h) > 0$	$2K(1+h) > 0$	min	$-K(1+2h)$
$(0, \pi)$	$2K(1-h) > 0$	$2K(1-h) > 0$	min	$-K(1-2h)$
$(0, \cos\phi = -h)$	0	$-K(1-h^2) < 0$	saddle	Kh^2

Table 3.1: The table lists the relevant critical points of E for a parallel field. There are two minima of equal energy separated by one saddle point. The points involving $p = \pm 1$ are not considered as they lead to infinities in the energy Hessian.

The energy approximation at the saddle point is

$$E_s \approx E_s^{(0)} - K(1-h^2)\Phi_s \tag{3.55}$$

where $\Phi_s = \phi - \tilde{\phi}$, with $\cos\tilde{\phi} = -h$, and $E_s^{(0)} = Kh^2$. So, the Hessian matrix at the saddle point is,

$$\mathbf{E}^s = \begin{pmatrix} -K(1-h^2) & 0 \\ 0 & 0 \end{pmatrix} \tag{3.56}$$

and,

$$|\det{}'\mathbf{E}^s| = K(1-h^2) \tag{3.57}$$

where the prime indicates that the zero eigenvalue has been removed from the Hessian. Also, in Equation (3.55), the coefficient over the 'p' coordinate is 0, yielding a subspace volume $v = 2$, since

$$\int_{-1}^{1} dp = 2. \tag{3.58}$$

So, plugging the following values into Equation (3.14), (the equation for the escape rate in the presence of k zero eigenvalues) with $k = 1$ and $N = 1$, the only non-zero eigenvalue at the saddle point is

$$\mu_{n_l} = |\det{}' \mathbf{E}^s| = K(1 - h^2), \tag{3.59}$$

the Hessian at the metastable minimum is

$$\mathbf{E}^A = K^2 (1 - h)^2 , \tag{3.60}$$

and the barrier height is

$$\Delta E = K (1 - h)^2 \tag{3.61}$$

so, the escape rate for a parallel field is $\Gamma_{||}$

$$\Gamma_{||} = \frac{\lambda_+}{\pi} \sqrt{\frac{1-h}{1+h}} \sqrt{\frac{\beta K}{\pi}} \exp\left\{-\beta K (1-h)^2\right\} \tag{3.62}$$

where, λ_+ is the positive eigenvalue of the Landau-Lifshitz equations. Again, to calculate λ_+, we linearise the Landau Lifshitz equations (A.21)(A.22) (cf. Appendix A) by replacing E with E_s so, using Equation (3.55)

$$\frac{\partial E}{\partial \phi} = \frac{\partial E_s}{\partial \phi} = -2K(1 - h^2)(\phi - \tilde{\phi})^2 \tag{3.63}$$

and the equations of motion for p and ϕ are,

$$\begin{aligned} \dot{p} &= -2K(1 - h^2)\phi \\ \dot{\phi} &= 2\alpha K(1 - h^2)\phi \end{aligned} \tag{3.64}$$

where $\alpha > 0$ is a damping parameter. We write the equations for $\dot{p}$ and $\dot{\phi}$ in matrix notation, so

$$\begin{pmatrix} \dot{p} \\ \dot{\phi} \end{pmatrix} = \begin{pmatrix} 0 & -2K(1-h^2) \\ 0 & 2\alpha K(1-h^2) \end{pmatrix} \begin{pmatrix} p \\ \phi \end{pmatrix}. \tag{3.65}$$

The eigenvalues of the matrix in Equation (3.65) are $\lambda = 2\alpha K(1-h^2)$ or $\lambda = 0$ so, $\lambda_+ = 2\alpha K(1-h^2)$.

In terms of h and K, we find that the escape rate, $\Gamma_{||}$, is

$$\Gamma_{||} = \frac{\alpha K}{\pi}(1-h)^{3/2}(1+h)^{1/2}\sqrt{\frac{\beta K}{\pi}}\exp\left\{-\beta K(1-h)^2\right\}. \tag{3.66}$$

Equation (3.66) is the result for the escape rate of a single noninteracting particle in a parallel external field where a zero appears in the energy Hessian matrix at the saddle point barrier.

Chapter 4

Two Particle Interaction

4.1 Introduction

We consider a system which is composed of two single domain ferromagnetic particles, and modeled by two magnetic vectors. The total potential energy of the particles consists of three terms [27][28], one involving the anisotropy K, one involving external field $\mathbf{H}$ and one involving the exchange interaction J [174]. The exchange interaction is isotropic but the external field is in the direction of the x-axis, which we have chosen as the easy axis of magnetisation. So, the model is similar to and may be thought of as a system of two single domain particles, as it were, "glued" together in a parallel external field, as in Section 3.5. An extra term in the energy function accounts for the so-called glue or interaction between the two magnetic vectors. The particle is viewed as having two unit vectors $\vec{\mathbf{m}}_1$ and

$\vec{\mathbf{m}}_2$ where $\vec{\mathbf{m}}_i = \frac{\mathbf{M}_i}{M_0}$, $i = 1, 2$. $\mathbf{M}_i$ is the i^{th} particle's magnetic vector (and M_0 is its magnitude). Again, we assume as in [30] that the saddle point, the metastable minimum and the stable minimum lie in the plane $\theta = \pi/2$ or $p = \cos\theta = 0$.

Depending on the value of the exchange-interaction coefficient, $j = \frac{J}{2K}$, $j \in (0, \infty)$, and the reduced field, $h = \frac{HM_0}{2K}$, $h \in [0, 1)$, the particles reside in a metastable state and cross a potential barrier to come to rest in a stable state. The particles are ferromagnetic, so we assume $\vec{\mathbf{m}}_1$ and $\vec{\mathbf{m}}_2$ begin and end the rotation in the same state or orientation and remain together (more or less throughout the rotation and) as they traverse a saddle point barrier, this is referred to as coherent relaxation. Coherent relaxation occurs when $j > 2$, but *may* also be the process of relaxation when $j \in (1, 2]$. When $j \in (1, 2]$ there is another, alternative or preferred, (depending on the energy height difference between the saddle point and the metastable minimum) barrier to the coherent relaxation barrier mentioned above. We will discuss this in greater detail later. If the exchange interaction is weak enough $j \in (0, 1]$ the particles' magnetic vectors can oppose each other and can fall into an antiferromagnetic 'trap' if a certain condition is met, that is if $j < 1 - h^2$. Also, when $j \in (0, 1]$ and $j > 1 - h^2$ we find there is the possibility of another turning point or points which are zeros of a fourth order polynomial.

4.2 Two Interacting Magnetic Particles

As usual we begin our study with a potential energy function $E = E(p, \phi)$. Our task is to find a full description of the energy profile (critical points or possible energy states) for the two particles, then we identify which critical points are wells and which are barriers. Then, based on this knowledge, we identify the possible relaxation processes (paths) and apply Langer's method. Since the model involves two particles with four degrees of freedom $(p_1, p_2, \phi_1, \phi_2)$, the energy Hessian will be a 4×4 matrix. In general, this fact will make difficult the identification of the nature of the turning points. The nature of the points can be indicated (if not determined) by evaluating the energy function E at a particular critical point, say A, we will label this particular value of E as $E|_A$, and comparing this to the energy at a point near the critical point in question to get the value of E, which we will label as $E|_{A+\Delta A}$, for each of the degrees of freedom.

In general, to determine the nature of a particular point, say the point $A(p_1, p_2, \phi_1, \phi_2)$ we need to move away from A in one of the directions, p_1, p_2, ϕ_1, ϕ_2 at a time, keeping all others constant. If all directions are decreasing, that is, if $E|_{A+\Delta A} - E|_A$ is negative everywhere, then the value of $E|_{A+\Delta A}$ is less than the value of $E|_A$ everywhere, so A is a maximum. But if $E|_{A+\Delta A} - E|_A$ is somewhere positive and somewhere negative near A, then A is a saddle point. If the value of $E|_{A+\Delta A}$ is everywhere greater than $E|_A$, then A is a minimum. This is a laborious task, but we are fortunate, as it turns out, because the Hessian matrices at the turning points

turn out to be sparse 4×4 matrices.

Hessian Matrices in the Interaction Particle Problem

The Hessian matrix at a turning point (say A) can, whether diagonalised or not, yield valuable information about the nature of turning point under consideration. The Hessian matrices are sparse since the entries

$$\left.\frac{\partial^2 E}{\partial p_i \phi_j}\right|_A = 0 \qquad i, j = 1, 2 \tag{4.1}$$

and it turns out we can modify the usual second derivative test for a function of two variables, as used in the single particle model, to take account of the increased number of variables. The Hessian matrices encountered in this model are of the form,

$$\mathbf{H} = \begin{pmatrix} e_{11} & e_{12} & 0 & 0 \\ e_{21} & e_{22} & 0 & 0 \\ 0 & 0 & e_{33} & e_{34} \\ 0 & 0 & e_{43} & e_{44} \end{pmatrix}. \tag{4.2}$$

The determinant of a matrix in this form can be found by considering two separate 2×2 matrices, where the product of the determinants of the smaller matrices equal the determinant of the 4×4 matrix. This can be used to reduce the amount of computations required to analyze a turning point of interest. To do this we form

the matrices,

$$\mathbf{H}_p = \begin{pmatrix} e_{11} & e_{12} \\ \\ e_{21} & e_{22} \end{pmatrix} \quad ; \quad \mathbf{H}_\phi = \begin{pmatrix} e_{33} & e_{34} \\ \\ e_{43} & e_{44} \end{pmatrix}. \tag{4.3}$$

Now (cf. Appendix D),

$$\det \mathbf{H} = \det \mathbf{H}_p \det \mathbf{H}_\phi \tag{4.4}$$

where the entries e_{lm} $l, m = 1, \ldots, 4$ in matrix $\mathbf{H}_p$ are the coefficients of the variables $p_i p_j$ $i, j = 1, 2$, and those in the matrix $\mathbf{H}_\phi$ are the coefficients of the $\phi_i \phi_j$ $i, j = 1, 2$ in the Taylor series expansion of the energy function $E(p_1, p_2, \phi_1, \phi_2)$ about the turning point A.

$$e_{ij} = \left. \frac{\partial^2 E}{\partial p_i \partial p_j} \right|_A \quad i, j = 1, 2 \tag{4.5}$$

and,

$$e_{lm} = \left. \frac{\partial^2 E}{\partial \phi_i \partial \phi_j} \right|_A \quad i, j = 1, 2. \;\; l, m = 3, 4. \tag{4.6}$$

Now, if

$$\det \mathbf{H} < 0 \tag{4.7}$$

then A is a saddle point, otherwise

$$\det \mathbf{H} \geq 0 \tag{4.8}$$

and we must look at the determinants of $\mathbf{H}_p$ and $\mathbf{H}_\phi$. Now, if

$$\det \mathbf{H}_p < 0 \quad \textit{and/or} \quad \det \mathbf{H}_\phi < 0 \tag{4.9}$$

then the point A is a saddle (the case where $\mathbf{H} = 0$ has been discussed in Chapter 3). We remark that the result in Equation (4.9), altough is theoretically possible, may contravene Langer's idea that there should be one and only one escape direction [13]. And, if

$$\det \mathbf{H}_p > 0 \quad and \quad \det \mathbf{H}_\phi > 0 \tag{4.10}$$

then A is either a maximum *or* a minimum and we must examine one diagonal entry in each of $\mathbf{H}_p$ and $\mathbf{H}_\phi$. Now, say we look at the diagonal entries

$$e_{11} = \left. \frac{\partial^2 E}{\partial^2 p_1} \right|_A \tag{4.11}$$

in $\mathbf{H}_p$, and

$$e_{33} = \left. \frac{\partial^2 E}{\partial^2 \phi_1} \right|_A \tag{4.12}$$

in $\mathbf{H}_\phi$, then, if the condition in Equation (4.10) is satisfied *and*

$$e_{11} < 0 \;\; and \;\; e_{33} < 0 \tag{4.13}$$

then A is a maximum, or if the condition in Equation (4.10) is satisfied *and*

$$e_{11} > 0 \;\; and \;\; e_{33} > 0 \tag{4.14}$$

then A is a minimum. If any of the e_{lm}, $l, m = 1, 2, 3, 4$ are zero we would have a zero eigenvalue in the Hessian and would have to deal with that situation separately as in [13], and explained here in Chapter 3. Thus, we may perform a second derivative

test (or tests) on the matrices $\mathbf{H}_p$ and $\mathbf{H}_\phi$ in a similar manner to the usual second derivative test with the single particle model. The test, when performed on $\mathbf{H}_p$ indicates the nature of the critical point in the p_i $i = 1, 2$ directions, whereas when performed on $\mathbf{H}_\phi$ indicates the nature of the critical point in the ϕ_i $i = 1, 2$ directions.

Also, the e_{ij} are real and since the order of differentiation in the mixed derivatives is not important, then $\mathbf{H}$ is a real square symmetric matrix, therefore we can find a matrix $\mathbf{S} = S_{ij}$ (which diagonalises $\mathbf{H}$) such that,

$$\mathbf{S}^t\mathbf{H}\mathbf{S} = \mathbf{S}^{-1}\mathbf{H}\mathbf{S} \tag{4.15}$$

is a diagonal matrix whose diagonal elements are the eigenvalues of $\mathbf{H}$, and

$$\det S_{ij} = 1 \tag{4.16}$$

since the columns of S_{ij} are vectors which form an orthogonal basis for $\mathbf{H}$. Equations (4.15) and (4.16) are standard results in linear algebra [198][199].

In summary, the (simple) interacting particle system considered here gives rise to 4×4 Hessian matrices at the turning points. If the Hessian at a particular point is positive we can draw *no conclusion* about the nature of that point. More analysis is required. If we go ahead and diagonalise the 4×4 matrix $\mathbf{H}$ then, if all the eigenvalues are strictly positive, the point is an absolute minimum. If there is a mixture of positive and negative signs, say two positive and two negative signs in the eigenvalues themselves, then $\mathbf{H} > 0$, but we have a saddle point. Finally, if all eigenvalues are strictly negative, the point is an absolute maximum.

Owing to the symmetry in the energy function (the existence of zero eigenvalues) and the fact that it is a function of the parameters j and h, there is no one definitive method of determining whether a point is a maximum, a minimum or a saddle. Indeed the nature of a point may change for certain values of the parameters. So to determine the reversal method (or escape path) followed by the particle, we must find all the turning points *for all* values of j and h. Also, the analysis can be made lengthy by the existence of equal eigenvalues or eigenvalues which are surd conjugates of each other, as we find with the interaction energy function considered here.

4.2.1 The Energy Function E for a System of Interacting Ferromagnetic Particles

We write the energy function for the interaction between two ferromagnetic particles as in [27].

$$E = -\frac{j}{2}\left(x_1x_2 + y_1y_2 + z_1z_2\right) - \frac{1}{2}\left(x_1^2 + x_2^2\right) - h\left(x_1 + x_2\right) \tag{4.17}$$

where the term $-\frac{j}{2}\left(x_1x_2 + y_1y_2 + z_1z_2\right)$ is the part of the total potential energy due to the interaction between the particles 1 and 2. Interaction is isotropic, that is, it acts equally in all directions. J is the magnitude of the interaction, $j = \frac{J}{2K}$ and $j > 0$. As before $h = \frac{HM_0}{2K}$ and $0 \leq h < 1$ is the 'reduced' field, H is the magnitude of the external field, M_0 is the magnitude of the magnetic vector and $K > 0$ is the

magnitude of the anisotropy. We chose the coordinate system as Equation (3.15), that is, spherical polar coordinates, $(1, \theta, \phi)$

$$\begin{aligned} x &= \sin\theta\cos\phi \\ y &= \sin\theta\sin\phi \\ z &= \cos\theta. \end{aligned} \tag{4.18}$$

So, rewriting the equation for E in this system we have,

$$\begin{aligned} E &= -\frac{j}{2}\left[\sin\theta_1\sin\theta_2\cos\left(\phi_1-\phi_2\right)+\cos\theta_1\cos\theta_2\right] \\ &- \frac{1}{2}\left[\sin^2\theta_1\cos^2\phi_1+\sin^2\theta_2\cos^2\phi_2\right]-h\left[\sin\theta_1\cos\phi_1+\sin\theta_2\cos\phi_2\right] \end{aligned} \tag{4.19}$$

Now, in order to apply Langer's method we again make the substitution $p = \cos\theta$, so the equation becomes,

$$\begin{aligned} E = &- \tfrac{j}{2}\left[\sqrt{1-p_1^2}\sqrt{1-p_2^2}\cos\left(\phi_1-\phi_2\right)+p_1p_2\right] \\ &- \tfrac{1}{2}\left[\left(1-p_1^2\right)\cos^2\phi_1+\left(1-p_2^2\right)\cos^2\phi_2\right] \\ &- h\left[\sqrt{1-p_1^2}\cos\phi_1+\sqrt{1-p_2^2}\cos\phi_2\right]. \end{aligned} \tag{4.20}$$

4.2.2 Partial Derivatives of E

$$\frac{\partial E}{\partial p_1} = -\frac{j}{2}\left[p_2-\frac{p_1\sqrt{1-p_2^2}}{\sqrt{1-p_1^2}}\cos\left(\phi_1-\phi_2\right)\right]+p_1\cos^2\phi_1+h\frac{p_1}{\sqrt{1-p_1^2}}\cos\phi_1 \tag{4.21}$$

$$\frac{\partial E}{\partial p_2} = -\frac{j}{2}\left[p_1-\frac{p_2\sqrt{1-p_1^2}}{\sqrt{1-p_2^2}}\cos\left(\phi_1-\phi_2\right)\right]+p_2\cos^2\phi_2+h\frac{p_2}{\sqrt{1-p_2^2}}\cos\phi_2 \tag{4.22}$$

$$\begin{aligned} \frac{\partial E}{\partial \phi_1} = \frac{j}{2}\sqrt{1-p_1^2}\sqrt{1-p_2^2}\sin\left(\phi_1-\phi_2\right)+\left(1-p_1^2\right)\cos\phi_1\sin\phi_1+ \\ +h\sqrt{1-p_1^2}\sin\phi_1 \end{aligned} \tag{4.23}$$

$$\frac{\partial E}{\partial \phi_2} = -\frac{j}{2}\sqrt{1-p_1^2}\sqrt{1-p_2^2}\sin(\phi_1-\phi_2) + \left(1-p_2^2\right)\cos\phi_2\sin\phi_2 + \\ +h\sqrt{1-p_2^2}\sin\phi_2 \qquad (4.24)$$

4.3 Analysis of the Energy Function E

4.3.1 Energy Profile 1: The turning points of E

Again, we assume (following [30]) the rotating particles will remain in one plane throughout the rotation. By inspection, we see that the plane

$$p_1 = p_2 = 0 \qquad (4.25)$$

forces

$$\frac{\partial E}{\partial p_1} = 0 \qquad (4.26)$$

and

$$\frac{\partial E}{\partial p_2} = 0. \qquad (4.27)$$

We then have the two equations,

$$\frac{\partial E}{\partial \phi_1} = \frac{j}{2}\sin(\phi_1-\phi_2) + \cos\phi_1\sin\phi_1 + h\sin\phi_1 \qquad (4.28)$$

$$\frac{\partial E}{\partial \phi_2} = -\frac{j}{2}\sin(\phi_1-\phi_2) + \cos\phi_2\sin\phi_2 + h\sin\phi_2. \qquad (4.29)$$

Now, setting

$$\frac{\partial E}{\partial \phi_1} = 0, \qquad (4.30)$$

with $p_1 = p_2 = 0$ yields,

$$\sin(\phi_2 - \phi_1) = \left[\frac{2}{j}\sin\phi_1(\cos\phi_1 + h)\right] \tag{4.31}$$

or,

$$\phi_2 = \phi_1 + \sin^{-1}\left[\frac{2}{j}\sin\phi_1(\cos\phi_1 + h)\right]. \tag{4.32}$$

And setting,

$$\frac{\partial E}{\partial \phi_2} = 0, \tag{4.33}$$

with $p_1 = p_2 = 0$ yields,

$$\sin(\phi_1 - \phi_2) = \left[\frac{2}{j}\sin\phi_2(\cos\phi_2 + h)\right] \tag{4.34}$$

or,

$$\phi_1 = \phi_2 + \sin^{-1}\left[\frac{2}{j}\sin\phi_2(\cos\phi_2 + h)\right]. \tag{4.35}$$

Equations (4.32) and (4.35) show that the solutions we seek (for ϕ_1 and ϕ_2) depend on each other. That is, we can solve for one, only if we know the other and vice versa. This interdependence doesn't seem very helpful in finding useful zeros to the partial differentials of E (i.e. Equations (4.23) and (4.24)). However, consider the following analysis:

the RHS of Equations (4.31) and (4.34) lie in the interval [-1, 1], since that is the range of the sine function. Also we have

$$\phi_i \in [0, 2\pi] \quad i = 1, 2. \tag{4.36}$$

So, if

$$(\phi_1 - \phi_2) \in [0, \pi] \tag{4.37}$$

then

$$\sin(\phi_1 - \phi_2) \in [0, 1], \tag{4.38}$$

and if

$$(\phi_1 - \phi_2) \in [\pi, 2\pi] \tag{4.39}$$

then

$$\sin(\phi_1 - \phi_2) \in [-1, 0]. \tag{4.40}$$

In order to find (useful) solutions to Equations (4.31) and (4.34) we will fix the *difference* between the azimuthal angles ϕ_1 and ϕ_2. Let

$$\phi_1 - \phi_2 = \mathcal{C}. \tag{4.41}$$

Now, when the difference is zero, $\mathcal{C} = 0$ and hence $\sin \mathcal{C} = 0$, so Equations (4.31) and (4.34) reduce to,

$$\frac{2}{j} \sin \phi_i (\cos \phi_i + h) = 0 \qquad i = 1, 2. \tag{4.42}$$

So,

$$\phi_i = 0 \quad or \quad \pi \quad or \quad \cos^{-1}(-h) \qquad i = 1, 2. \tag{4.43}$$

So, we have the following solutions $(p_1, p_2, \phi_1, \phi_2)$ to the partial differential equations;

$$(0,0,0,0)\,,\ (0,0,\pi,\pi)\,,\ (0,0,\pi,0)\,,\ (0,0,0,\pi)\,,\ \left(0,0,\cos^{-1}(-h)\,,\cos^{-1}(-h)\right) \tag{4.44}$$

If the difference is non-zero, we have $\phi_1 - \phi_2 = \mathcal{C}$, (but $\mathcal{C} \neq 0$). Now, let $\sin\mathcal{C} = c$ so, $c \in [-1, 0)$ or $c \in (0, 1]$,

$$\begin{aligned} c &= \tfrac{2}{j}\sin\phi_2\,(\cos\phi_2 + h) \\ -c &= \tfrac{2}{j}\sin\phi_1\,(\cos\phi_1 + h)\,. \end{aligned} \tag{4.45}$$

Squaring both sides of the above two equations yields two (equivalent) quartic equations in powers of $q_1 = \cos\phi_1$ and $q_2 = \cos\phi_2$,

$$\frac{(jc)^2}{4} = \left(1 - q_1^2\right)(q_1 + h)^2 \tag{4.46}$$

and

$$\frac{(jc)^2}{4} = \left(1 - q_2^2\right)(q_2 + h)^2 \tag{4.47}$$

or

$$q_i^4 + 2hq_i^3 - (1 - h^2)q_i^2 - 2hq_i - h^2 + \frac{(jc)^2}{4} = 0 \tag{4.48}$$

where $q_i = \cos\phi_i$ $i = 1, 2$. The quartic equation, Equation (4.48), can be solved for various values of $c \in [-1, 1]$. This is not dealt with in this thesis, but the reader is referred to [27] and [28] for a discussion on how this case is implicated in a multi-step process for the rotation of the particle when the exchange interaction is less than a critical value, that is when $j < 1 - h^2$ and,

$$c = \pm\sqrt{\frac{j - (1 - h^2)}{j - 1}}. \tag{4.49}$$

We will restrict ourselves to dealing with the following turning points of E, $(p_1, p_2, \phi_1, \phi_2)$ in (4.44), again they are

$$(0,0,0,0),\ (0,0,\pi,\pi),\ (0,0,\pi,0),\ (0,0,0,\pi), (0,0,\tilde{\phi}_1,\tilde{\phi}_2) \tag{4.50}$$

where, $\tilde{\phi}_i = \cos^{-1}(-h)$, $i = 1, 2$.

4.3.2 The Second Order Partial Derivatives of E

The second derivatives of E are,

$$\frac{\partial^2 E}{\partial p_1^2} = \frac{j}{2}\cos(\phi_1 - \phi_2)\sqrt{\frac{1-p_2^2}{(1-p_1^2)^3}} + \cos^2\phi_1 + h\frac{\cos\phi_1}{\sqrt{(1-p_1^2)^3}} \tag{4.51}$$

$$\frac{\partial^2 E}{\partial p_2^2} = \frac{j}{2}\cos(\phi_1 - \phi_2)\sqrt{\frac{1-p_1^2}{(1-p_2^2)^3}} + \cos^2\phi_2 + h\frac{\cos\phi_2}{\sqrt{(1-p_2^2)^3}} \tag{4.52}$$

$$\begin{aligned}\frac{\partial^2 E}{\partial \phi_1^2} &= \frac{j}{2}\sqrt{(1-p_1^2)(1-p_2^2)}\cos(\phi_1 - \phi_2) + \\ &+(1-p_1^2)(\cos^2\phi_1 - \sin^2\phi_1) + h\sqrt{1-p_1^2}\cos\phi_1\end{aligned} \tag{4.53}$$

$$\begin{aligned}\frac{\partial^2 E}{\partial \phi_2^2} &= \frac{j}{2}\sqrt{(1-p_1^2)(1-p_2^2)}\cos(\phi_1 - \phi_2) + \\ &+(1-p_2^2)(\cos^2\phi_2 - \sin^2\phi_2) + h\sqrt{1-p_2^2}\cos\phi_2\end{aligned} \tag{4.54}$$

$$\frac{\partial^2 E}{\partial p_1 \partial p_2} = -\frac{j}{2}\left[1 + \frac{p_1 p_2}{\sqrt{(1-p_1^2)(1-p_2^2)}}\cos(\phi_1 - \phi_2)\right] \tag{4.55}$$

$$\frac{\partial^2 E}{\partial \phi_1 \partial \phi_2} = -\frac{j}{2}\sqrt{(1-p_1^2)(1-p_2^2)}\cos(\phi_1 - \phi_2) \tag{4.56}$$

$$\frac{\partial^2 E}{\partial p_1 \partial \phi_1} = -\frac{j}{2} p_1 \sin(\phi_1 - \phi_2) \sqrt{\frac{1-p_2^2}{1-p_1^2}} - 2p_1 \cos\phi_1 \sin\phi_1 - h \sin\phi_1 \frac{p_1}{\sqrt{1-p_1^2}} \quad (4.57)$$

$$\frac{\partial^2 E}{\partial p_1 \partial \phi_2} = \frac{j}{2} p_1 \sqrt{\frac{1-p_2^2}{1-p_1^2}} \sin(\phi_1 - \phi_2) \quad (4.58)$$

$$\frac{\partial^2 E}{\partial p_2 \partial \phi_1} = -\frac{j}{2} p_2 \sqrt{\frac{1-p_1^2}{1-p_2^2}} \sin(\phi_1 - \phi_2) \quad (4.59)$$

$$\frac{\partial^2 E}{\partial p_2 \partial \phi_2} = -\frac{j}{2} p_2 \sin(\phi_1 - \phi_2) \sqrt{\frac{1-p_1^2}{1-p_2^2}} - 2p_2 \cos\phi_2 \sin\phi_2 - h \sin\phi_2 \frac{p_2}{\sqrt{1-p_2^2}} \quad (4.60)$$

Note: since $p_1 = p_2 = 0$, the right hand sides of Equations (4.57) to (4.60) are exactly 0.

4.3.3 Energy Profile 2: Analysis of the Turning Points of E

In order to determine the true identity of the turning points of E, and thus describe the so-called "energy landscape" of E we must examine each of the points by the process described above. Such an analysis shows that the eigenvalues of the energy Hessian at the point $(0,0,0,0)$ are strictly positive everywhere for all values of the parameters j and h. The energy at $(0,0,0,0)$ is $E^{(0)} = -\frac{j}{2} - 1 - 2h$ and the Hessian matrix is,

$$\begin{pmatrix} \frac{j}{2}+1+h & -\frac{j}{2} & 0 & 0 \\ -\frac{j}{2} & \frac{j}{2}+1+h & 0 & 0 \\ 0 & 0 & \frac{j}{2}+1+h & -\frac{j}{2} \\ 0 & 0 & -\frac{j}{2} & \frac{j}{2}+1+h \end{pmatrix} \quad (4.61)$$

with eigenvalues,

$$\{j+1+h, 1+h, j+1+h, 1+h\} \tag{4.62}$$

which are all strictly positive. So, $(0,0,0,0)$ is a minimum, and as we will see next it is a stable state of the system.

The energy at $(0,0,\pi,\pi)$ is $E^{(0)} = -\frac{j}{2} - 1 + 2h$ and the Hessian matrix is,

$$\begin{pmatrix} j+1-h & 0 & 0 & 0 \\ 0 & 1-h & 0 & 0 \\ 0 & 0 & j+1-h & 0 \\ 0 & 0 & 0 & 1-h \end{pmatrix} \tag{4.63}$$

with eigenvalues,

$$\{j+1-h, 1-h, j+1-h, 1-h\}\,. \tag{4.64}$$

These are also always positive for all values of the parameters j and h, so $(0,0,\pi,\pi)$ is a minimum, but the point is at a higher energy than $(0,0,0,0)$ so it is a metastable state of the system.

Now, we turn our attention to the possible saddle points and first examine the point $(0,0,\cos\phi_1 = -h, \cos\phi_2 = -h)$, which has energy

$$E = -\frac{j}{2} + h^2 \tag{4.65}$$

and a Hessian matrix,

$$\begin{pmatrix} -\frac{j}{2} & \frac{j}{2} & 0 & 0 \\ \frac{j}{2} & -\frac{j}{2} & 0 & 0 \\ 0 & 0 & \frac{j}{2}+1-h^2 & -\frac{j}{2} \\ 0 & 0 & -\frac{j}{2} & \frac{j}{2}+1-h^2 \end{pmatrix} \tag{4.66}$$

with eigenvalues,

$$\left\{0, j, j-(1-h^2), -(1-h^2)\right\}. \tag{4.67}$$

So, the point $(0, 0, \cos\phi_1 = -h, \cos\phi_2 = -h)$ has at least one negative direction for all values of j and h, and at least one positive direction, therefore it is a saddle point. This point can assume a second negative eigenvalue $j-(1-h^2)$ when $j < (1-h^2)$ (i.e. $j \in (0, 1]$ but, of course, this bound on j is not absolute assurance of a negative eigenvalue $j-(1-h^2)$). Lastly, this eigenvalue is strictly positive when $j > (1-h^2)$. We see later that the eigenvalue $j-(1-h^2)$ is always positive when the barrier $(0, 0, \cos\phi_1 = -h, \cos\phi_2 = -h)$ is active. Also, we note that Langer says there should be one and only one negative eigenvalue at the saddle so that the process can be described as a 'nucleating' one [13]. Next, we can examine either of the points $(0, 0, \pi, 0)$ or $(0, 0, 0, \pi)$ as their Hessian matrices have a common structure and the same eigenvalues. Both these points have energy

$$E = \frac{j}{2} - 1. \tag{4.68}$$

The Hessian matrices are,

$$\mathbf{H}_{(\pi,0)} = \begin{pmatrix} -\frac{j}{2} - h + 1 & -\frac{j}{2} & 0 & 0 \\ -\frac{j}{2} & -\frac{j}{2} + h + 1 & 0 & 0 \\ 0 & 0 & -\frac{j}{2} - h + 1 & \frac{j}{2} \\ 0 & 0 & \frac{j}{2} & -\frac{j}{2} + h + 1 \end{pmatrix} \tag{4.69}$$

and,

$$\mathbf{H}_{(0,\pi)} = \begin{pmatrix} -\frac{j}{2} + h + 1 & -\frac{j}{2} & 0 & 0 \\ -\frac{j}{2} & -\frac{j}{2} - h + 1 & 0 & 0 \\ 0 & 0 & -\frac{j}{2} + h + 1 & \frac{j}{2} \\ 0 & 0 & \frac{j}{2} & -\frac{j}{2} - h + 1 \end{pmatrix} \tag{4.70}$$

where $H_{0,\pi}$ is the Hessian at $(0, 0, \pi, 0)$ and $H_{\pi,0}$ is that at $(0, 0, 0, \pi)$.

Now, examining the matrix $\mathbf{H}_{(0,\pi)}$ we can consider the two, 2×2 matrices,

$$\mathbf{H}_p = \begin{pmatrix} -\frac{j}{2} + h + 1 & -\frac{j}{2} \\ -\frac{j}{2} & -\frac{j}{2} - h + 1 \end{pmatrix}, \mathbf{H}_\phi = \begin{pmatrix} -\frac{j}{2} + h + 1 & \frac{j}{2} \\ \frac{j}{2} & -\frac{j}{2} - h + 1 \end{pmatrix} \tag{4.71}$$

both of which have identical eigenvalues, thus further reducing the analysis, which are,

$$\left\{ \frac{-j + 2 + \sqrt{4h^2 + j^2}}{2}, \frac{-j + 2 - \sqrt{4h^2 + j^2}}{2} \right\}, \tag{4.72}$$

where the eigenvalue $\frac{-j+2+\sqrt{4h^2+j^2}}{2}$ occurs twice and the eigenvalue $\frac{-j+2-\sqrt{4h^2+j^2}}{2}$ occurs twice in each of Equations (4.70) and (4.69) making in all four eigenvalues in

either of two states $(0, 0, \pi, 0)$ or $(0, 0, 0, \pi)$. Also,

$$\det \mathbf{H}_p = \det \mathbf{H}_\phi = -j + \left(1 - h^2\right). \tag{4.73}$$

Now, we seek bounds on j which determine the nature of all possible saddle points and when they may be involved in any resulting switching process. First, we remark that the points $(0, 0, \pi, 0)$ or $(0, 0, 0, \pi)$ will be involved in an escape rate calculation when the energy barrier they present is equal to or lower than the energy barrier of the point $(0, 0, \cos\phi_1 = -h, \cos\phi_2 = -h)$ only (see Equations (4.65) and (4.68)), that is *iff*,

$$\frac{j}{2} - 1 \leq -\frac{j}{2} + h^2 \tag{4.74}$$

or

$$j \leq 1 + h^2 \tag{4.75}$$

which is possible as long as

$$1 \leq j < 2 \tag{4.76}$$

since, in our set-up,

$$\begin{gathered} 0 \leq h < 1 \\ j > 0. \end{gathered} \tag{4.77}$$

So, the barrier $(0, 0, \cos\phi_1 = -h, \cos\phi_2 = -h)$ will be the only barrier coming into play when $j > 1 + h^2$. The eigenvalues of $\mathbf{H}_{(0,\pi)}$ and of $\mathbf{H}_{(\pi,0)}$ are simultaneously

positive when,

$$j < 1 - h^2 \quad and \quad \left|\sqrt{4h^2 + j^2}\right| < 2 - j, \tag{4.78}$$

The points $(0, 0, \pi, 0), (0, 0, 0, \pi)$ are minima when, $0 < j < 1$, which is the region where $j < 1 - h^2$. They are simultaneously negative when,

$$j < 1 - h^2 \quad and \quad \left|\sqrt{4h^2 + j^2}\right| < j - 2, \tag{4.79}$$

but the inequalities in (4.79) are (obviously) incompatible in the region $0 < j < 1$, so we can conclude that the points never represent a maximum. See Appendix E for further confirmation of these results. The results for all turning points $(p_1, p_2, \phi_1, \phi_2)$ are summarized in the below table (cf. Table 4.1). The eigenvalues can be of alternate sign and therefore the points represent a saddle point when

$$j > 1 - h^2, \tag{4.80}$$

which is possible when $0 < j \leq 1$ and strictly true when $j > 1$. Also, we remark that the nature of these points is indeterminate when,

$$j = 1 - h^2. \tag{4.81}$$

4.4 Conclusion: Particle Rotation

The above analysis indicates at least two possible ways in which the particle or magnetic moment can reverse its magnetisation from its starting point $(0, 0, \pi, \pi)$ to

Point	**Type**	j **Bound**	**Energy**
$(0,0,0,0)$	min	$j > 0$	$-\frac{j}{2} - 1 - 2h$
$(0,0,\pi,\pi)$	min	$j > 0$	$-\frac{j}{2} - 1 + 2h$
$(0,0,\pi,0)$	min/sad min if sad if saddle indet	$0 < j < 1$ $j < 1 - h^2$ $j > 1 - h^2$ $1 < j < \infty$ $j = 1 - h^2$	$E = \frac{j}{2} - 1$ but used iff $j < 1 + h^2$
$(0,0,0,\pi)$	min/sad saddle indet	Same as the point $(0,0,\pi,0)$	$\frac{j}{2} - 1$
$(0,0,\tilde{\phi},\tilde{\phi})$	saddle	$j > 0$	$-\frac{j}{2} + h^2$

Table 4.1: The different turning points of E

the position $(0,0,0,0)$ depending on the values of j and h. The first, which we shall refer to as ferromagnetic ordering, is

$$A = (0,0,\pi,\pi) \rightarrow C = (0,0,\cos\phi_1 = -h, \cos\phi_2 = -h) \rightarrow B = (0,0,0,0) \quad (4.82)$$

where we have labeled the points to comply with Fig. 1.1. This rotation mechanism or path is followed strictly when $j > 2$ but is also possible when $1 \leq j < 2$ and $j \geq 1+h^2$. The second rotation mechanism, referred to as antiferromagnetic ordering

is,

$$A = (0, 0, \pi, \pi) \rightarrow C1 = (0, 0, 0, \pi) \rightarrow B = (0, 0, 0, 0)$$

$$or \tag{4.83}$$

$$A = (0, 0, \pi, \pi) \rightarrow C2 = (0, 0, \pi, 0) \rightarrow B = (0, 0, 0, 0)$$

which is the preferred path when $(1 - h^2) < j < (1 + h^2)$, (so $0 < j < 2$), that is, when $C1$ and $C2$ are saddle points and the energy barrier is lower than that of C. We note that when $C1$ and $C2$ are saddle points they each have two equal and negative eigenvalues which is not as Langer proposed but can be catered for in the theory and we have modified the calculation of q, the flux of particles (j in [125]), to allow for saddle points with more than one negative direction (cf. Appendix B). Also, when $j = 2$ the particle will (have the choice to) cross one of two barriers C or $C1 = C2$, but when $0 < j < 1$ and $j < 1 - h^2$, $C1$ and $C2$ are minima, and the particle can get 'stuck' in one of two *potential wells*, which are metastable states. This may be caused by weak interaction and/or a weak field. The metastable states $C1$ and $C2$ may form part of the two-step relaxation process, which also involves a saddle point (or points) which is a solution (or which are solutions) to the quartic equation, Equation (4.48). For a discussion of the two step relaxation process see references [27, 28].

4.5 Energy Approximations

4.5.1 Ferromagnetic Ordering

At the saddle point $(0, 0, \cos\phi_1 = -h, \cos\phi_2 = -h)$, the Taylor series approximation of the energy $E = E_s$ is,

$$E_s \approx E_s^{(0)} + \frac{1}{2}\left[\frac{j}{2}p_1^2 + 2\left(\frac{-j}{2}\right)p_1p_2 + \frac{j}{2}p_2^2 + \left(\frac{j}{2} + h^2 - 1\right)\left(\phi_1 - \tilde{\phi}\right)^2 + 2\left(\frac{-j}{2}\right)\left(\phi_1 - \tilde{\phi}\right)\left(\phi_2 - \tilde{\phi}\right) + \left(\frac{j}{2} + h^2 - 1\right)\left(\phi_2 - \tilde{\phi}\right)^2\right] \quad (4.84)$$

where $E_s^{(0)} = E(0, 0, \cos\phi_1 = -h, \cos\phi_2 = -h) = -\frac{j}{2} + h^2$, $\tilde{\phi} = \cos^{-1}(-h)$.

Now we follow the notation of Equation (2.29) and write,

$$E \approx E_s^{(0)} + \frac{1}{2}\begin{pmatrix} p_1, p_2, \Phi_1, \Phi_2 \end{pmatrix}\begin{pmatrix} -\frac{j}{2} & \frac{j}{2} & 0 & 0 \\ \frac{j}{2} & -\frac{j}{2} & 0 & 0 \\ 0 & 0 & \frac{j}{2} + 1 - h^2 & -\frac{j}{2} \\ 0 & 0 & -\frac{j}{2} & \frac{j}{2} + 1 - h^2 \end{pmatrix}\begin{pmatrix} p_1 \\ p_2 \\ \Phi_1 \\ \Phi_2 \end{pmatrix} \quad (4.85)$$

where $\Phi_i = \phi_i - \tilde{\phi}, \quad i = 1, 2$. After some algebraic manipulation, (see Appendix F), we have the diagonalised Hessian form we seek, which is,

$$E \approx E_s^{(0)} + \begin{pmatrix} \eta_1, \eta_2, \eta_3, \eta_4 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & j & 0 & 0 \\ 0 & 0 & j - (1 - h^2) & 0 \\ 0 & 0 & 0 & -(1 - h^2) \end{pmatrix}\begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \eta_4 \end{pmatrix} \quad (4.86)$$

where the η_i are the transformation coordinates which diagonalise the Hessian (e.g. $\eta_1 = \frac{p_1 + p_2}{\sqrt{2}}$ cf Appendix F). The eigenvalues of the energy Hessian, denoted by the

μ's in Chapter 3, are the coefficients of the η variables in the expansion of the energy near the saddle point. Note that the coefficient of the variable η_1 is 0, $\eta_1 \in [-1, 1]$, so this will contribute a factor $v = 2$ in the numerator of the escape rate formula, since

$$\int_{-1}^{1} d\eta_1 = 2 \tag{4.87}$$

is the volume of the one dimensional η_1 space. The eigenvalues of the energy Hessian at the saddle point are,

$$\left\{0, j, j - (1 - h^2), -(1 - h^2)\right\}. \tag{4.88}$$

At the metastable minimum, $(0, 0, \pi, \pi)$ the energy approximation is,

$$E_m \approx E_m^{(0)} + \frac{1}{2}\left[\left(\frac{j}{2} + 1 - h\right) p_1^2 + 2\left(\frac{-j}{2}\right) p_1 p_2 + \left(\frac{j}{2} + 1 - h\right) p_2^2 + \right. \tag{4.89}$$
$$\left.\left(\frac{j}{2} + 1 - h\right)(\phi_1 - \pi)^2 + 2\left(\frac{-j}{2}\right)(\phi_1 - \pi)(\phi_2 - \pi) + \left(\frac{j}{2} + 1 - h\right)(\phi_2 - \pi)^2\right]$$

which, after a similar procedure as in the case of the saddle point we have,

$$E \approx E_m^{(0)} + \frac{1}{2}\left[(j + 1 - h)\left(\frac{p_1 - p_2}{\sqrt{2}}\right)^2 + (1 - h)\left(\frac{p_1 + p_2}{\sqrt{2}}\right)^2\right. \tag{4.90}$$
$$\left. + (j + 1 - h)\left(\frac{\Phi_1 - \Phi_2}{\sqrt{2}}\right)^2 + (1 - h)\left(\frac{\Phi_1 + \Phi_2}{\sqrt{2}}\right)^2\right]$$

where, $\Phi_i = \phi_i - \pi$, $i = 1, 2$ and the equations (F.5) hold for the transformation to η space. And the diagonalised form of the energy Hessian matrix is

$$E \approx E_m^{(0)} + \begin{pmatrix} \eta_1, \eta_2, \eta_3, \eta_4 \end{pmatrix} \begin{pmatrix} j+1-h & 0 & 0 & 0 \\ 0 & 1-h & 0 & 0 \\ 0 & 0 & j+1-h & 0 \\ 0 & 0 & 0 & 1-h \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \eta_4 \end{pmatrix} \quad (4.91)$$

So, the metastable state eigenvalues are,

$$\{j+1-h, 1-h, j+1-h, 1-h\}. \quad (4.92)$$

In both approximations, the Jacobean [125] for the transformation to η space has determinant 1.

4.5.2 Antiferromagnetic Ordering

The same metastable and stable states apply to this type of rotation as apply to the ferromagnetic case. We have seen that the Hessian matrices for the points $(0, 0, \pi, 0), (0, 0, 0, \pi)$ are, for our purposes, very similar, so we confine ourselves to calculating the energy approximation involving $\mathbf{H}_{(\pi,0)}$, thus,

$$E \approx E_{AF}^{(0)} + \frac{1}{2} \begin{pmatrix} p_1, p_2, \Phi_1, \Phi_2 \end{pmatrix} \begin{pmatrix} -\frac{j}{2} - h + 1 & -\frac{j}{2} & 0 & 0 \\ -\frac{j}{2} & -\frac{j}{2} + h + 1 & 0 & 0 \\ 0 & 0 & -\frac{j}{2} - h + 1 & \frac{j}{2} \\ 0 & 0 & \frac{j}{2} & -\frac{j}{2} + h + 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ \Phi_1 \\ \Phi_2 \end{pmatrix} \quad (4.93)$$

where $E_{AF}^{(0)} = \frac{j}{2} - 1$ [see Equation (4.68)] is the energy at the two points $(0, 0, 0, \pi)$ and $(0, 0, \pi, 0)$. The algebraic details of the diagonalisation of this matrix are not

as simple as for the metastable state of the saddle point above, however the matrix which diagonalises $\mathbf{H}_{(\pi,0)}$ is given in Appendix G.

4.6 Calculation of the Escape Rates

4.6.1 Ferromagnetic Escape Rate

Using the modified Langer formula derived in Chapter 3, i.e. Equation (3.14), we have $\upsilon = 2$ and,

$$\det \mathbf{E}^A = (1-h)^2(j+1-h)^2 \tag{4.94}$$

and

$$|\det{}' \mathbf{E}^s| = j\left(1-h^2\right)\left[j-\left(1-h^2\right)\right] \tag{4.95}$$

so the escape rate for a two-particle system with interaction and ferromagnetic ordering, Γ_F is,

$$\Gamma_F = \frac{\lambda_{+_F}}{2\pi}\frac{2}{\sqrt{2\pi k_B T}}\frac{(1-h)(j+1-h)}{\sqrt{j\left(1-h^2\right)\left(j-(1-h^2)\right)}}\exp\left\{-\frac{(1-h)^2}{k_B T}\right\} \tag{4.96}$$

where $\lambda_{+_F} = \alpha(1-h^2)$ is the positive eigenvalue of the Landau-Lifshitz equations with $\alpha = a > 0$ and $b = 1$ (see Appendix A). So,

$$\Gamma_{_F} = A_{_F}\exp\left\{-\frac{(1-h)^2}{k_B T}\right\} \tag{4.97}$$

where,

$$A_{_F} = \frac{\alpha}{\pi}\frac{1}{\sqrt{2\pi k_B T}}\frac{(1-h)(j+1-h)}{\sqrt{j(\frac{j}{(1-h^2)}-1)}}. \tag{4.98}$$

Now, there are a number of things to note about this result;

- In the limit $j \to \infty$ we regain the escape rate for a single particle in a parallel external field, Equation (3.66).
- $j \neq 0$.
- This formula is valid when $j > 1 + h^2$.
- It may also play a part in the calculation of the escape rate when $j = 1 + h^2$.
- The eigenvalue $j - (1 - h^2)$ is *never* negative or zero when this escape rate is effective.

4.6.2 Antiferromagnetic Escape Rate

In this case, there are no identically zero eigenvalues, so we can use Langer's formula with nonzero eigenvalues, Equation (2.39) and we have

$$\det \mathbf{E}^A = (1-h)^2(j+1-h)^2 \tag{4.99}$$

and

$$|\det \mathbf{E}^s| = \left[j - \left(1-h^2\right)\right]^2 \tag{4.100}$$

so the escape rate, Γ_{AF} is,

$$\Gamma_{AF} = A_{_{AF}} \exp\left\{-\frac{j-2h}{k_B T}\right\} \tag{4.101}$$

where,

$$A_{_{AF}} = \frac{Re\left\{\lambda_{+_{AF}}\right\}}{2\pi}\left(\frac{(1-h)(j+1-h)}{j-(1-h^2)}\right). \tag{4.102}$$

Note that,

1. this formula is valid when $1-h^2 < j < 1+h^2$, so the denominator $j-(1-h^2)$ is always positive and non-zero.

2. $Re\left\{\lambda_{+_{AF}}\right\}$ is the real part of the largest positive eigenvalue of the Landau-Lifshitz equations with $E = E_{AF}$.

It turns out that the eigenvalues of the Landau-Lifshitz equations for this case are complex numbers and are not given here as they are long expressions in the parameters a, b, j, h (cf. Appendix A). However, the relevant 4×4 matrix is given in Appendix H from which the eigenvalues are easily calculated on a desktop computer with a computation software package such as **DERIVE**$^{\text{TM}}$, either symbolically or numerically to the required precision. Also, this escape rate applies to both of the points $(0,0,\pi,0)$ and $(0,0,0,\pi)$.

4.6.3 Escape Rate when $j = 1+h^2$

When $j = 1+h^2$ the barrier heights for the ferromagnetic case and the antiferromagnetic case are equal. So, the total escape rate will be

$$\Gamma = \Gamma_{_{Tot}} \tag{4.103}$$

where

$$\Gamma_{_{Tot}} = \Gamma_F + 2\Gamma_{AF} \tag{4.104}$$

$$= (A_{_F} + 2A_{_{AF}}) \exp\left\{-\frac{(1-h)^2}{k_B T}\right\} \tag{4.105}$$

$$= \left(\frac{\alpha\sqrt{1-h^4}}{(1+h^2)\sqrt{\pi k_B T}} + \frac{Re\left\{\lambda_{+_{AF}}\right\}}{2\pi h}\right) \frac{(1-h)(2-h+h^2)}{2h} \exp\left\{-\frac{(1-h)^2}{k_B T}\right\} \tag{4.106}$$

This escape rate applies when $j = 1 + h^2$ and involves the three barriers, $(0, 0, 0, \pi)$, $(0, 0, \pi, 0)$ and $(0, 0, \cos\phi_1 = -h, \cos\phi_2 = -h)$.

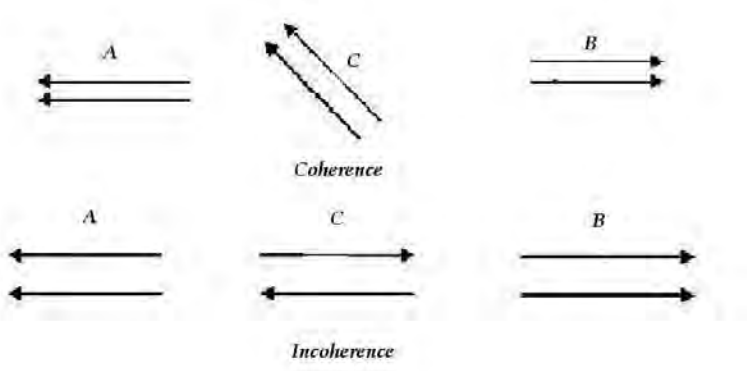

Figure 4.1: The rotation processes for different values of the exchange interaction coefficient. A, B and C represent the metastable, stable and saddle points respectively. The top diagram relates to the scenario when $j > 1 + h^2$. The particles rotate together, referred to as coherent relaxation. This happens when the exchange interaction is relatively strong ($j > 2$) and the two particles behave as one. The bottom diagram applies when $j < 1 + h^2$, the particles rotate one after the other, referred to as incoherent relaxation, due to weak exchange interaction $j < 2$. Below the threshold $j = 1$, the point C can form a metastable well where the particles may become trapped.

Chapter 5

Conclusion

We have seen that in the application of Langer's theory to the model of a single domain ferromagnetic particle, the chosen coordinate system necessitates certain substitutions in the energy function. The use of spherical polar coordinates of Equation (2.1) leads to the substitution $p = \cos\theta$ in the single particle problem and $p_i = \cos\theta_i$, $i = 1, 2$ in the interacting particle problem. This type of substitution is nonlinear and therefore all subsequent calculations carried out on the energy function in the context of Langer's theory must be consistent with this substitution. Any other choice can lead to integrals of the type in Equation (3.16). In fact, without the substitution $p = \cos\theta$ in spherical polar coordinates we cannot apply Langer's method. All that is required, after making the substitution is that the energy profile consist of a metastable well, a stable well and a sufficiently high barrier, or barriers. The barriers should be sufficiently high to ensure a Maxwell-Boltzmann distribution is

maintained in the well and the internal dynamics of the system are the dominant dynamical feature. We have seen that the energy Hessian in the Taylor series expansion of the energy function about the critical points is not covariant under nonlinear transformation. So, for example, in the interacting particle problem, if we had chosen the z-axis as the easy axis (as in [23] for the single particle), we would have had

$$E = -\frac{j}{2}\left[\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos\varphi\right] - \frac{1}{2}\left(\cos^2\theta_1 + \cos^2\theta_2\right) - h\left(\cos\theta_1 + \cos\theta_2\right) \quad (5.1)$$

where $\varphi = \phi_1 - \phi_2$, which in Langer's theory becomes,

$$E = -\frac{j}{2}\left[p_1 p_2 + \sqrt{1-p_1^2}\sqrt{1-p_2^2}\cos\varphi\right] - \frac{1}{2}\left(p_1^2 + p_2^2\right) - h\left(p_1 + p_2\right). \quad (5.2)$$

which presents some difficulties in implementing the theory, such as the loss of certain turning points. Also, as in [27, 28], the energy function is reduced to three variables (p_1, p_2, φ) and thus the number of (zero or non-zero) eigenvalues for the energy Hessians is 3 instead of 4. But these as just some of the problems associated with implementing Langer's theory. The biggest problem is that, as the system becomes more complicated, the process of finding the turning points becomes more difficult. The result is that, we can express the turning points, which are the roots of the partial differential equations for the energy function, as functions of the coordinates only. We then make certain assumptions and use mathematical devices to reduce the number of variables in the equations for the turning points.

In the interacting particle problem we assume the particle is a rigid rotor, as

in [30], which allows us to assume that the particle remains in one plane ($p_1 = p_2 = 0$) throughout the rotation. Then, all the turning points (in this plane) are solutions of a fourth order polynomial, which can be solved only if we fix the angle $(\phi_1 - \phi_2)$ between the rotors. We have found solutions for the turning points when the difference $(\phi_1 - \phi_2)$ is zero or π, and we have been able to draw some (qualified but plausible) conclusions about the relaxation process for two interacting particles. These conclusions are based, partly on our experience of the calculations for the single particle cases and partly on the assumptions we made during the calculations. But the picture is still incomplete. We need to build up a better picture of the turning points by studying the quartic equation in Equation (4.48).

5.1 Further Study

5.1.1 Equation (4.48)

Our calculations for the interacting particle do not apply to all values of the interaction coefficient j. When $j < 1 - h^2$ the energy profile or 'landscape' acquires a pair of metastable minima $(0, 0, 0, \pi)$ and $(0, 0, \pi, 0)$ (which are saddle points when $j > 1 - h^2$). So, the following question arises. What, if any, barrier does the particle need to overcome when it is in the state $(0, 0, 0, \pi)$ or $(0, 0, \pi, 0)$ and $j < (1 - h^2)$? Such a barrier would be solutions to the quartic equation, Equation (4.48),

$$q_i^4 + 2hq_i^3 - (1 - h^2)q_i^2 - 2hq_i - h^2 + \frac{(jc)^2}{4} = 0 \tag{5.3}$$

where $q_i = cos\phi_i$ $i = 1, 2$, $c = \sin \mathcal{C}$ and $\mathcal{C} = \phi_1 - \phi_2$. We know that this quartic is the key to describing the energy landscape in the plane $p_1 = p_2 = 0$. Maybe the quartic equation could be solved in general for specific values of $c = \sin(\phi_1 - \phi_2)$, but the results are likely to be almost incomprehensible. Perhaps a profile of turning points could be 'built up' by solving the equation for certain values of $c = \sin(\phi_1 - \phi_2)$ and the coefficients j and h, chosen such that $j < 1 - h^2$, $j > 1 - h^2$ and $j = 1 - h^2$. This seems to be the most obvious choice and method of investigation as the task could easily be set-out in an incremental format (increments of c in the interval $[-1, 1]$). The results could be then tested as to their nature, in a similar (algorithmic) method to that used in Chapter 4 (since the Hessian is sparse in the plane $p_1 = p_2 = 0$). This study could be the subject of further investigation and could yield yet more information, and indeed a completely new theory, about the reversal path of a single domain ferromagnetic particle for all values of j. Also we have not considered points outside the plane $p_1 = p_2 = 0$.

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Appendix A

Derivation of the Landau-Lifshitz Equations

From the starting point of the noiseless Gilbert equation [32] pg.72 with $\alpha = \eta$,

$$\frac{\partial \mathbf{M}}{\partial t} = \gamma \left(\frac{\partial E}{\partial \mathbf{M}} + \alpha\gamma \frac{\partial E}{\partial \mathbf{M}} \times \mathbf{M} \right) \times \mathbf{M} \tag{A.1}$$

where $\mathbf{M}$ is the magnetisation vector $\{M_x, M_y, M_z\}$, we wish to derive the dynamical equations which apply in the vicinity of the barrier. These are the Landau-Lifshitz equations for $\dot{p}$ and $\dot{\phi}$.

Let $\mathbf{m}$ be a unit vector in the direction of $\mathbf{M}$; so $\mathbf{M} = M_0\mathbf{m}$, and the magnitude of $\mathbf{M}$ is M_0. The vector $\mathbf{m}$ is on the unit sphere, see Figure 2.1.

Now,

$$\dot{\mathbf{m}} = \dot{\hat{\mathbf{r}}} \tag{A.2}$$

and

$$\dot{\hat{\mathbf{r}}} = \frac{\partial \hat{\mathbf{r}}}{\partial \theta}\dot{\theta} + \frac{\partial \hat{\mathbf{r}}}{\partial \phi}\dot{\phi} + \frac{\partial \hat{\mathbf{r}}}{\partial r}\dot{r}. \tag{A.3}$$

but

$$r = 1 \Rightarrow \dot{r} = 0.$$

Also,

$$\begin{aligned} \tfrac{\partial \hat{\mathbf{r}}}{\partial \theta} &= \hat{\boldsymbol{\theta}} \\ \tfrac{\partial \hat{\mathbf{r}}}{\partial \phi} &= \sin\theta\, \hat{\boldsymbol{\phi}} \end{aligned} \tag{A.4}$$

and

$$\hat{\boldsymbol{\theta}} = -\hat{\mathbf{p}}$$

since $p = \cos\theta$ decreases as θ increases in the interval $[0, \pi]$. So,

$$\dot{\hat{\mathbf{r}}} = \dot{\theta}\hat{\boldsymbol{\theta}} + \sin\theta\dot{\phi}\hat{\boldsymbol{\phi}}. \tag{A.5}$$

or

$$\frac{\partial \hat{\mathbf{r}}}{\partial p} = \frac{\partial \hat{\mathbf{r}}}{\partial \theta}\frac{\partial \theta}{\partial p} = -\frac{1}{\sin\theta}\hat{\boldsymbol{\theta}} = \frac{\hat{\mathbf{p}}}{\sqrt{1-p^2}} \tag{A.6}$$

so,

$$\dot{\hat{\mathbf{r}}} = \frac{\dot{p}}{\sqrt{1-p^2}}\hat{\mathbf{p}} + \dot{\phi}\sqrt{1-p^2}\hat{\boldsymbol{\phi}}. \tag{A.7}$$

Also, $\boldsymbol{\nabla}$ in spherical polar coordinates is

$$\boldsymbol{\nabla} = \hat{\mathbf{r}}\frac{\partial}{\partial r} + \hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi} \tag{A.8}$$

now $\frac{\partial E}{\partial r} = 0$ since $E \neq E(r)$, so, since $r = |\hat{\mathbf{r}}| = 1$

$$\boldsymbol{\nabla} E = \frac{\partial E}{\partial \theta}\hat{\boldsymbol{\theta}} + \frac{1}{sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\phi}}. \tag{A.9}$$

With

$$\hat{\mathbf{r}} \times \hat{\boldsymbol{\theta}} = \hat{\boldsymbol{\phi}},\ \hat{\boldsymbol{\theta}} \times \hat{\boldsymbol{\phi}} = \hat{\mathbf{r}},\ \hat{\boldsymbol{\phi}} \times \hat{\mathbf{r}} = \hat{\boldsymbol{\theta}}$$

and

$$\mathbf{A} \times \mathbf{B} = -\mathbf{B} \times \mathbf{A}.$$

We have,

$$\vec{\mathbf{m}} \times \boldsymbol{\nabla} E = \hat{\mathbf{r}} \times \left(\frac{\partial E}{\partial \theta}\hat{\boldsymbol{\theta}} + \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\phi}}\right) \tag{A.10}$$

$$= \frac{\partial E}{\partial \theta}\hat{\boldsymbol{\phi}} - \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\theta}} \tag{A.11}$$

$$= \frac{\partial E}{\partial p}\frac{dp}{d\theta}\hat{\boldsymbol{\phi}} - \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\theta}} \tag{A.12}$$

$$= -\sin\theta\frac{\partial E}{\partial p}\hat{\boldsymbol{\phi}} - \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\theta}} \tag{A.13}$$

that is,

$$\mathbf{m}\times\boldsymbol{\nabla}E = \sqrt{1-p^2}\frac{\partial E}{\partial p}\hat{\boldsymbol{\phi}} + \frac{1}{\sqrt{1-p^2}}\frac{\partial E}{\partial \phi}\hat{\mathbf{p}} \tag{A.14}$$

Also,

$$\{\mathbf{m}\times\boldsymbol{\nabla}E\}\times\mathbf{m} = \frac{\partial E}{\partial \theta}\hat{\boldsymbol{\theta}} + \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\phi}} \tag{A.15}$$

$$= \frac{\partial E}{\partial \theta}\hat{\boldsymbol{\theta}} + \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\phi}} \tag{A.16}$$

$$= \sin\theta\frac{\partial E}{\partial p}\hat{\mathbf{p}} + \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\phi}} \tag{A.17}$$

$$\{\mathbf{m}\times\boldsymbol{\nabla}E\}\times\mathbf{m} = \sqrt{1-p^2}\frac{\partial E}{\partial p}\hat{\mathbf{p}} + \frac{1}{\sqrt{1-p^2}}\frac{\partial E}{\partial \phi}\hat{\boldsymbol{\phi}} \tag{A.18}$$

Now, $\mathbf{m} = \frac{\mathbf{M}}{|M_0|}$, so equation (A.1) becomes,

$$\dot{\mathbf{m}} = b(\mathbf{m}\times\boldsymbol{\nabla}E) + a(\mathbf{m}\times\boldsymbol{\nabla}E)\times\mathbf{m} \tag{A.19}$$

so

$$\frac{\dot{p}}{\sqrt{1-p^2}}\hat{\mathbf{p}} + \dot{\phi}\sqrt{1-p^2}\hat{\boldsymbol{\phi}} = \left(\frac{b}{\sqrt{1-p^2}}\frac{\partial E}{\partial \phi} + a\sqrt{1-p^2}\frac{\partial E}{\partial p}\right)\hat{\mathbf{p}} + \left(-b\sqrt{1-p^2}\frac{\partial E}{\partial p} + \frac{a}{\sqrt{1-p^2}}\frac{\partial E}{\partial \phi}\right)\hat{\boldsymbol{\phi}} \tag{A.20}$$

where $b = -\gamma$ and $a = -\alpha\gamma$. So, putting it all together and equating co-efficients of $\hat{\mathbf{p}}$ and $\hat{\boldsymbol{\phi}}$ we have the coupled equations

$$\dot{p} = b\frac{\partial E}{\partial \phi} + a\left(1 - p^2\right)\frac{\partial E}{\partial p} \tag{A.21}$$

and,

$$\dot{\phi} = -b\frac{\partial E}{\partial p} + \frac{a}{1 - p^2}\frac{\partial E}{\partial \phi} \tag{A.22}$$

which we write in matrix notation, so

$$\begin{pmatrix} \dot{p} \\ \dot{\phi} \end{pmatrix} = \begin{pmatrix} a(1-p^2) & b \\ -b & \frac{a}{1-p^2} \end{pmatrix} \begin{pmatrix} \frac{\partial E}{\partial p} \\ \frac{\partial E}{\partial \phi} \end{pmatrix}. \tag{A.23}$$

The 2×2 matrix in equation (A.23) is referred to as the transport matrix. In practice these equations (A.21) and (A.22) are "linearised" at the barrier top by repacing E with the energy approximation about the barrier for the particular model in question, and 'p' is replaced with the value of p at the barrier. We then solve the resulting auxiliary equations, referred to as the transition equations, for the eigenvalue λ_+, which will be the largest postive eigenvalue of the transition matrix.

Appendix B

Calculation of the Flux over the Barrier, q, for many Negative Eigenvalues

The following appendix is an extension of appendix **IV.II**, page 600 of [125] $j = q$, to accommodate the presence of more than one negative eigenvalue in the Hessian Matrix for the saddle point. We start with equation (4.109) of [125]

$$q = \int \cdots \int \sum_j U_i J_i(\{\eta\}) \delta(u) d\eta_1 \cdots d\eta_{2N} \tag{B.1}$$

$$q = \sqrt{\frac{k_B T}{2\pi}} \int \cdots \int \sum_j U_i M_{ij} U_j Z^{-1} \exp\left\{-\frac{E}{k_B T}\right\} \exp\left\{-\frac{1}{2}\frac{u^2}{k_B T}\right\} \delta(u) d\eta_1 \cdots d\eta_{2N} \tag{B.2}$$

where, $E = E(\{\eta\})$. At the barrier point C in Fig.2.2 the energy is

$$E_s \approx E_s^{(0)} + \frac{1}{2}\sum_{i,j} e_{ij}(\eta_i - \tilde{\eta}_i)(\eta_j - \tilde{\eta}_j) + \mathcal{O}(\eta). \tag{B.3}$$

$$q = \sqrt{\frac{k_B T}{2\pi}} \frac{\sum_{i,j} U_i M_{ij} U_j}{Z} \int \cdots \int \exp\left\{ -\frac{E}{k_B T} \right\} \delta(u) d\eta_1 \cdots d\eta_{2N}. \tag{B.4}$$

Since

$$\exp\left\{ -\frac{1}{2} \frac{u^2}{k_B T} \right\} \delta(u) = \delta(u) \tag{B.5}$$

$$q \approx \sqrt{\frac{k_B T}{2\pi}} \frac{\lambda_+}{2\pi} Z^{-1} \exp\left\{ -\frac{E_s^{(0)}}{k_B T} \right\} \times$$
$$\int \cdots \int \exp\left\{ -\frac{1}{2} \frac{1}{k_B T} \sum_{i,j} e_{ij} (\eta_i - \tilde{\eta}_i)(\eta_j - \tilde{\eta}_j) + ik \sum_l U_l (\eta_l - \tilde{\eta}_l) \right\} d\eta dk \tag{B.6}$$

where we have substituted the energy $E = E_s$ about the barrier point $\{\tilde{\eta}\}$, and

$$d\eta \equiv d\eta_1 \cdots d\eta_{2N}. \tag{B.7}$$

Now, define the matrix $\mathbf{S}$

$$\mathbf{S} = (S_{ij}) \tag{B.8}$$

and the vector $\mathbf{x} = (x_j)$ by the equation

$$x_i \equiv \sum_j S_{ij} \left(\eta_j - \tilde{\eta}_j \right) \tag{B.9}$$

then, we have,

$$\sum_{i,j} e_{ij} (\eta_i - \tilde{\eta}_i)(\eta_j - \tilde{\eta}_j) = \sum_{l=1}^{2N} \mu_l x_l^2 \tag{B.10}$$

where,

$$\mu_1 \leq \mu_2 \leq \cdots \leq \mu_m < 0 \tag{B.11}$$

and

$$\mu_j > 0, \qquad m \leq j \leq 2N. \tag{B.12}$$

The entries of $\mathbf{S}$ are constants, given by

$$\frac{\partial x_i}{\partial \eta_j} = S_{ij}. \tag{B.13}$$

Hence the Jacobean of the transformation (B.9) is given by

$$J = \begin{vmatrix} \frac{\partial x_1}{\partial \eta_1} & \cdots & \frac{\partial x_{2N}}{\partial \eta_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial x_1}{\partial \eta_{2N}} & \cdots & \frac{\partial x_{2N}}{\partial \eta_{2N}} \end{vmatrix} = \det(\mathbf{S}). \tag{B.14}$$

Langer [13] states that this transformation is orthogonal since $\mathbf{E}$ is symmetric, so

$$J = \det \mathbf{S} = 1 \tag{B.15}$$

and

$$S_{ij}^{-1} = S_{ij}^{t} \tag{B.16}$$

Now changing to x-space we have

$$q \approx \sqrt{\frac{k_B T}{2\pi}} \frac{1}{Z} \frac{\lambda_+}{2\pi} \exp\left\{ -\frac{E_s^{(0)}}{k_B T} \right\} \times$$
$$\int\int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum_j \mu_j \left(x_j^2 - \frac{2ikU_j}{\beta} \sum_l S_{jl} x_l \right) \right\} J dx_1 \cdots dx_{2N} dk. \tag{B.17}$$

Let

$$I = \int\int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum_j \mu_j (x_j^2 - \frac{2ikU_j}{\beta} \sum_l S_{jl} x_l \right\} J dx_1 \cdots dx_{2N} dk. \tag{B.18}$$

So,

$$q \approx \sqrt{\frac{k_B T}{2\pi}} \frac{1}{Z} \frac{\lambda_+}{2\pi} \exp\left\{-\frac{E_s^{(0)}}{k_B T}\right\} I. \tag{B.19}$$

Now, separating the first m μ out from the $2N$ μ we can write the above integral I as,

$$\int\int\cdots\int \exp\left\{-\frac{\beta}{2}\left(\sum_{j=1}^{m}\mu_j x_j^2 + \sum_{j=m+1}^{2N}\mu_j x_j^2 - \sum_j\sum_l \frac{2ikU_j}{\beta}S_{jl}x_l\right)\right\} J dx_1\cdots dx_{2N}dk.$$

Now,

$$I = J\int\int\cdots\int \exp\left\{-\frac{\beta}{2}\left(\sum_{j=1}^{m}\mu_j x_j^2 + \sum_{m+1}^{2N}\mu_j x_j^2 - \sum_l \frac{2ik}{\beta}\tilde{U}_l x_l\right)\right\} dx_m dx_{2N} dk \tag{B.20}$$

where,

$$\begin{aligned} \tilde{U}_l &= \textstyle\sum_j U_j S_{jl} \\ dx_m &= dx_1 dx_2\cdots dx_m \qquad . \\ dx_{2N} &= dx_{m+1}dx_{m+2}\cdots dx_{2N} \end{aligned} \tag{B.21}$$

So,

$$\begin{aligned} I = J\int\Bigg[\int\cdots\int \exp\left\{-\frac{\beta}{2}\sum_{j=1}^{m}\left(\mu_j x_j^2 - \frac{2ik}{\beta}\tilde{U}_j x_j\right)\right\} dx_m \times \\ \int\cdots\int \exp\left\{-\frac{\beta}{2}\sum_{m+1}^{2N}\left(\mu_j x_j^2 - \frac{2ik}{\beta}\tilde{U}_j x_j\right)\right\} dx_{2N}\Bigg] dk \end{aligned} \tag{B.22}$$

$$\begin{aligned} = J\int\Bigg[\int\cdots\int \exp\left\{-\frac{\beta}{2}\sum_{j=1}^{m}\left(\mu_j x_j^2 - \frac{2ik\tilde{U}_j}{\beta}x_j\right)\right\} dx_m \times \\ \int\cdots\int \exp\left\{-\frac{\beta}{2}\sum_{m+1}^{2N}\mu_j\left(x_j^2 - \frac{2ik}{\beta\mu_j}\tilde{U}_j x_j + \frac{i^2k^2\tilde{U}_j^2}{\beta\mu_j^2}\right)\right\} dx_{2N} \times \\ \exp\left\{-\frac{\beta}{2}\sum_{m+1}2N\frac{k^2\tilde{U}_j^2}{\beta^2\mu_j}\right\}\Bigg] dk \end{aligned} \tag{B.23}$$

$$= J \int \left[\int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum_{j=1}^{m} \left(\mu_j x_j^2 - \frac{2ik\tilde{U}_j}{\beta} x_j \right) \right\} dx_m \times \right.$$
$$\left. \prod_{m+1}^{2N} \exp\left\{ -\frac{k^2 \tilde{U}_j^2}{2\beta\mu_j} \right\} \int \exp\left\{ -\frac{\beta\mu_j}{2} \left(x_j - \frac{ik\tilde{U}_j}{\beta\mu_j} \right)^2 \right\} dx_{2N} \right] dk \tag{B.24}$$

$$= J \int \left[\int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum_{j=1}^{m} \left(\mu_j x_j^2 - \frac{2ik\tilde{U}_j}{\beta} x_j \right) \right\} dx_m \prod_{m+1}^{2N} \exp\left\{ -\frac{k^2 \tilde{U}_j^2}{2\beta\mu_j} \right\} \sqrt{\frac{2\pi}{\beta\mu_j}} \right] dk$$

$$= J \prod_{j=m+1}^{2N} \sqrt{\frac{2\pi}{\beta\mu_j}} \int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum_{j=1}^{m} \left(\mu_j x_j^2 \right) \right\} \exp\left\{ \sum_{m+1}^{2N} -\frac{k^2 \tilde{U}_j^2}{2\beta\mu_j} + \sum_{j=1}^{m} ik\tilde{U}_j x_j \right\} dk \, d\eta_m$$

$$= J \prod_{m+1}^{2N} \sqrt{\frac{2\pi}{\beta\mu_j}} \int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum_{j=1}^{m} \left(\mu_j x_j^2 \right) \right\} \exp\left\{ -\frac{-k^2}{2\beta} \sum_{m+1}^{2N} \frac{\tilde{U}_j^2}{\mu_j} + ik \sum_{j=1}^{m} \tilde{U}_j x_j \right\} dk \, dx_m$$

Next, complete the square on k to get,

$$\begin{aligned} &= J \prod_{m+1}^{2N} \sqrt{\frac{2\pi}{\beta\mu_j}} \int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum_{j=1}^{m} \left(\mu_j x_j^2 \right) \right\} \times \\ &\times \int \exp\left\{ \frac{-1}{2\beta} \sum_{m+1}^{2N} \frac{\tilde{U}_l^2}{\mu_l} \left(k^2 - \frac{\sum_j 2\beta i \tilde{U}_j x_j}{\left(\sum_{m+1}^{2N} \frac{\tilde{U}_l^2}{\mu_l} \right)} k + \frac{\beta^2 i^2 \sum_{j=1}^{m} \tilde{U}_j^2 \eta_j^2}{\left(\sum_{m+1}^{2N} \frac{\tilde{U}_l^2}{\mu_l} \right)^2} \right) \right\} \\ &\times \exp\left\{ \frac{-\beta}{2} \frac{\sum_{j=1}^{m} \tilde{U}_j^2 x_j^2}{\left(\sum_{m+1}^{2N} \frac{\tilde{U}_l^2}{\mu_l} \right)} \right\} dk \, dx_m \end{aligned} \tag{B.25}$$

and complete the square on the $\sum_{m+1}^{2N} \mu_j x_j$ to get

$$\begin{aligned} &= J \prod_{m+1}^{2N} \sqrt{\frac{2\pi}{\beta\mu_j}} \int \exp\left\{ \frac{-\beta}{2} \left(\sum \mu_j + \frac{\sum_{j=1}^{m} \tilde{U}_j}{\left(\sum_{m+1}^{2N} \frac{\tilde{U}_l^2}{\mu_l} \right)^2} \right) x_j^2 \right\} \times \\ &\qquad \int \exp\left\{ \frac{-1}{2\beta} \sum_{m+1}^{2N} \frac{\tilde{U}_l^2}{\mu_l} \left(k - \frac{i\beta \sum \tilde{U}_j x_j}{\left(\sum_{m+1}^{2N} \frac{\tilde{U}_l^2}{\mu_l} \right)^2} \right)^2 \right\} dk \, dx_m \end{aligned} \tag{B.26}$$

$$= J\prod_{m+1}^{2N}\sqrt{\frac{2\pi}{\beta\mu_j}}\sqrt{\frac{2\pi\beta}{\sum_{m+1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}}}\sqrt{\frac{2\pi}{\beta}}\left[\sum_j \mu_j + \frac{\sum_{j=1}^{m}\tilde{U}_j}{\left(\sum_{m+1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}\right)^2}\right]^{-\frac{1}{2}} \tag{B.27}$$

$$= J\prod_{m+1}^{2N}\sqrt{\frac{2\pi}{\beta\mu_j}}\sqrt{\frac{2\pi\beta}{\sum_{m+1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}}}\sqrt{\frac{2\pi}{\beta\sum_{j=1}^{m}|\mu_j|}}\left[-1 + \frac{\sum_{j=1}^{m}\frac{\tilde{U}_j}{|\mu_j|}}{\left(\sum_{m+1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}\right)^2}\right]^{-\frac{1}{2}} \tag{B.28}$$

since $\mu_1 < \mu_2 < \cdots < \mu_m < 0$, and $\mu_{m+1} > \mu_{m+2} > \cdots > \mu_{2N} > 0$. So,

$$I = J\prod_{j=1}^{2N}\sqrt{\frac{2\pi}{\beta|\mu_j|}}\sqrt{2\pi\beta}\left[\sum_{l=m+1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}\right]^{-\frac{1}{2}}\left[-1 + \frac{\left(\sum_{j=1}^{m}\frac{\tilde{U}_j}{|\mu_j|}\right)}{\left(\sum_{l=m+1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}\right)}\right]^{-\frac{1}{2}} \tag{B.29}$$

$$= J\prod_{j=1}^{2N}\sqrt{\frac{2\pi}{\beta|\mu_j|}}\sqrt{2\pi\beta}\left[-\sum_{l=1}^{2N}\frac{\tilde{U}_l^2}{|\mu_l|}\right]^{-\frac{1}{2}}. \tag{B.30}$$

So,

$$q = \frac{\lambda_+}{Z}\frac{\exp\left\{-\beta E_s^{(0)}\right\}}{2\pi}J\prod_{j=1}^{2N}\sqrt{\frac{2\pi}{\beta|\mu_j|}}\sqrt{2\pi\beta}\left[-\sum_{l=1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}\right]^{-\frac{1}{2}} \tag{B.31}$$

$$= \frac{\lambda_+}{Z}\frac{\exp\left\{-\beta E_s^{(0)}\right\}}{2\pi}J\prod_{j=1}^{2N}\sqrt{\frac{2\pi}{\beta|\mu_j|}}\left[-\sum_{l=1}^{2N}\frac{\tilde{U}_l^2}{\mu_l}\right]^{-\frac{1}{2}}. \tag{B.32}$$

Now, let

$$\mathbf{M} = \begin{pmatrix} \mu_1 & 0 & 0 & \cdots & 0 \\ 0 & \mu_2 & 0 & \cdots & 0 \\ 0 & 0 & \mu_3 \cdots & 0 & \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \mu_{2N} \end{pmatrix} \tag{B.33}$$

$$\mathbf{M} = \mathbf{S}^t\mathbf{E}^s\mathbf{S}. \tag{B.34}$$

Hence,

$$\det \mathbf{M} = \det \mathbf{E}^s \left[\det \left(\mathbf{S}\right)\right]^2 \tag{B.35}$$

$$\det \mathbf{M} = \det \left(\mathbf{E}^s\right) J^2 \tag{B.36}$$

$$\det \mathbf{M} = \prod_{j=1}^{2N} \mu_j \tag{B.37}$$

for j distinct non-zero eigenvalues μ and so,

$$\prod_{j=1}^{2N} \sqrt{\frac{2\pi}{\beta \left|\mu_j\right|}} = \left|\det \left[\frac{\mathbf{E}^s}{2\pi k_B T}\right]\right|^{-\frac{1}{2}} \left(\frac{1}{\det \mathbf{S}}\right) \tag{B.38}$$

using Equation (B.14)

$$J \prod_{j=1}^{2N} \sqrt{\frac{2\pi}{\beta \left|\mu_j\right|}} = \left|\det \left[\frac{\mathbf{E}^s}{2\pi k_B T}\right]\right|^{-\frac{1}{2}}. \tag{B.39}$$

Also,

$$\mathbf{M}^{-1} = \begin{pmatrix} \frac{1}{\mu_1} & 0 & 0 & \cdots & 0 \\ 0 & \frac{1}{\mu_2} & 0 & \cdots & 0 \\ 0 & 0 & \frac{1}{\mu_3} \cdots & 0 & \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \frac{1}{\mu_{2N}} \end{pmatrix} \tag{B.40}$$

$$\mathbf{M}^{-1} = \mathbf{S}^{-1} \left(\mathbf{E}^s\right)^{-1} \left(\mathbf{S}^t\right)^{-1} \tag{B.41}$$

or,

$$\mathbf{S}\mathbf{M}^{-1}\mathbf{S}^t = \left(\mathbf{E}^s\right)^{-1} = \left(e_{ij}\right)^{-1}. \tag{B.42}$$

Now,

$$\sum_{ij} U_i e_{ij} U_j^{-1} = \sum_{i,j,k,l} U_i S_{ik} M_{kl}^{-1} S_{lj}^t U_j$$
$$= \sum_{k,l} \tilde{U}_k M_{kl}^{-1} \tilde{U}_l \tag{B.43}$$

$$= \sum_{k,l} \tilde{U}_k \frac{1}{\mu_k} \delta_{kl} \tilde{U}_l \tag{B.44}$$

$$= \sum_{k} \frac{\tilde{U}_k}{\mu_k} \tilde{U}_k \tag{B.45}$$

$$= \sum_{k} \frac{\tilde{U}_k^2}{\mu_k}. \tag{B.46}$$

Now, since $\sum_{i,j} U_i e_{ij}^{-1} U_j < 0$ [125], we see

$$\left(- \sum_{k} \frac{\tilde{U}_k^2}{\mu_k} \right)^{-\frac{1}{2}} = \left| \sum_{ij} U_i e_{ij}^{-1} U_j \right|^{-\frac{1}{2}} \tag{B.47}$$

and hence,

$$q = \frac{\sum_{ij} U_i M_{ij} U_j}{\left| \sum_{ij} U_i e_{ij}^{-1} U_j \right|^{\frac{1}{2}}} \frac{1}{2\pi} \left| \det \frac{\mathbf{E}^s}{2\pi k_B T} \right|^{-\frac{1}{2}} Z^{-1} \exp\left\{ -\beta E_s^{(0)} \right\} \tag{B.48}$$

which is the current of particles (flux) through the plane $u = 0$ near the barrier and not parallel to the direction of flow.

Appendix C

Calculation of the number of particles in the metastable well N_A

$$N_A = \int \dots \int \rho_{eq}\, d\eta_1 \dots d\eta_{2N} \tag{C.1}$$

$$= Z^{-1} \int \dots \int \exp\{-\beta E_A\}\, d\eta_1 \dots d\eta_{2N} \tag{C.2}$$

The energy approximation in the well (the point A in Fig.2.2) is,

$$E_A = E_A^{(0)} + \frac{1}{2} \sum_{ij} a_{ij} \left(\eta_i - \tilde{\eta}_i\right) \left(\eta_j - \tilde{\eta}_j\right) \tag{C.3}$$

So we substitute the approximate for the energy to get

$$N_A = \frac{1}{Z} \int \dots \int e^{-\beta E_A^{(0)}} \exp\left\{ -\frac{\beta}{2} \sum_{ij} a_{ij} (\eta_i - \tilde{\eta}_i)(\eta_j - \tilde{\eta}_j) \right\} d\eta_1 \dots \eta_{2N} \tag{C.4}$$

Define the vector **x** as in **Appendix B**,

$$x_i = \sum_j S_{ij} \left(\eta_j - \tilde{\eta}_j\right) \tag{C.5}$$

So,

$$\frac{1}{2}\sum_{ij} a_{ij}\left(\eta_i - \tilde{\eta}_i\right)\left(\eta_j - \tilde{\eta}_j\right) = \frac{1}{2}\sum_{l} \mu_l x_l^2 \tag{C.6}$$

$$N_A = \frac{1}{Z}\int \ldots \int e^{-\beta E_A^{(0)}} \exp\left\{-\frac{\beta}{2}\sum_{l} \mu_l x_l^2\right\} J d\eta_1 \ldots \eta_{2N} \tag{C.7}$$

where

$$J = \det\left(S_{ij}\right) = \det\left(\mathbf{S}\right) \tag{C.8}$$

So,

$$N_A = \frac{1}{Z} e^{-\beta E_A^{(0)}} J \prod_{l=1}^{2N} \sqrt{\frac{2\pi}{\beta\mu_l}}. \tag{C.9}$$

Let $\mathbf{M}$ be a diagonal matrix of the eigenvalues of $\mathbf{E}_A = (a_{ij})_{i,j=1}^{2N}$

$$\mathbf{S}^t \mathbf{E}^A \mathbf{S} = \mathbf{M} \tag{C.10}$$

and

$$\det \mathbf{S} = 1 \tag{C.11}$$

since $\mathbf{E}_A$ is symmetric. So,

$$\left[\det\left(\mathbf{S}\right)\right]^2 \det\left(\mathbf{E}^A\right) \det\left(\mathbf{M}\right) = \prod_{i=1}^{2N} \mu_i \tag{C.12}$$

$$\det\left(\frac{\mathbf{E}^A}{2\pi k_B T}\right) = \prod_{i=1}^{2N} \frac{\beta\mu_i}{2\pi} \tag{C.13}$$

Then,

$$\prod_{i=1}^{2N} \sqrt{\frac{2\pi}{\beta\mu_i}} = \left[\det\left(\frac{\mathbf{E}^s}{2\pi k_B T}\right)\right]^{-1/2} \tag{C.14}$$

So,

$$N_A = Z^{-1} e^{-\beta E_A^{(0)}} \prod_{l=1}^{2N} \sqrt{\frac{2\pi}{\beta \mu_l}} \tag{C.15}$$

$$= Z^{-1} e^{-\beta E_A^{(0)}} \left[\det \left(\frac{\mathbf{E}^A}{2\pi k_B T} \right) \right]^{-1/2} \tag{C.16}$$

is the number of particles in the metastable minimum (well).

Appendix D

Proof of Equation (4.4)

Consider the 4×4 matrix $\mathbf{H}$, with positive constants a, b, c, d, e, f, g, and h,

$$\mathbf{H} = \begin{pmatrix} a & b & 0 & 0 \\ c & d & 0 & 0 \\ 0 & 0 & e & f \\ 0 & 0 & g & h \end{pmatrix} \tag{D.1}$$

Expand $\mathbf{H}$ about the first row,

$$\det \mathbf{H} = a \begin{vmatrix} d & 0 & 0 \\ 0 & e & f \\ 0 & g & h \end{vmatrix} - b \begin{vmatrix} c & 0 & 0 \\ 0 & e & f \\ 0 & g & h \end{vmatrix}, \tag{D.2}$$

then,

$$\det \mathbf{H} = ad(eh - gf) - bc(eh - gf) \tag{D.3}$$

i.e.,

$$\det \mathbf{H} = (ad - bc)(eh - gf) \tag{D.4}$$

$$\det \mathbf{H} = \det \mathbf{H}_p \det \mathbf{H}_\phi \tag{D.5}$$

which is equation (4.71) where,

$$\mathbf{H}_p = \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} e_{11} & e_{12} \\ e_{21} & e_{22} \end{pmatrix} \tag{D.6}$$

and,

$$\mathbf{H}_\phi = \begin{pmatrix} e & f \\ g & h \end{pmatrix} = \begin{pmatrix} e_{33} & e_{34} \\ e_{43} & e_{44} \end{pmatrix} \tag{D.7}$$

Appendix E

The Nature of the Points $(0, 0, 0, \pi)$ and $(0, 0, \pi, 0)$

The following is a supporting argument of the nature of the points $(0, 0, 0, \pi)$ and $(0, 0, \pi, 0)$.

With respect to the matrix

$$\mathbf{H}_p = \begin{pmatrix} -\frac{j}{2} + h + 1 & -\frac{j}{2} \\ -\frac{j}{2} & -\frac{j}{2} - h + 1 \end{pmatrix}, \tag{E.1}$$

three situations present themselves

1. When $\det \mathbf{H}_p < 0$ the points are saddle points.

2. When $\det \mathbf{H}_p > 0$, and $-\frac{j}{2} - h + 1 > 0$ the points are minima.

3. When $\det \mathbf{H}_p > 0$, and $-\frac{j}{2} - h + 1 < 0$ the points are maxima.

Now

$$\det \mathbf{H}_p = -\left[j - \left(1 - h^2\right)\right] \tag{E.2}$$

and for a maximum

$$\det \mathbf{H}_p > 0 \tag{E.3}$$

that is,

$$j < \left(1 - h^2\right) \tag{E.4}$$

and

$$j > 2(1 - h) \tag{E.5}$$

which are obviously incompatible.

For a saddle point,

$$\det \mathbf{H}_p < 0 \tag{E.6}$$

or

$$j > 1 - h^2 \tag{E.7}$$

so, (in terms of the bound on j) we are assured of a saddle point when $j > 1$, and there is a possibility of a saddle point when $0 < j < 1$.

For a minimum we must have,

$$j < 2(1 - h) \tag{E.8}$$

and

$$\det \mathbf{H}_p > 0 \tag{E.9}$$

or

$$j < 1 - h^2 \tag{E.10}$$

which can only happen when $0 < j < 1$. So, when $0 < j < 1$ the points maybe either saddle points or minima, depending on the direction of the inequality

$$j \gtrless 1 - h^2. \tag{E.11}$$

When

$$j = 1 - h^2 \tag{E.12}$$

the analysis is indeterminate. Also, the eigenvalues of the matrices $\mathbf{H}_{(0,\pi)}$ and $\mathbf{H}_{(\pi,0)}$ are equal. There are two eigenvalues which occur twice, so in all, there are four eigenvalues, $c_{1,3}$ and $c_{2,4}$ where,

$$c_{1,3} = -\frac{j}{2} + 1 + \frac{1}{2}\sqrt{4h^2 + j^2} \tag{E.13}$$

and

$$c_{2,4} = -\frac{j}{2} + 1 - \frac{1}{2}\sqrt{4h^2 + j^2} \tag{E.14}$$

Now, we want to find values of j and h which make $c_{1,3}$ and$c_{2,4}$ simultaneously positive or simultaneously negative, in which case the 'antiferromagnetic' points $C1$ and $C2$ of equation (4.83) are minima or maxima respectively, so, we write the inequalities

$$\begin{aligned} c_{1,3} &< 0 \\ c_{2,4} &< 0 \end{aligned} \tag{E.15}$$

which is true iff,

$$-(j-2) < \sqrt{4h^2 + j^2} < j - 2 \tag{E.16}$$

i.e.

$$\left|\sqrt{4h^2 + j^2}\right| < (j-2) \tag{E.17}$$

with $j > 2$. This is the region where the points $(0, 0, 0, \pi)$ and $(0, 0, \pi, 0)$ are maxima. But again this is inconsistent with equation (E.7), so there can be no maximum at these points.

To see where they are minima we write,

$$\begin{aligned} c_{1,3} &> 0 \\ c_{2,4} &> 0 \end{aligned} \tag{E.18}$$

and this is possible when,

$$\left|\sqrt{4h^2 + j^2}\right| < (2-j) \tag{E.19}$$

with $0 < j < 2$. This is the region were the points are minima.

To find values of j and h which make the points a saddle we simply multiply the eigenvalues together and set the result < 0. So,

$$c_{1,3} \times c_{2,4} = \det \mathbf{H}_p = -\left[j - \left(1 - h^2\right)\right] \tag{E.20}$$

or

$$j > (1 - h^2) \tag{E.21}$$

where, $j \geq 1$ ensures a saddle point but also $0 < j < 1$ is possible since $0 \leq h < 1$, as before.

Appendix F

Algebraic Manipulations which Diagonalise the Hessian Matrix at the Barrier when $j > 2$

The following shows the algebraic manipulations which yield the eigenvalues of the energy Hessian matrix and the coordinates η at the saddle point for the case $j > 1 - h^2$. We show the calculation for the barrier top (saddle point) only, as the metasable minimum calculation is very similiar. Also, we give the matrix which diagonalises the hessian, which is the matrix S_{ij} above, i.e the Jacobean for the transformation into η-space.

Since the Hessian matrix is symmetric, we use the method of completing the square, so

$$E_s \approx E_s^{(0)} + \frac{1}{2}\left[\frac{j}{2}p_1^2 + 2\left(\frac{-j}{2}\right)p_1p_2 + \frac{j}{2}p_2^2 + \left(\frac{j}{2} + h^2 - 1\right)\left(\phi_1 - \tilde{\phi}\right)^2 + \right. \tag{F.1}$$

$$2\left(\frac{-j}{2}\right)\left(\phi_1-\tilde{\phi}\right)\left(\phi_2-\tilde{\phi}\right)+\left(\frac{j}{2}+h^2-1\right)\left(\phi_2-\tilde{\phi}\right)^2\Bigg]$$

where $E_s^{(0)} = E(0,0,\cos\phi_1 = -h, \cos\phi_2 = -h) = -\frac{j}{2} + h^2$, $\tilde{\phi} = \cos^{-1}(-h)$.

Or, on tidying up,

$$E_s \approx E_s^{(0)} + \frac{1}{2}\left[\frac{j}{2}p_1^2 - jp_1p_2 + \frac{j}{2}p_2^2 + \left(\frac{j}{2} - \frac{1-h^2}{2}\right)\Phi_1^2 - \left(\frac{1-h^2}{2}\right)\Phi_1^2 + \right. \tag{F.2}$$
$$\left. j\Phi_1\Phi_2 + \left(\frac{j}{2} - \frac{1-h^2}{2}\right)\Phi_2^2 - \frac{1-h^2}{2}\Phi_2^2 - (1-h^2)\Phi_1\Phi_2 + (1-h^2)\Phi_1\Phi_2\right]$$

where, $\Phi_i = \phi_i - \tilde{\phi}_i$ $i = 1, 2$. So, E_s can be written,

$$E_s \approx E_s^{(0)} + \frac{1}{2}\left[\frac{j}{2}(p_1-p_2)^2 + \left(\frac{j}{2} - \frac{1-h^2}{2}\right)\Phi_1^2 - \left(j - (1-h^2)\right)\Phi_1\Phi_2 + \right.$$
$$\left. \left(\frac{j}{2} - \frac{1-h^2}{2}\right)\Phi_2^2 - \frac{1-h^2}{2}\Phi_1^2 - (1-h^2)\Phi_1\Phi_2 - \frac{1-h^2}{2}\Phi_2^2\right] \tag{F.3}$$

Or,

$$E_s \approx E_s^{(0)} + \tfrac{1}{2}\left[j\left(\tfrac{p_1-p_2}{\sqrt{2}}\right)^2 + \left(j-(1-h^2)\right)\left(\tfrac{\Phi_1-\Phi_2}{\sqrt{2}}\right)^2 - (1-h^2)\left(\tfrac{\Phi_1+\Phi_2}{\sqrt{2}}\right)^2\right] \tag{F.4}$$

where, the variables $\frac{p_1 \pm p_2}{\sqrt{2}}$ and $\frac{\Phi_1 \pm \Phi_2}{\sqrt{2}}$ form the Jacobean [125] which diagonalise the Hessian matrix part of the energy approximation (c.f. Chapter 2).

$$\begin{aligned} \eta_1 &= \tfrac{p_1+p_2}{\sqrt{2}} \\ \eta_2 &= \tfrac{p_1-p_2}{\sqrt{2}} \\ \eta_3 &= \tfrac{\Phi_1+\Phi_2}{\sqrt{2}} \\ \eta_4 &= \tfrac{\Phi_1-\Phi_2}{\sqrt{2}} \end{aligned} \tag{F.5}$$

so,

$$S_{ij} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix}. \tag{F.6}$$

So, for this saddle point the Equation (B.34) above yields,

$$\mathbf{M} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & j & 0 & 0 \\ 0 & 0 & j-(1-h^2) & 0 \\ 0 & 0 & 0 & -(1-h^2) \end{pmatrix}. \tag{F.7}$$

The eigenvalues of the energy Hessian are the diagonal elements of $\mathbf{M}$, or the coefficents of the η_i, $(i = 1, .., 4)$ variables. At the saddle point these eigenvalues are,

$$\left\{0, j, j-(1-h^2), -(1-h^2)\right\} \tag{F.8}$$

Note that the coefficient of the variable η_1 is 0 and the possible range of values of η_1 is $[-1, 1]$, so this will contribute a factor $v = 2$ in the numerator of the escape rate formula to account for the volume of the one-dimensional space associated with the variable η_1.

Appendix G

Antiferromagnetic Hessians

The Hessians for the antiferromagnetic states $(0,0,0,\pi)$ and $(0,0,\pi,0)$ are (c.f. Equations (4.70) and (4.69)),

$$\mathbf{H}_{(0,\pi)} = \begin{pmatrix} -\frac{j}{2}+h+1 & -\frac{j}{2} & 0 & 0 \\ -\frac{j}{2} & -\frac{j}{2}-h+1 & 0 & 0 \\ 0 & 0 & -\frac{j}{2}+h+1 & \frac{j}{2} \\ 0 & 0 & \frac{j}{2} & -\frac{j}{2}-h+1 \end{pmatrix} \tag{G.1}$$

and,

$$\mathbf{H}_{(\pi,0)} = \begin{pmatrix} -\frac{j}{2}-h+1 & -\frac{j}{2} & 0 & 0 \\ -\frac{j}{2} & -\frac{j}{2}+h+1 & 0 & 0 \\ 0 & 0 & -\frac{j}{2}-h+1 & \frac{j}{2} \\ 0 & 0 & \frac{j}{2} & -\frac{j}{2}+h+1 \end{pmatrix} \tag{G.2}$$

There are two non-zero eigenvalues, which occur twice

$$1 - \frac{j}{2} \pm \frac{1}{2}\sqrt{j^2 + 4h^2} \tag{G.3}$$

So, in the range $1 < j < 2$ there are two negative eigenvalues and two positive, this is catered for in the calculation of the flux over the barrier in Appendix B.

$$\det \mathbf{H}_{(0,\pi)} = \det \mathbf{H}_{(\pi,0)} = (j - (1 - h^2))^2 \tag{G.4}$$

These are essentially the same in terms of the algebraic treatment so we concentrate on (G.2) The matrix which diagonalises the Hessian matrix is S_{ij}, i.e. the matrix in equation (G.5) which appears in equation (B.42), which for the matrix (G.2) is,

$$\begin{pmatrix} \frac{-\sqrt{j^2+4h^2}+2h}{j} & 1 & 0 & 0 \\ 1 & \frac{\sqrt{j^2+4h^2}-2h}{j} & 0 & 0 \\ 0 & 0 & \frac{-\sqrt{j^2+4h^2}-2h}{j} & 1 \\ 0 & 0 & 1 & \frac{\sqrt{j^2+4h^2}+2h}{j} \end{pmatrix} \tag{G.5}$$

The determinant of this matrix is the constant $J = \frac{4}{j^2}(4h^2 + j^2)$, This determinant can be normalised by applying the Gram-Schmidt process [199].

Appendix H

Calculation of λ_+ in equation (4.102)

To calculate λ_+ for the states $(0,0,0,\pi)$ and $(0,0,\pi,0)$ (which are the same) we expand the energy function of equation (4.20) in a Taylor series about one of the points, say $(0,0,0,\pi)$ to get the energy approximation,

$$\begin{aligned} E_{AF} \approx E_{AF}^{(0)} \quad &+\tfrac{1}{2}\left[\left(-\tfrac{j}{2}-h+1\right)p_1^2 - jp_1p_2 + \left(-\tfrac{j}{2}+h+1\right)p_2^2 + \right. \\ &\left.\left(-\tfrac{j}{2}-h+1\right)\Phi_1^2 + j\Phi_1\Phi_2 + \left(-\tfrac{j}{2}+h+1\right)\Phi_2^2\right] \end{aligned} \tag{H.1}$$

where $\Phi_1 = \phi$, and $\Phi_2 = \phi_2 - \pi$. And the equations of dynamics (A.21)(A.22) in matrix form are

$$\begin{pmatrix} \dot{p_1} \\ \dot{p_2} \\ \dot{\Phi_2} \\ \dot{\Phi_2} \end{pmatrix} = \begin{pmatrix} a\left(\frac{-j}{2}+1-h\right) & \frac{-aj}{2} & b\left(\frac{-j}{2}+1-h\right) & \frac{bj}{2} \\ \frac{-aj}{2} & a\left(\frac{-j}{2}+1+h\right) & \frac{bj}{2} & b\left(\frac{-j}{2}+1-h\right) \\ b\left(\frac{-j}{2}+1-h\right) & \frac{bj}{2} & a\left(\frac{-j}{2}+1-h\right) & \frac{aj}{2} \\ \frac{bj}{2} & -b\left(\frac{-j}{2}+1+h\right) & \frac{aj}{2} & a\left(\frac{-j}{2}+1+h\right) \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ \Phi_2 \\ \Phi_2 \end{pmatrix} \tag{H.2}$$

where a, b are coefficients of the Landau-Lifschitz equation in **Appendix A**. We omit the eigenvalues of the 4×4 matrix which are complex numbers and long expressions which are best left to a computer.