Drift-Diffusion of a vacancy in inhomogeneous media and its material constants. A Fokker-Planck equation approach with an application to foreign exchange data.

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Abstract

This study derived the mobility and diffusion coefficients of a Fokker-Planck equation describing a vacancy hopping in inhomogeneous media in one dimension under a directed stress. The study used the general master equation as a basis for a physical model because of the mesoscopic view that the change in average concentration is inadequate to describe small fluctuations in a system and that a probabilistic approach is needed. By van Kampen's system-size expansion a master equation was expanded to obtain a non-linear Fokker-Planck equation of the diffusive type. The Einstein relation was obtained and satisfied. As an application to a physical system we considered the simple one dimension case of a point defect diffusing by a hopping mechanism under an applied stress using data obtained from the implantation of krypton ions on a pre-existing stress state in polycrystalline titanium. From this data we estimated the stress gradient and from literature used the vacancy migration enthalpy to find the diffusion coefficients, and by the Einstein relation, the mobility, the coefficients of a Fokker-Planck equation. As an application to a non physical system the study set up a Fokker-Planck equation which described incremental changes in foreign exchange (FX) prices. The Fokker-Planck equation was completely determined by the drift and diffusion coefficients extracted directly from the actual FX prices. The purpose here was to show the importance of a 'physical model' or the existence of the Markov property for the establishment of a Fokker-Planck equation and by starting from a master equation for non physical systems which would make for better understanding of the underlying statistical equations of motion of the fluctuating system.

Contents

1. Introduction

2. Drift-Diffusion and the Markov property

3. Statistical derivation of Diffusion and the Fokker-Planck Equation from the Master Equation

4. Solutions to the Fokker-Planck Equation

5. Application to a Physical System

6. Application to a Non Physical System

6. Conclusion

Appendix

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Amigos para siempre

CHAPTER 1

Introduction

1.1 Introduction

The twentieth century started with random walks and diffusion processes promising exciting developments in the pure sciences (Pearson 1905 [1], Lord Rayleigh 1905 [2], Einstein 1905 with the introduction of drift in the random walk [3]), and the social sciences (Bachelier 1900 investigating stock market prices under Poincarè) [4]. It has since, under the guidance of physicists, engineers and materials scientists developed and delivered beyond our expectations in such diverse areas as bio-technology, speculative price modelling, population dynamics, materials science and medicine, and promises so much more for the information technology sector.

Statistical reasoning was used by both Maxwell and Boltzman in their gas theories to give only possible states of a system without any time evolution of that system. It was Lord Rayleigh [2] who applied stochastic modelling to natural systems in the early 1900s, but for some reason Einstein's work on Brownian motion is regarded as the starting point for modelling using probabilistic methods. For phenomena involving systems of individual particles, such as diffusion processes (really any physical system containing an atomic constant), it has been found that jump processes and its associate master equation are more wholesome and mathematically rigorous in modelling both the deterministic motion and fluctuations which arise out of the individual jumps. A master equation is an integro-differential equation for the time evolution of the probability to integration over the microscopic jumps between states.

However, it is the Fokker-Planck equation [5], a special type of master equation, which has gained favour over the past decades as a powerful tool modelling these fluctuating subsystems, or systems containing noise. The Fokker-Planck equation was first used by Fokker (1914) and by Planck (1917) to describe the Brownian motion of particles in fluids. In this system it is the position which fluctuates because of the unpredictable way in which the fluid molecules kick around the particle. Because of these fluctuations one is unable to give a position of the particle, only some probability of finding the particle in some region. It is the Fokker-Planck equation which gives an 'equation of motion' for this probability density. Fokker-Planck equations are widely used in solid-state physics, chemical physics, theoretical biology and circuit theory [5]. Recently, Fokker-Planck equations have been used to describe non physical systems such as the evaluation of financial risk and price changes in the financial markets [6-12].

The goal of this study was to model the diffusion of a point defect (vacancy) in one dimension in inhomogeneous media in the presence of an external potential by means of a Fokker-Planck equation, and to consider a Fokker-Planck approach to modelling drift-diffusion processes in physical and non physical media. The study started with formulating the diffusion equation from Fick's first law and the continuity equation, and discussed its limitations when applied to diffusion of point defects in solids. The proper form of the diffusion equation for inhomogeneous media was defined and discussed as well.

The formulation of the Fokker-Planck equation for the diffusing vacancy in inhomogeneous media consisted of two parts. The first part outlined the physical process of diffusion - hopping. In this model of diffusion we considered a vacancy that hopped in one dimension from one trap to the next (closest neighbour) with time spent in each trap just enough to erase the memory of previous hopping, *i.e.* a Markovian process. This hopping model used was a modified version of the one used by van Kampen to model particle hopping in an inhomogeneous medium [13-16]. In van Kampen's model particles were allowed to jump over several neighbouring sites but for this study, because of the mechanism of vacancy diffusion, only nearest neighbour sites were permissible. From this Markovian process we constructed the stochastic master equation as a first approximation from which the Fokker-Planck equation was extracted via the Ω-expansion method of van Kampen [16]. The study then briefly discussed the solutions to the Fokker-Planck equation and the homogeneous diffusion equation obtained using the commercially available software, MATLAB® [17].

As an application to a physical system we considered the simple one dimensional case of a point defect diffusing by a hopping mechanism under an applied stress using data obtained by M. Härting *et al* in 'Near Surface Stress Determination in Kr-implanted Polycrystalline Titanium by the X-Ray $\sin^2 \Psi$-Method' [18]. From this data we estimated the stress gradient, and from literature, used the vacancy migration enthalpy to find the diffusion coefficients, and by the Einstein relation, the mobility.

As an application to a non physical system the study set up a Fokker-Planck equation which would describe incremental changes in foreign exchange (FX) prices, and in so doing would quantify the deterministic and random influences on the statistics of FX prices [19-23]. However, unlike using the hopping model as a first approximation to setup the master equation for vacancy diffusion, here the Fokker-Planck equation was directly derived from the FX data. To setup the master equation for this system one would have needed intimate knowledge of the trading mechanisms and agent behaviour used to generate the macroscopic and fluctuating parts of the system. From analyses of the extracted drift and diffusion coefficients the study makes some brief comments on the statistical processes underlying speculative price changes. The purpose here was to show that the same approach, namely a Fokker-Planck equation, could be applied to non material systems provided the Markov property was satisfied. Also, that the use of a 'physical model' or starting from the master equation in non physical systems would make for better understanding of the underlying statistical equations of motion of the fluctuating system.

The study concludes firstly with some brief comments on the media coefficients obtained in the formulated Fokker-Planck equation for a diffusing vacancy in inhomogeneous media as well as the implications of its solution. Secondly we comment on the importance of starting from a 'physical' model, to deduce the mechanics of the individual 'particles' of non physical systems.

Chapter 2

Drift-Diffusion and the Markov Property

2.1 Diffusion and Drift Processes

Diffusion is the passive transport of particles, driven by thermal motion, from areas of high concentration to areas of low concentration. Classical examples are smoke from a chimney dissipating into the air and a drop of dye added to clear water. Under a directed stress, such as an external potential, the particles still move around in a random motion, but in addition there is on average a net motion along the direction of the force field. Diffusion under an applied stress is called drift. The diffusion of point defects in one dimension under a directed stress can find application in ion beam irradiation and certain applications in semiconductor technology [24], and is discussed in many areas of classical physics, plasma physics and charge transport in semiconductors [25]. To fully understand the influences of pressure and stress on diffusion processes one has to consider both the effects on the point defect concentrations [26,27,28] and on the point defect mobilities [26,29,30].

There are two main reasons for studying diffusion in solids [31]. The first is to understand the changes that occur in solids at high temperatures for diffusion processes such as precipitation, oxidation, creep, annealing, *etc*. The second reason for studying diffusion is to learn about point defects and their movement.

One such method of diffusion is called vacancy diffusion. In all crystals there are some lattice sites that are unoccupied. It is these unoccupied lattice sites that are called vacancies. When an atom from an adjacent site jumps into the vacant site, the atom is said to have diffused by a hopping mechanism. From the theory of specific heat, atoms in a crystal oscillate around their equilibrium positions, and occasionally these oscillations become violent enough to allow an atom to change sites. It is the jumping of atoms from one site to another which gives rise to diffusion in solids. For an atom to escape its bonds and diffuse into an adjacent site it has to acquire enough thermal energy. With an increase in temperature comes an increase in the natural vibrational energy of the atoms so that an atom with enough energy is able to jump into that vacancy, of course leaving a vacant site behind as it does so.

In figure 2.1.1 a schematic of volume change to a simple crystal lattice associated with vacancy diffusion is shown. A vacancy is created by an atom moving from the interior of the crystal to a surface site. This is vacancy formation. Migration of a vacancy (diffusion) is obtained when an atom adjacent to the vacant site moves into the unoccupied site [26]. Vacancy diffusion is an important assisting mechanism during the deformation of minerals at moderate temperatures. An example of vacancy diffusion is that of Sb in Silicon [26,32].

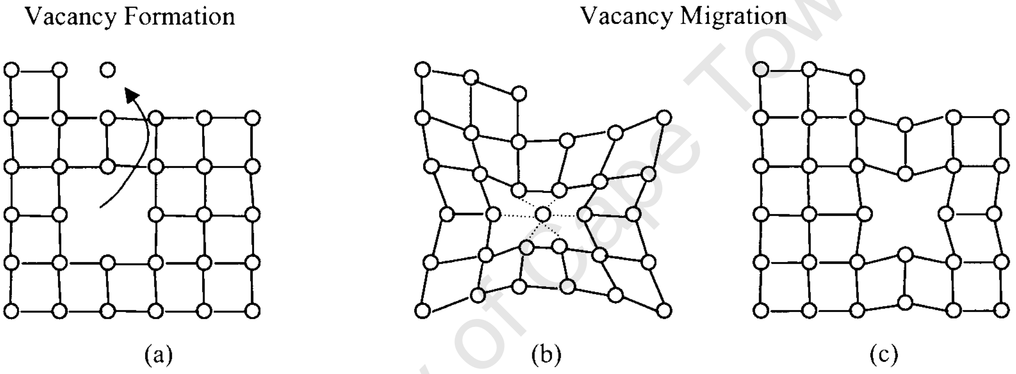

Figure 2.1.1 (a) Vacancy formation takes place with an atom moving to the surface. (b) Vacancy diffusion takes place when an adjacent atom moves into the vacant site. (c) A newly formed vacancy showing vacancies diffusing to the right in the crystal lattice [15].

Our laws of diffusion are phenomenological - a mathematical description derived by observation of the physical system [33]. In 1807 Fourier developed a mathematical description for heat transfer due to random molecular motions which is essentially a diffusive transfer of kinetic energy,

$$f = -k\nabla T, \tag{2.1.1}$$

where f is the heat flux, k is the thermal conductivity and T the temperature. Half a century later Fick, through his pioneering work, observing the diffusive mixing of salt and water, found that the magnitude of the mass flux is proportional and directly opposite to the magnitude of the concentration gradient at that point. Fick's first law describes steady-state diffusion

$$J = -D\nabla P, \tag{2.1.2}$$

where J is the diffusant flux (number of particles crossing a unit area per unit time), D is the proportionality constant (diffusion coefficient) and ∇P the concentration gradient. For thermally activated processes, like vacancy diffusion, the diffusion coefficient D is generally described by the empirical equation

$$D = D_0\, \mathrm{e}^{(\frac{-H}{k_B T})}, \tag{2.1.3}$$

where D_0 is a temperature independent factor, H is the activation energy or enthalpy and k_B the Boltzman constant.

Using random walk theory we are able to derive Fick's first law describing the diffusion of a vacancy from one atom plane to another by considering a primitive cubic lattice with one dimension geometry, as shown in figure 2.1.2. We assume a concentration gradient in the x-direction, $P(x,y,z) = P(x)$, *i.e.* along the $\langle 100 \rangle$ x-axis. Also, the number of vacancies per unit area, n, on any lattice plane perpendicular to the x-direction is computable using $P(x)$, *i.e.* the number of vacancies on 1 cm^2 area on plane 1 is n_1. In such a discrete system $dx \approx a$, the lattice constant, as shown in figure 2.1.2..

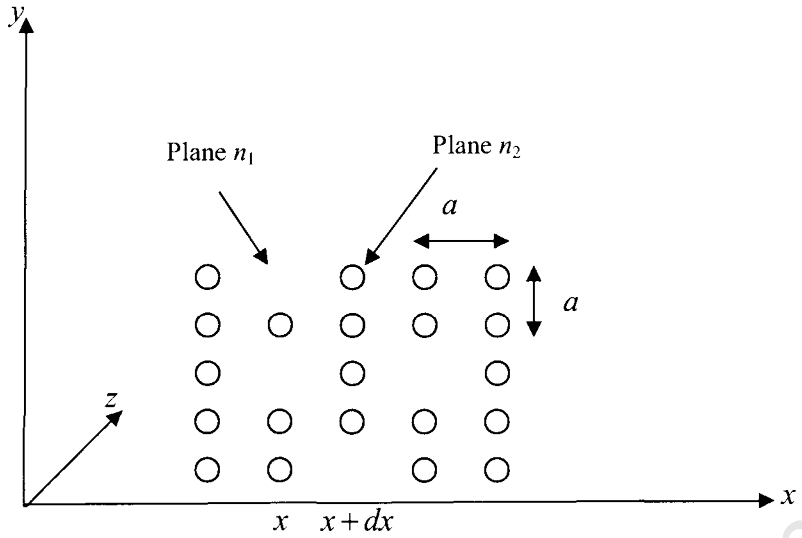

Figure 2.1.2 Diffusion of a vacancy in a primitive cubic lattice from atomic planes n_1 to n_2.

Thus the number of vacancies on 1 cm^2 area on plane n_1 and n_2 are respectively

$$n_1 = aP(x) \text{ and} \tag{2.1.4}$$

$$n_2 = aP(x+a)\,. \tag{2.1.5}$$

Next consider jump rates in the +x-direction with

$$r_{1\to2} = \text{jump rate from plane } n_1 \text{ to } n_2 \tag{2.1.6a}$$

$$r_{2\to1} = \text{jump rate from plane } n_2 \text{ to } n_1\,. \tag{2.1.6b}$$

Because of the number of nearest neighbours, $\frac{1}{6}$ of the total number of jumps of a vacancy is in either the positive or negative x-direction, *i.e.*

$$r_{1\to2}(T) = r_{2\to1}(T) = \frac{1}{6}r(T)\,. \tag{2.1.7}$$

The jump rate, r, is given by the Arrhenius factor

$$r = v_0 e^{\frac{H^M}{kT}}, \tag{2.1.8}$$

where v_0 is the vibration frequency of the particle and H^M the enthalpy of migration. The current of vacancies flowing out of plane n_1 into plane n_2 is given by

$$J_{1\to 2} = n_1 r_{1\to 2}, \tag{2.1.9a}$$

which is compensated to some degree by the current flowing into n_1 given by

$$J_{2\to 1} = n_2 r_{2\to 1}. \tag{2.1.9b}$$

The two components of the current are then

$$J_{1\to 2} = \frac{r}{6} aP(x) \text{ and} \tag{2.1.10a}$$

$$J_{2\to 1} = \frac{r}{6} aP(x+a). \tag{2.1.10b}$$

The net current in the x-direction between the two planes is the difference between the two partial currents, *i.e.*

$$J_x = J_{1\to 2} - J_{2\to 1}$$

$$= -\frac{ar}{6}[P(x+a) - P(x)] \tag{2.1.11}$$

$$= -(\frac{a^2 r}{6})\frac{dP(x)}{dx} = -D\frac{dP(x)}{dx}, \tag{2.1.12}$$

which is Fick's first law for the diffusion of vacancies in a primitive cubic lattice. But what if there was a driving force present? Well, if ΔV is a potential difference between the two planes such that there is a driving force in the x-direction then equation (2.1.9) becomes, to first order,

$$J_{1\to 2} = n_1 r_{1\to 2} = n_1 r e^{\frac{\Delta V}{kT}} \approx n_1 r(1+\frac{\Delta V}{kT}) = n_1 r(1+\frac{aq\Delta V}{2kT}) = n_1 r(1+\frac{aF}{2kT}) \text{ and} \tag{2.1.13a}$$

$$J_{2\to 1} = n_2 r_{2\to 1} = n_2 r e^{\frac{\Delta V}{kT}} \approx n_2 r(1-\frac{\Delta V}{kT}) = n_2 r(1-\frac{aq\Delta V}{2kT}) = n_2 r(1-\frac{aF}{2kT}). \tag{2.1.13b}$$

But for a simple random walk the jump rate does not depend on the direction of the jump so that $r = r_{2\to 1} = r_{1\to 2}$. The net vacancy or particle flux in a presence of a constant force between planes n_1 and n_2 is now

$$J_x = r(n_1 - n_2) + \frac{aF}{2kT} r(n_1 + n_2)$$

$$J_x = -(\frac{a^2 r}{6})\frac{dP(x)}{dx} + (\frac{a^2 r}{6})P(x)\frac{F}{kT}$$

$$J_x = -D\frac{dP(x)}{dx} + DP(x)\frac{F}{kT}. \tag{2.1.14}$$

Fick's second law, also called the linear diffusion equation, describes transient diffusion or non steady-state diffusion where the diffusivity is independent of the concentration. In the absence drift this is

$$\frac{\partial P}{\partial t} = -\nabla \cdot \dot{J} = D\frac{\partial^2 P}{\partial x^2}. \tag{2.1.15}$$

2.2 The Diffusion Equation

Consider a vacancy diffusing in a homogeneous medium with a homogeneous temperature and external force acting on the point defect with potential *V*, like that given in equation (2.1.14). From Einstein's analyses on Brownian motion the diffusion coefficient and mobility are related by

$$D = \mu kT, \tag{2.2.1}$$

arriving at the continuity equation,

$$J = -(P\mu\nabla V + D\nabla P), \tag{2.2.2}$$

from which most authors construct the diffusion equation

$$\frac{\partial P}{\partial t} = \nabla \cdot [(\mu \nabla V)P + D\nabla P], \tag{2.2.3}$$

where P, J, μ and D are the probability density, diffusion flow of the diffusing particle, mobility and diffusion tensor, respectively [35]. The mobility, μ, and diffusion tensor D are material constants of the medium. The first term gives the stress assisted diffusion or drift in the potential force field *V*, and the latter term is the diffusional drift given by Fick's law. In thermal equilibrium the stationary solution of equation (2.2.3) is

$$P = const\ \mathrm{e}^{(\frac{-V}{T})}. \tag{2.2.4}$$

Substituting (2.2.4) into (2.2.3) one gets the Einstein relation [4]

$$D = \mu kT. \tag{2.2.5}$$

But these equations describe diffusion in homogeneous media. The question is, what are (2.2.3) and (2.2.5) when μ and D vary in space [4]? An alternative form of the diffusion equation to (2.2.3) has been proposed [14] *i.e.*

$$\frac{\partial P}{\partial t} = \nabla \cdot [P(\mu \nabla V) + \nabla \cdot DP]. \tag{2.2.6}$$

This can be rewritten as

$$\frac{\partial P}{\partial t} = \nabla \cdot [P(\mu \nabla V + \nabla \cdot D) + D \nabla P]. \tag{2.2.7}$$

This form of the diffusion equation differs by an additional drift term, $\nabla \cdot D$, often called the 'spurious drift' [13] or 'noise-induced drift' [5]. The term $P(\mu \nabla V)$ is deterministic in nature while $D \nabla P$ is caused by the stochastic nature of the system. However, what ever the form of the diffusion equation it must be of the following

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}[(\mu V' - k)P + D\frac{\partial P}{\partial x}], \tag{2.2.8}$$

where kP is the unknown extra drift and μ and D are the unknown media coefficients [5].

2.3 Carrier Transport in a Semiconductor as an Example of a Drift–Diffusion Process

The motion of free carriers (charged particles) in a semiconductor leads to a current. It is the sum of two transport mechanisms or current, the drift and diffusion current. Drift is obtained when the free carriers experience a force in an electric field, due to an externally applied voltage. The second motion is the movement of carriers from areas of high concentration to areas of low concentration due to the thermal energy and the associated random motion of carriers.

With an application of an external voltage, the electrostatic force causes the carriers to accelerate which reach a constant average velocity, *v*, due to the collisions with impurities and lattice vibrations. The ratio of the velocity to the applied field is called the mobility[*], μ. Consider a current carried by an electron population in a semiconductor crystal. The drift current, I_f, is the total charge in the semiconductor, Q, divided by the time needed to travel from one electrode to the other

$$I_f = \frac{Q}{t_r} = \frac{Q}{L/v}, \qquad (2.3.1)$$

where t_r is the transit time of a particle, travelling with velocity, *v*, over the distance *L*, see figure 2.3.1 below.

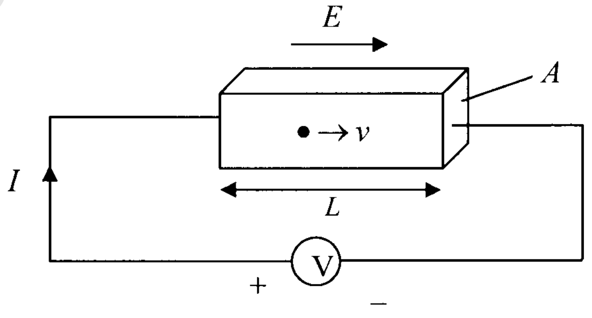

Figure 2.3.1 Drift of a carrier with velocity, *v*, due to an applied electric field, E.

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[*] which differs from the general definition by a factor of the electronic charge *e* (see section 2.2).

In the absence of an electric field the carriers move about in a random motion frequently changing direction. When an electric field is applied the carriers still move around in a random motion but in addition there is on average a net motion along the direction of the field. Applying Newton's Law

$$F = ma = m\frac{md\langle v\rangle}{dt}, \tag{2.3.2}$$

which is the difference between the electrostatic force and the scattering force due to the loss in momentum at the time of scattering. The scattering force is given by the momentum divided by the average time between scattering events, so that

$$F = qE - \frac{m\langle v\rangle}{\tau} \tag{2.3.3}$$

for some particle, maybe an electron, with charge q. Equating the equations (2.3.2) and (2.3.3) gives the average electron velocity

$$qE = m\frac{d\langle v\rangle}{dt} + \frac{m\langle v\rangle}{\tau}. \tag{2.3.4}$$

In the steady-state situation the electron has already accelerated to a constant average velocity which is proportional to the applied electric field, and we define the mobility as

$$\mu = \frac{\Delta|v|}{|E|} = \frac{q\tau}{m}. \tag{2.3.5}$$

The electron drift current depends on the electric field, electron density, and the electron mobility, *i.e.*

$$J_f = n\mu qE, \tag{2.3.6}$$

which is equivalent to the second term in equation (2.1.14).

Diffusion of carriers is obtained by creating a carrier density gradient by varying the doping density in a semiconductor or by applying a thermal gradient. It is thermal energy which drives the diffusion process so that at absolute zero there is no diffusion. The thermal energy has a random nature which requires statistical analyses of electron transport, but working with averages produces similar results. Consider the thermal velocity, v_{th}, which is the average velocity of the electrons going left or right in one dimension, (see figure 2.3.2). The collision time is the time during which electrons will move with the same velocity before a collision occurs with an atom or another electron. The mean free path is the average length an electron will travel between collisions. These three averages are related by

$$v_{th} = \frac{l}{\tau}. \tag{2.3.7}$$

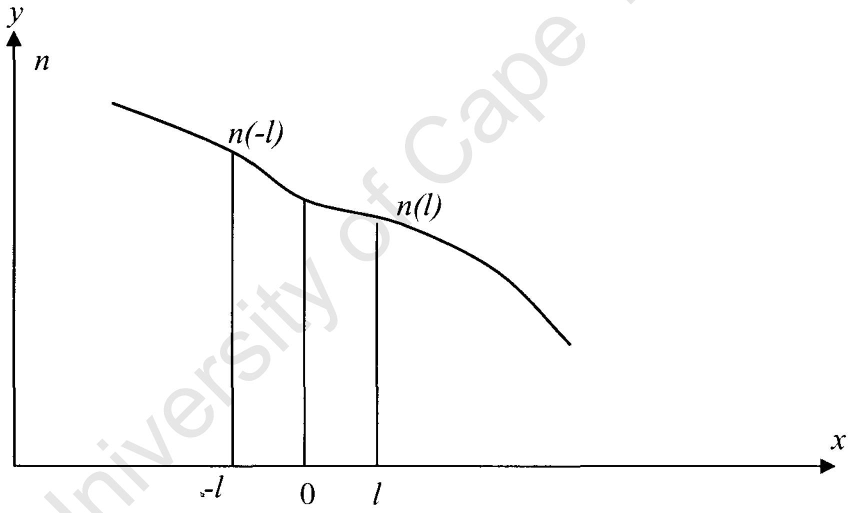

Figure 2.3.2 The flux of electrons moving down a concentration gradient.

The total flux of electrons moving from the left to the right is

$$\Phi_n = \Phi_{n,\text{left}\rightarrow\text{right}} - \Phi_{n,\text{right}\rightarrow\text{left}} = \frac{1}{2} v_{th}[n(x=-l) - n(x=l)], \tag{2.3.8}$$

at $x = 0$. But because the mean free path is small we can write the total flux as

$$\Phi_n = -lv_{th} \frac{n(x=l) - n(x=-l)}{2l} = -lv_{th} \frac{dn}{dx}. \tag{2.3.9}$$

The electron diffusion current equals this flux times the charge of an electron,

$$J_d = -q\Phi_n = qlv_{th} \frac{dn}{dx}. \tag{2.3.10}$$

Replacing the product of the thermal velocity and the mean free path with the diffusion constant, D_n,

$$J_d = qD_n \frac{dn}{dx}. \tag{2.3.11}$$

From the Einstein relation, equation (2.2.1) we have

$$J_f = kT\mu \frac{dn}{dx}. \tag{2.3.12}$$

The total current density due to all the electrons is then

$$J_n = J_f + J_d = kT\mu \frac{dn}{dx} + qD_n \frac{dn}{dx}. \tag{2.3.13}$$

2.4 Diffusion in non material systems

Physicists have made substantial contributions to the modelling of complex stochastic systems by using proven tools and methodologies developed in statistical mechanics and theoretical physics [6,7,9]. With the physics background they have complimented established disciplines in economics, biology and risk and asset management as well as 'cross-fertilising' others. One such instance of cross-fertilisation of disciplines is the similarity between the short time dynamics of foreign exchange (FX) price changes and fully developed hydrodynamic turbulence. Moreover, the financial markets have shown themselves to be equally highly complex but also well defined and closely monitored. Virtually every transaction is recorded down to resolutions of a few seconds. Turbulence is the blending of order and disorder that occurs in fluid flows [36]. The analogy to FX data would be periods of stable prices followed by sudden extreme fluctuations, *i.e.*, the energy flow in fluids is analogous to the flow of information in financial markets. This similarity allows the physicist to setup effective equations of motion for changes in FX prices, such as a Fokker-Planck equation, and to calculate the drift and diffusion coefficients of the financial security in question. The correct description and comparison of these coefficients could tell us more about the deterministic and stochastic influences on the transactions and trading mechanisms affecting price changes.

2.5 So why a Fokker-Planck equation approach?

A simple and convenient way of describing any diffusing system mathematically is with differential equations for changes in concentrations (Fick's first law). But differential equations are deterministic in nature and will always evolve in the same way regardless of the system's initial state. These differential equations are easily solved but provide a rather limited and often misleading solution when working with systems which contain a fluctuating subsystem, for example diffusion in inhomogeneous media. More accurate models are obtained when using a Fokker-Planck equation to model fluctuating systems. This is especially true when one has a diffusing system which has low reactants (diffusion in solids is a slow and rather transient process), making it misleading to talk about a change in mean concentrations [37]. In such systems, having low fluctuations in concentration, the discrete number of particles becomes more important than the average concentration.

Thus, what we need is a model that appreciates the finer (low in number) fluctuations in a system! What we need is a mesoscopic view of a diffusing system. In a mesoscopic model, the fluctuating system is caused by the discrete nature of that system. For example the density of a gas fluctuates because gases consist of molecules; current fluctuations exist because the current is made up of electrons; and radio-active decay fluctuates owing to the individuality of the nuclei [3]. In the mesoscopic model each 'reaction' occurs with a certain probability giving a stochastic process. It is the Fokker-Planck equation which gives the probability density for such systems with different system's states over time, an equation of motion for the probability density. Thus using stochastic integration, a probabilistic method, one is able to describe the system within a more rigorous mathematical framework [38]. The Fokker-Planck equation, in one dimension and independent of time is

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x} D^{(1)}(x)P + \frac{1}{2}\frac{\partial^2}{\partial x^2} D^{(2)}(x)P\,, \tag{2.5.1}$$

where $D^{(1)}(x)$ is the drift or convection term and $D^{(2)}(x) > 0$ the diffusion term or fluctuating term.

Chapter 3

Statistical derivation of Diffusion and the Fokker-Planck Equation from the Master Equation

3.1 Markov processes

To set up a general master equation from which a Fokker-Planck equation can be approximated via the system-size expansion, consider a system whose properties can be described in terms of a single stochastic variable, X. Then let the following be:

I. the probability density that the stochastic variable X has a value x_1 at time t_1 is

$$P(x_1 t_1)\,; \tag{3.1.1}$$

II. the joint probability density that the stochastic variable X has a value x_1 at time t_1 and x_2 at time t_2 is

$$P(x_2 t_2, x_1 t_1)\,; \tag{3.1.2}$$

III. the joint probability density that the stochastic variable X has a value x_1 at time t_1, x_2 at time t_2,..., x_n at time t_n is

$$P(x_n t_n, x_{n-1} t_{n-1}, \ldots, x_2 t_2, x_1 t_1); \tag{3.1.3}$$

IV. the conditional probability that the stochastic variable X has a value x_2 at time t_2 given that it had a value x_1 at time t_1 is

$$P(x_2 t_2 | x_1 t_1)\,. \tag{3.1.4}$$

The conditional probability density is also defined by the identity

$$P(x_2t_2, x_1t_1) = P(x_2t_2 \left| x_1t_1 \right.) P(x_1t_1)\,. \tag{3.1.5}$$

The joint probability densities have the following properties:

I. are positive *i.e.* $P_n \geq 0$; (3.1.6)

II. can be reduced *i.e.*

$$\int P(x_nt_n, \ldots, x_2t_2, x_1t_1)dx_n = P(x_{n-1}t_{n-1}, \ldots, x_2t_2, x_1t_1) \text{ and} \tag{3.1.7}$$

III. they can be normalised

$$\int P(x_1t_1)dx_1 = 1. \tag{3.1.8}$$

Combining equations (3.1.5) and (3.1.7) gives the probability densities at different times,

$$P(x_2t_2) = \int P(x_2t_2 \left| t_1x_1 \right.) P(x_1t_1) dx_1, \tag{3.1.9}$$

where the conditional probability $P(x_2t_2 \left| x_1t_1 \right.)$ can also be normalised *i.e.*

$$\int P(x_2t_2 \left| x_1t_1 \right.) dx_2 = 1. \tag{3.1.10}$$

Finally the joint transitional probability density can now be defined by

$$P(x_{k+l}t_{k+l}, \ldots, x_{k+1}t_{k+1} \left| x_kt_k, \ldots, x_1t_1 \right.) = \frac{P(x_{k+l}t_{k+l}, \ldots, x_1t_1)}{P(x_kt_k, \ldots, x_1t_1)}, \tag{3.1.11}$$

where $P(x_{k+l}t_{k+l}, \ldots, x_{k+1}t_{k+1} \left| x_kt_k, \ldots, x_1t_1 \right.)$ is the joint conditional probability density that the stochastic variable X has values $(x_{k+l}t_{k+l}, \ldots, x_{k+1}t_{k+1})$ given that ($x_kt_k, \ldots, x_1t_1$) are fixed.

The statistics of a Markov process are fully determined by the two functions $P(x_1t_1)$ and $P(x_2t_2|x_1t_1)$. For instance the three-variable joint probability density can be decomposed,

$$P(x_3t_3,x_2t_2,x_1t_1)=P(x_3t_3|x_2t_2,x_1t_1)P(x_2t_2,x_1t_1)=$$
$$P(x_3t_3|x_2t_2)P(x_2t_2,x_1t_1)\,P(x_1t_1). \tag{3.1.12}$$

Continuing this algorithm one finds successively all probabilities. Now, integrating over x_2, one obtains

$$P(x_3t_3,x_1t_1)=P(x_1t_1)\int P(x_3t_3|x_2t_2)P(x_2t_2|x_1t_1)dx_2. \tag{3.1.13}$$

Dividing by $P(x_1t_1)$, assuming $t_3\geq t_2\geq t_1$ and using (3.1.11) one obtains the Chapman-Kolmogorov equation

$$P(x_3t_3|x_1t_1)=\int P(x_3t_3|x_2t_2)P(x_2t_2|x_1t_1)dx_2. \tag{3.1.14}$$

A graphical display of this equation is given in figure 3.1.1. The transition probability from x_1 at time t_1 to state x_3 at time t_3 is equal to the transition probability from x_1 at time t_1 to x_2 at time t_2 multiplied by the transition probability from x_2 at time t_2 to x_3 at time t_3 for all possible x_2 [5].

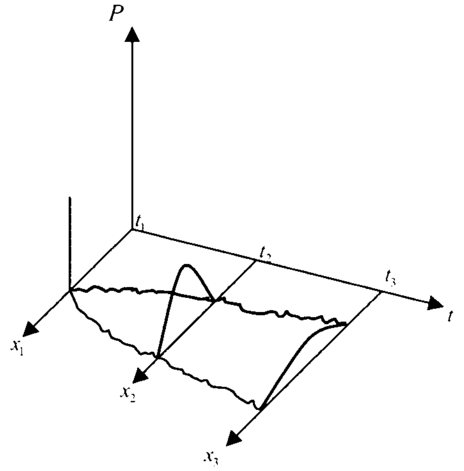

Figure 3.1.1 Transition probabilities at times t_2 and t_3 with a sharp initial value at t_1 [5].

3.2 The Master Equation

The master equation is an integro-differential equation for the time evolution of the probability

$$\frac{\partial P(x,t)}{\partial t} = \int [W_t(x|x')P_1(x',t) - W_t(x'|x)P_1(x,t)]dx'. \tag{3.2.1}$$

The master equation describes the rate of change of the probability $P(x,t)$, *i.e.* $\frac{\partial P(x,t)}{\partial t}$, due to transitions into the state *n* from all other states, *i.e.* $W_t(x|x')P(x',t)$ and due to the transitions out of state *n* into all other states, *i.e.* $W_t(x'|x)P(x,t)$. It is a gain-loss equation for the probability of each state *n* [13].

3.3 Hopping Model

The hopping model was originally introduced to discuss electron transport in solid materials [16]. In this model of diffusion one considers a particle that hops between states in one dimension where both the temperature and the properties of the medium are inhomogeneous. A particle hops from one trap to the next with time spent in each trap long enough to erase the memory of previous hopping, and so hopping is therefore Markovian. Each trap consist of an internal potential of depth *H* so that the escape probability per unit time is given by

$$c\, e^{[\frac{-H}{k_B T(x')}]}, \tag{3.3.1}$$

where k_B is the Boltzman constant (enter the mesoscopic property). If the particle has enough thermal vibrational energy, $k_B T(x')$, it surmounts the energy barrier, *H*, and travels to the left or to right with equal probability in the absence of an external force, as shown in figure 3.3.1.

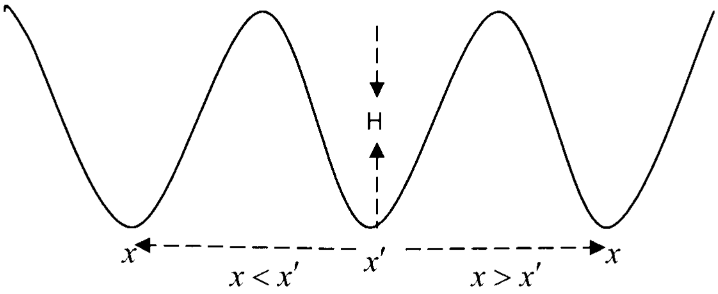

Figure 3.3.1 A particle is at an initial position x'. Upon obtaining enough thermal vibrational energy, $k_B T(x')$, it travels to the left or to the right, to position x, with equal probability in the absence of a force.

But suppose there was an external potential V present such that $\frac{dV}{dx} > 0$. Then for $x < x'$, $c\mathrm{e}^{[\frac{-H}{k_B T(x')}]}$ is sufficient for the hop to take place. For $x > x'$ an additional energy is required to hop to the right *i.e.* $c\mathrm{e}^{[\frac{-H(x)-V(x)+V(x')}{k_B T(x')}]}$, (see figure 3.3.2).

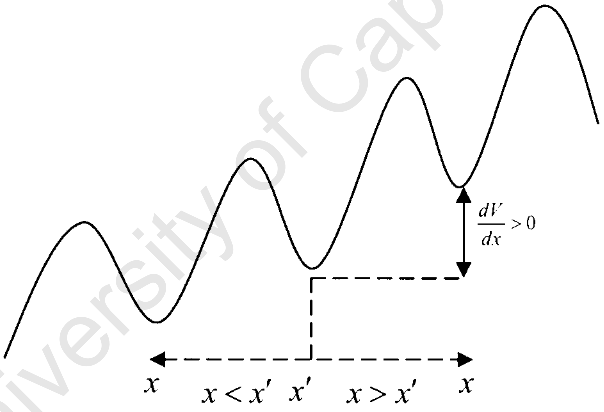

Figure 3.3.2 With an external potential V present, the escape probability to jump to the left requires only $c\mathrm{e}^{[\frac{-H}{k_B T(x')}]}$ while jumping to the right or 'uphill' requires an additional energy of $V(x) - V(x')$, giving $c\mathrm{e}^{[\frac{-H(x)-V(x)+V(x')}{k_B T(x')}]}$.

Taking all this into account one arrives at a gain-loss equation for the probability density $P(x, t)$, which has the general form of the master equation,

$$\frac{\partial P(x,t)}{\partial t} = \int [W(x|x')P(x',t) - W(x'|x)P(x,t)]dx' . \qquad (3.3.2)$$

3.4 The Fokker-Planck Approximation

Jump processes such as that given by the master equation are difficult to work with, as sample paths are discontinuous. This problem is overcome by approximating the master equation with a Fokker-Planck equation. The approximation is a Taylor expansion around the state *x*, truncated after the second derivative, giving a continuous approximation of the flows between states [39]. It is only in rare cases that master equations can be solved explicitly, such as a one-step master equation [13]. Thus an approximation method is more often needed to solve the master equation. Many methods are used in literature to expand the master equation [38] described by van Kampen as 'ad hoc prescriptions for cutting off higher moments of the fluctuations'. This study makes use of the Ω-expansion, introducing a system size parameter Ω, as used by van Kampen [13]. Ω is also referred to as the expansion parameter and has to be chosen so that it appears in the master equation in the transition probability function, $W(x|x')$. Also, it governs the size of the jumps, such that for 'large' Ω the jumps are relatively small. The precise definition of this parameter depends on the system, but loosely stated is: 'if a random variable represents the number of particles in a box, one may choose Ω as the volume of the box', [39].

By setting $x = \frac{X}{\Omega}$ the general form of the master equation (3.3.2) can be written as

$$\frac{\partial P(x,t)}{\partial t} = \int [W_\Omega(X|X')P(X',t) - W_\Omega(X'|X)P(X,t)]dX' \qquad (3.4.1)$$

The jump probability per unit time or transition probability, *W*, is now written as a function of the starting point and jump length, $r = X - X'$ *i.e.*

$$W_\Omega(X|X') = W_\Omega(X';X-X') = W_\Omega(X';r) \text{ also} \qquad (3.4.2)$$

$$W_\Omega(X';X-X') = \Phi(\frac{X'}{\Omega};X-X') = \Phi(x';r) \text{ and} \qquad (3.4.3)$$

$$W_\Omega(X'|X) = \Phi(\frac{X}{\Omega};X) = \Phi(x;-r)\,, \tag{3.4.4}$$

where Φ is some function of two variables $x' = \dfrac{X'}{\Omega}$ and r [6]. The distinction between X and x is one between extensive (say number of point defects) and intensive (concentration of point defects) variables respectively [38].

Now, allowing for an arbitrary factor $f(\Omega)$, affecting the time scale only, the final form of W is

$$W_\Omega(x|x') = f(\Omega)[\Phi_0(x';r) + \Omega^{-1}\,\Phi_1(x';r) + \Omega^{-2}\Phi_2(x';r) + \Omega^{-3}\Phi_3....] \tag{3.4.5}$$

This is true in all applications one meets in practice and is called the canonical form. If the transition probability per unit time does not fit this form the expansion in Ω^{-1} will not work [13].

Substituting the equation (3.4.5) into the master equation (3.4.1) and changing the integration variable from x' to r one obtains

$$\frac{\partial P(x,t)}{\partial t} = \Omega^{-1} f(\Omega)\int[\Phi_0(x-\frac{r}{\Omega},r) + \Omega^{-1}\Phi_1(x-\frac{r}{\Omega},r) + \Omega^{-2}\Phi_2(x-\frac{r}{\Omega},r)...]P(x-\frac{r}{\Omega},t)dr$$

$$-\Omega^{-1} f(\Omega)\int[\Phi_0(x,-r) + \Omega^{-1}\Phi_1(x,-r) + \Omega^{-1}\Phi_1(x,-r)...]dr\cdot P(x,t)\,. \tag{3.4.6}$$

The shift from x to $x-\dfrac{r}{\Omega}$ gives rise to the Taylor expansion and upon truncating after the second derivative one obtains, after cancelling terms of Ω^{-1},

$$\frac{\partial P(x,t)}{\partial t} = -\Omega^{-2} f(\Omega)\frac{\partial}{\partial x}[P(x,t)\int r\{\Phi_0(x,r) + \Omega^{-1}\Phi_1(x,r) + \Omega^{-2}\Phi_2(x,r)...\}dr]$$

$$+\frac{1}{2}\Omega^{-3} f(\Omega)\frac{\partial^2}{\partial x^2}[P(x,t)\int r^2\{\Phi_0(x,r) + \Omega^{-1}\Phi_1(x,r) + \Omega^{-2}\Phi_2(x,r)...\}dr]\,. \tag{3.4.7}$$

Rescaling time by setting $\Omega^{-2} f(\Omega) t = \tau$ and rescaling jump moments,

$$\alpha_{\nu,\lambda}(x) = \int r^{\nu} \Phi_{\lambda}(x;r) dr, \tag{3.4.8}$$

the two lines of integrals become respectively

$$\alpha_1(x) = \alpha_{1.0}(x) + \Omega^{-1}\alpha_{1.1}(x) + \Omega^{-2}\alpha_{1.2}(x) + \ldots \tag{3.4.9}$$

$$\alpha_2(x) = \alpha_{2.0}(x) + \Omega^{-1}\alpha_{2.1}(x) + \Omega^{-2}\alpha_{2.2}(x) + \ldots \quad . \tag{3.4.10}$$

Thus the master equation (3.1.7) becomes

$$\begin{aligned}\frac{\partial P(x,t)}{\partial t} &= \Omega^{-2} f(\Omega)[-\frac{\partial}{\partial x}\alpha_{1,1}(x)P + \frac{1}{2}\frac{\partial^2}{\partial x^2}\alpha_{2.0}(x)P] \\ &+\Omega^{-3} f(\Omega)[\frac{1}{2}\frac{\partial^2}{\partial x^2}\alpha_{2.1}(x)P - \frac{\partial}{\partial x}\alpha_{2.1}(x)P].\end{aligned} \tag{3.4.11}$$

When $\alpha_{1.0}(x) = 0$, one obtains

$$\frac{\partial P(x,\tau)}{\partial \tau} = -\frac{\partial}{\partial x}\alpha_{1,1}(x)P + \frac{1}{2}\frac{\partial^2}{\partial x^2}\alpha_{2.0}(x)P, \tag{3.4.12}$$

a nonlinear Fokker-Planck equation called the diffusive type, which is the one obtained and used in this study. It contains no macroscopic equation and is true for all master equations where Ω^0 cancels out. It also occurs when one has diffusion taking place under a directed stress. Here, for diffusion under a directed force, the random jumps and drift are independent of each other [40].

3.5 The transition probabilities

Our particle hops in the presence of a stress in the form of an external applied potential $V(x)$ such that $\frac{dV(x)}{dx} > 0$. It is trapped in a potential well (see section 3.3) unless it has enough thermal energy, *H*, to escape the trap. Once out of the trap, at position x', the particle either 'rolls down' to the left $(x < x')$ or 'climbs up' the energy slope to the right $(x > x')$ until meeting another trap at position *x*. To travel to the right it needs additional energy $\Delta V(x) = V(x) - V(x')$. The probability per unit time for a vacancy to gain enough energy to travel is

$$\text{Downhill, } (x < x')\text{: } c\Omega g(\Omega|x - x'|)\,\mathrm{e}^{[\frac{-H(x)}{k_B T(x')}]} \tag{3.5.1a}$$

$$\text{Uphill, } (x > x')\text{: } c\Omega g(\Omega|x - x'|)\,\mathrm{e}^{[\frac{-[H(x)+V(x)-V(x')]}{k_B T(x')}]}, \tag{3.5.1b}$$

where $g(\Omega)$ is a factor affecting the time scale only. These two equations establish the jump probabilities, $W(x|x')$, of our master equation (3.3.2).

3.6 The mobility and diffusion constants

The master equation for the drift-diffusion of a particle in inhomogeneous media in an external potential is

$$\frac{\partial P(x,t)}{\partial t} = \int_x^{\infty} W(x|x')P(x',t)dx' - \int_{-\infty}^{x} W(x'|x)dx' \cdot P(x',t) \qquad x < x' \tag{3.6.1a}$$

$$+ \int_{-\infty}^{x} W(x|x')P(x',t)dx' - \int_x^{\infty} W(x'|x)dx' \cdot P(x',t) \qquad x > x'. \tag{3.6.1b}$$

The jumps $|x - x'|$ are of order Ω^{-1} and so one can use the Taylor expansion to solve equation (3.6.1) for large Ω [14]. One can change the integration variable from x' to $r = \Omega|x - x'|$ and can set $x' = x + \frac{r}{\Omega}$ and $x' = x - \frac{r}{\Omega}$ respectively. Using the above the jump probabilities (equation 3.5.1) per unit time, $W(x|x')$ becomes

$$W(x'|r) = \Omega g(x+\frac{r}{\Omega},r)\,\mathrm{e}^{[\frac{-H(x)}{k_B T(x')}]} \text{ for } r<0 \text{ and} \tag{3.6.2}$$

$$W(x'|r) = \Omega g(x-\frac{r}{\Omega},r)\,\mathrm{e}^{\{\frac{-[H(x)+V(x)-V(x+\frac{r}{\Omega},r)]}{k_B T(x)}\}} \text{ for } r>0\,. \tag{3.6.3}$$

The master equation (3.6.1) now becomes

$$\frac{\partial P(x,t)}{\partial t} = \int_0^\infty drg(x+\frac{r}{\Omega},r)\,\mathrm{e}^{[\frac{-H(x)}{k_B T(x')}]} P(x+\frac{r}{\Omega},t)$$

$$-\int_0^\infty drg(x,-r)\,\mathrm{e}^{[\frac{-H(x)}{k_B T(x')}]} P(x,t)$$

$$+\int_0^\infty drg(x-\frac{r}{\Omega},r)\,\mathrm{e}^{\{\frac{-[H(x)+V(x)-V(x-\frac{r}{\Omega},r)]}{k_B T(x)}\}} P(x-\frac{r}{\Omega},t)$$

$$-\int_0^\infty drg(x,-r)\,\mathrm{e}^{[\frac{-H(x)}{k_B T(x)}]} P(x,t)\,. \tag{3.6.4}$$

Exercising the Taylor expansion from x to $\pm\frac{r}{\Omega}$, respectively, the result for

$r<0$:(Downhill)

$$\Omega^{-2} f(\Omega)\frac{\partial}{\partial x}[P(x,t)\int_0^\infty r\{\Phi_0(x,r)+\Omega^{-1}\Phi_1(x,r)+\Omega^{-2}\Phi_2(x,r)...\}\,dr]e^{[\frac{-H(x)}{k_B T}]}$$

$$+\frac{1}{2\Omega^3}\frac{\partial^2}{\partial x^2}[P(x,t)\int_0^\infty r^2\{\Phi_0(x,r)+\Omega^{-1}\Phi_1(x,r)+\Omega^{-2}\Phi_2(x,r)...\}\,dr]e^{[\frac{-H(x)}{k_B T}]} \tag{3.6.5}$$

and

$r>0$:(Uphill)

$$\Omega^{-2} f(\Omega)\frac{\partial}{\partial x}[P(x,t)\int_0^\infty r\{\Phi_0(x,r)+\Omega^{-1}\Phi_1(x,r)+\Omega^{-2}\Phi_2(x,r)...\}\,dr]\mathrm{e}^{\{\frac{-[H(x)+V(x)-V(x-\frac{r}{\Omega},r)]}{k_B T(x)}\}}$$

$$+\frac{1}{2\Omega^3}\frac{\partial^2}{\partial x^2}[P(x,t)\int_0^\infty r^2\{\Phi_0(x,r)+\Omega^{-1}\Phi_1(x,r)+\Omega^{-2}\Phi_2(x,r)...\}\,dr]e^{[\frac{-H(x)}{k_B T}]}\,. \tag{3.6.6}$$

Summing these equations, the terms of order Ω^{-2} cancel, and to order Ω^{-3}

$$\frac{\partial P(x,t)}{\partial t} = -\Omega^{-3} f(\Omega) \frac{\partial}{\partial x}[P(x,t)\int_0^\infty rV'(x,r)\{\Phi_0(x,r)+\Omega^{-1}\Phi_1(x,r)$$

$$+\Omega^{-3}\Phi_2(x,r)\ldots\} dr]e^{[\frac{-H(x)}{k_B T}]}$$

$$+\frac{1}{\Omega^3}\frac{\partial^2}{\partial x^2}[P(x,t)\int_0^\infty r^2\{\Phi_0(x,r)+\Omega^{-1}\Phi_1(x,r)+\Omega^{-2}\Phi_2(x,r)\ldots\} dr]e^{[\frac{-H(x)}{k_B T}]} . \tag{3.6.7}$$

Rescaling time and jump moments as in equations (3.4.9) and (3.4.10), the Fokker-Planck equation is

$$\frac{\partial P(x,t)}{\partial t} = \frac{c}{\Omega^2}[\frac{\partial}{\partial x}(\frac{V'(x)}{k_B T(x)})e^{[\frac{-H(x)}{k_B T}]} P + \frac{\partial^2}{\partial x^2} e^{[\frac{-H(x)}{k_B T}]} P], \tag{3.6.8}$$

which upon rearranging terms

$$\frac{\partial P(x,t)}{\partial t} = \frac{c}{\Omega^2}\frac{\partial}{\partial x}[\frac{V'(x)}{k_B T(x)} e^{[\frac{-H(x)}{k_B T}]} P + \frac{\partial}{\partial x} e^{[\frac{-H(x)}{k_B T}]} P]. \tag{3.6.9}$$

This is the Fokker-Planck equation for a vacancy diffusing by a hopping mechanism in inhomogeneous media. It has the canonical form of equation (3.4.12). Comparing with equation (2.2.3) one can identify the mobility and diffusion coefficients, respectively

$$\mu(x) = \frac{c}{\Omega^2 T(x)} e^{\frac{-H}{k_B T(x)}}, \tag{3.6.10}$$

$$D(x) = \frac{c}{\Omega^2} e^{\frac{-H}{k_B T(x)}}; \tag{3.6.11}$$

thus satisfying the Einstein relation (2.2.1).

Chapter 4

Solutions to the Fokker-Planck Equation

4.1 Stationary solution

The general one dimensional Fokker-Planck equation (2.5.1), reproduced here is

$$\frac{\partial P(x(t))}{\partial t} = -\frac{\partial}{\partial x} D^{(1)}(x)P + \frac{1}{2}\frac{\partial^2}{\partial x^2} D^{(2)}(x)P \tag{4.1.1}$$

with time-independent drift and diffusion coefficients, $D^{(1)}(x)$ and $D^{(2)}(x)$, respectively.

By a suitable transformation $x' \equiv y = y(x)$ one can rewrite the x-dependent diffusion coefficient as

$$D'^{(2)} \equiv D = (\frac{dy}{dx})^2 D^{(2)}(x), \tag{4.1.2}$$

and the drift by

$$D'^{(1)}(y) = \frac{dy}{dx} D^{(1)}(x) + \frac{d^2 y}{dx^2} D^{(2)}(x) \text{ [5].} \tag{4.1.3}$$

The transformed Fokker-Planck equation is

$$\frac{\partial P'(y,t)}{\partial t} = [-\frac{\partial}{\partial y} D'^{(1)}(y) + D\frac{\partial^2}{\partial y^2}]P'(y,t), \tag{4.1.4}$$

where $D = const$. We are able to rewrite the above equation with a constant diffusion coefficient,

$$\frac{\partial P(x,t)}{\partial t} = [-\frac{\partial}{\partial x} f'(x) + D\frac{\partial^2}{\partial x^2}]P, \tag{4.1.5}$$

where

$$f(x) = -\int_0^x D^{(1)}(x)dx' \qquad (4.1.6)$$

is a potential. For stationary solutions $\frac{\partial P(x,t)}{\partial t} = const;$ so one can write

$$0 = -\frac{\partial}{\partial x}[D^{(1)}(x)P^s(x) - \frac{1}{2}\frac{\partial}{\partial x}\{D^{(2)}(x)P^s(x)\}]. \qquad (4.1.7)$$

For one dimension we find the solution when the term inside the square brackets is zero

$$0 = D^{(1)}(x)P^s - \frac{1}{2}\frac{\partial}{\partial x}\{D^{(2)}P^s\}. \qquad (4.1.8)$$

Then

$$D^{(1)}(x)P^s = \frac{D^{(1)}(x)}{D^{(2)}(x)}\{D^{(2)}(x)P^s\} = \frac{\partial}{\partial x}D^{(2)}(x)P^s. \qquad (4.1.9)$$

Assuming $D^{(2)}$ and P^s are not equal to zero, we integrate equation (4.1.9) giving

$$P^s(x) = \frac{const}{D^{(2)}(x)}\exp^{[\int_0^x \frac{D^{(1)}(y)}{D^{(2)}(y)}dy]} \qquad (4.1.10)$$

as the stationary solution.

Returning to the Fokker-Planck equation for the drift-diffusing vacancy obtained in section 3.6, *i.e.*, equation (3.6.9), the stationary solution is then (by equation 4.1.10)

$$P^s(x) = const.\exp^{\left\{\frac{H(x)}{k_B T}\right\}} \exp^{[-\int_0^x \frac{V'(y)}{k_B T(y)} dy]} . \qquad (4.1.11)$$

The integration constant has to be chosen such that P^s is normalised. The factor $\exp^{\left\{\frac{H(x)}{k_B T}\right\}}$ gives the probability for each potential well to be occupied while the last factor is the effect of the external potential field. Thus in the absence of an external field the stationary solution is simply

$$P^s(x) = h(x) = const \exp^{\left\{\frac{H(x)}{k_B T}\right\}}, \qquad (4.1.12)$$

which is also the stationary solution to the diffusion equation (equation 2.2.3). Inserting this solution into the canonical form of the diffusion equation, (equation 2.2.8) we obtain

$$\frac{d}{dx}[\mu V' - k + D\frac{h'}{h} - D\frac{V'}{T}]P^s = 0, \qquad (4.1.13)$$

which states that the diffusion flow, J, must be constant. If V' grows fast enough so that $J = 0$ *i.e.*, no particles can enter or leave, implies that the factor in the brackets must vanish. We can therefore conclude, assuming V has this property, that the Einstein relation, (2.2.1), holds even when, μ, D and T depend on x [14]. This illustrates the importance of starting from a physical model, so that not only a correct translation between the microscopic model and the derived mesoscopic diffusion equation can take place, but also because it has serious implications for numerical modelling of diffusive systems, *e.g.*, Monte Carlo methods [35].

4.2 Solution by Numerical Methods

To obtain non stationary solutions for the Fokker-Planck equation is not an easy exercise, and only for special drift and diffusion coefficients can one obtain such solutions. In fact, for large times and for certain restrictions on the drift, diffusion and boundary conditions it can be proved that if a stationary solution exists then every solution must decay to the stationary solution [5]. With this in mind we tentatively proceed to solve both the homogenous diffusion equation (2.1.15) and the Fokker-Planck equation (2.5.1, 4.1.1) using the complex but accurate finite element method used by the *pdepe* routine of the commercially available mathematical software MATLAB® (Release 14 with service pack 2, February 2005).

The *pdepe* function solves initial boundary value problems for systems of partial differential equations in one dimensional space and time in the form of

$$c(x,t,P,\frac{\partial P}{\partial x})\frac{\partial P}{\partial t} = x^{-m}\frac{\partial}{\partial x}(x^{m}f(x,t,P,\frac{\partial P}{\partial x})) + s(x,t,P,\frac{\partial P}{\partial x}), \qquad (4.2.1)$$

where $c(x,t,P,\frac{\partial P}{\partial x})$ is a diagonal matrix defining an elliptic or parabolic partial differential equation, $f(x,t,P,\frac{\partial P}{\partial x})$ is the flux term, $s(x,t,P,\frac{\partial P}{\partial x})$ is the source term and m = 0, 1 or 2 decides the geometry of the problem such as a slab, cylinder or sphere. Thus we need to rewrite the diffusion equation (2.1.15) and the Fokker-Planck equation (4.1.1) in the form of equation (4.2.1) and then identify the flux and source terms. But first we establish the boundary and initial conditions for equations (2.1.15) and (4.1.1) in the next section.

4.2.1 Diffusion equation

Consider the one dimensional homogenous diffusion equation (Fick's 2nd law, equation (2.1.15)).

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2},$$

where $P(x,t)$ is the concentration at time t a distance x along a thin rod. To solve this partial differential equation one needs both initial conditions, that is the concentration at $t=0$, $P(x,t=0)$, and the boundary conditions at the end points of the rod, say $x=a$ and $x=b$. We choose the boundary conditions such that $P(x=a,t)=P_a$ and $P(x=b,t)=P_b$ that is the value of P is held constant at the ends.

The initial condition is

$$P(x,t=0)=f(x), \tag{4.2.1.1}$$

where $f(x)$ gives the impurity concentration distribution at $t=0$, *i.e.*, the Dirichlet problem. Consider now the inhomogeneous diffusion equation in one dimension,

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2} + g(x,t). \tag{4.2.1.2}$$

With $-\infty < x < \infty$, $t \geq 0$ and the initial condition $P(x,0)=f(x)$, where g and f are arbitrary functions. This is the Cauchy problem. The physical problem is an infinite bar which is subjected to a heat source $g(x,t)$ which may vary in time and along the length of the bar. The solution of the above equation is the sum of

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2} + g(x,t), \quad -\infty < x < \infty,\ t \geq 0 \tag{4.2.1.3a}$$

$$P(x,0)=0$$

and

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2}, \qquad -\infty < x < \infty,\ t \geq 0 \qquad (4.2.1.3b)$$
$$P(x,0) = f(x).$$

We set $g(x,t) = \delta(x-y)\delta(t-\tau)$, which represents an instantaneous unit heat input at time τ and position y, and assume the same homogeneous initial and boundary conditions as in the general case. Then

$$P(x,t) = G(x-y,t-\tau). \qquad (4.2.1.4)$$

The solution to equation (4.2.1.3a), is the Green's function. Because of the linearity of the diffusion equation, the solution to the general problem is given by the superposition formula as

$$\begin{aligned} P(x,t) &= \int_{y=-\infty}^{\infty}\int_{\tau=0}^{t} G(x-y,t-\tau)g(y,\tau)d\tau dy \\ &= \int_{y=-\infty}^{\infty}\int_{\tau=0}^{\tau} \frac{g(y,\tau)}{\sqrt{4\pi(t-\tau)}} e^{-\left(\frac{(x-y)^2}{4(t-\tau)}\right)} d\tau dy, \end{aligned} \qquad (4.2.1.5)$$

and the forcing term as

$$g(x,t) = \int_{0}^{\infty}\int_{-\infty}^{\infty} g(y,\tau)\delta(t-\tau)\delta(x-y)dyd\tau \ [35]. \qquad (4.2.1.6)$$

The second problem, equation (4.2.1.3b), is the same as

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2} + g(t)f(x), \ -\infty < x < \infty,\ t \geq 0 \qquad (4.2.1.7)$$
$$P(x,0) = 0 .$$

Setting $g(y,t)$ in equation (4.3.1.5) equal to $g(t)f(x)$ we get

$$P(x,t) = \frac{1}{\sqrt{4\pi t}} \int_{y=-\infty}^{\infty} f(y) e^{-\{\frac{(x-y)^2}{4t}\}} dy . \qquad (4.2.1.8)$$

Thus the solution to equation (4.2.1.2) is the sum of equations (4.2.1.5) and (4.2.1.8). The initial condition is

$$P(x,0) = \lim_{t\to 0} \int_{-\infty}^{\infty} f(y) \frac{e^{-\{\frac{(x-y)^2}{4t}\}}}{\sqrt{4\pi t}} dy = \int_{-\infty}^{\infty} f(y)\delta(x-y)dy = f(x) . \qquad (4.2.1.9)$$

Now returning to the homogenous diffusion equation (equation 2.1.15), subject to the Dirichlet conditions as described above, we can set the initial condition equation (4.2.1.1) to equation (4.2.1.9). We may use

$$P(x,t=0) = f(x) = \frac{5}{8} \frac{e^{-\{\frac{(x+7)^2}{4}\}}}{\sqrt{4\pi}} \qquad (4.2.1.10)$$

and

$$P(x,t=0) = f(x) = \frac{5}{8} \frac{e^{-\{\frac{(x+7)^2}{4}\}}}{\sqrt{4\pi}} + \frac{2}{8} \frac{e^{-\{\frac{(x-1)^2}{4}\}}}{\sqrt{4\pi}} + \frac{1}{8} \frac{e^{-\{\frac{(x-6)^2}{4}\}}}{\sqrt{4\pi}} \text{ [41,42]} \qquad (4.2.1.11)$$

as a trimodal initial condition. See figures 4.2.1.1 and 4.2.1.2 respectively for plots of these functions.

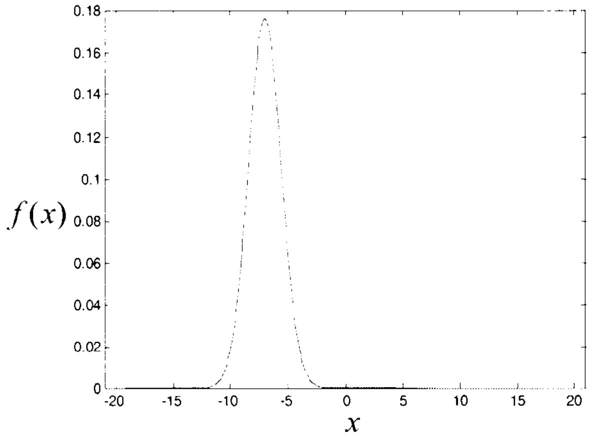

Figure 4.2.1.1 Plot of the initial condition according to equation (4.2.1.10).

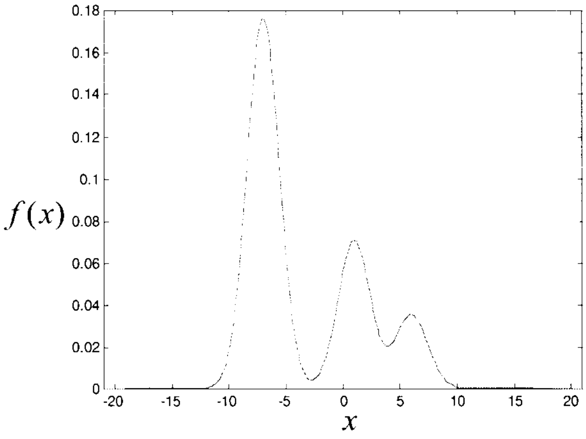

Figure 4.2.1.2 Plot of the initial condition according to equation (4.2.1.11).

Rewriting the diffusion equation (equation 2.1.15) in the form of equation (4.2.1) we get

$$1(\frac{\partial P}{\partial t}) = 1\frac{\partial P}{\partial x}\frac{\partial P}{\partial x} + 0. \qquad (4.2.1.12)$$

Therefore

$$c(x,t,P,\frac{\partial P}{\partial x}) = 1, \qquad (4.2.1.13)$$

$$f(x,t,P,\frac{\partial P}{\partial x}) = \frac{\partial P}{\partial x}, \qquad (4.2.1.14)$$

and

$$s(x,t,P,\frac{\partial P}{\partial x}) = 0. \qquad (4.2.1.15)$$

4.2.2 Fokker-Planck Equation

Returning to the one dimensional Fokker-Planck equation (4.1.1), with time-independent drift and diffusion coefficients, $D^{(1)}(x)$ and $D^{(2)}(x)$, respectively, we consider the Ornstein-Uhlenbeck process where the drift coefficient is linear and the diffusion coefficient is constant, *i.e.*,

$$D^{(1)}(x) = -\gamma x\,;\ D^{(2)}(x) = D = const\,; \tag{4.2.2.1}$$

$$\frac{\partial P(x(t))}{\partial t} = \gamma\frac{\partial P}{\partial x}(xP) + D\frac{\partial^2 P}{\partial x^2}. \tag{4.2.2.2}$$

Using the same boundary conditions and initial condition, for the homogenous diffusion equation (Fick's 2nd law *i.e.* equation (2.1.15)) we solve equation (4.2.2.2) for different values of γ. But first we have to rewrite equation (4.2.2.2) in the form of equation (4.2.1) *i.e.*

$$1(\frac{\partial P}{\partial t}) = 1\frac{\partial P}{\partial x}\frac{\partial P}{\partial x} + \gamma x\frac{\partial P}{\partial x} + \gamma P. \tag{4.2.2.3}$$

Therefore

$$c(x,t,P,\frac{\partial P}{\partial x}) = 1, \tag{4.2.2.4}$$

$$f(x,t,P,\frac{\partial P}{\partial x}) = \frac{\partial P}{\partial x}, \tag{4.2.2.5}$$

and

$$s(x,t,P,\frac{\partial P}{\partial x}) = \gamma x\frac{\partial P}{\partial x} + \gamma P. \qquad 4.2.2.6)$$

4.3 Results

The MATLAB® program, diffusion_Model (see appendix A1), solves Fick's 2nd law, equation (2.1.15), with boundary conditions $P(x=a,t)=P_a$ and $P(x=b,t)=P_b$, and initial condition equation (4.2.1.10). The solution profile of its density functions, as a function of x and t, is given in figures 4.3.1 (a) and (b) respectively.

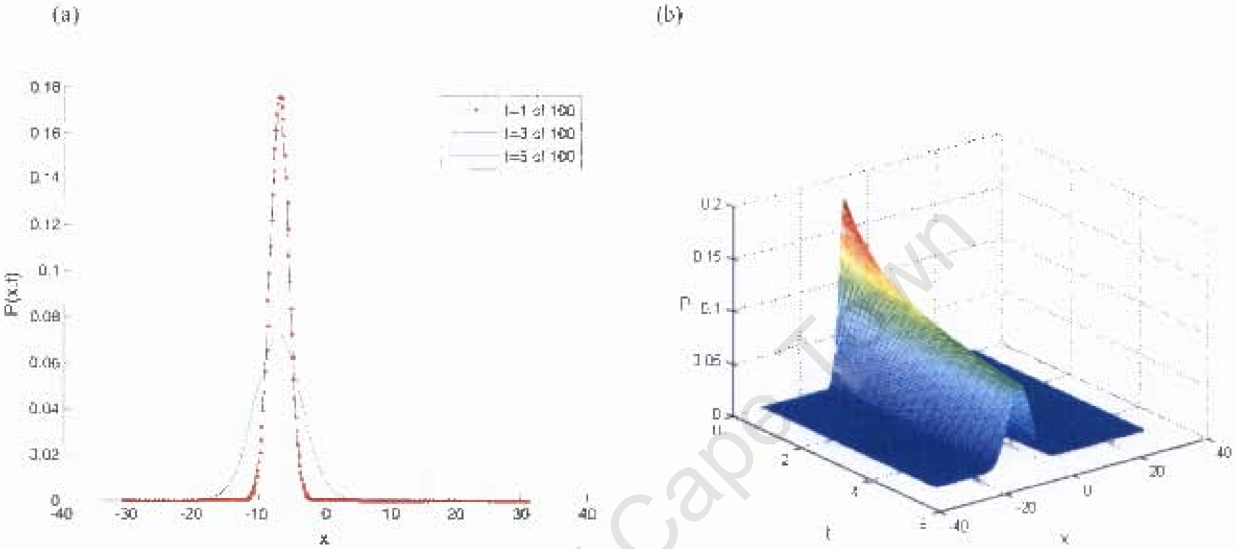

Figure 4.3.1 Solution profile of Fick's 2nd Law for (a) the probability density as a function of x and in (b) the probability density as a function of x and t. The initial condition is equation 4.2.1.10. For values of Δt and Δx there are 100 values of t ranging from 0 to 5 and 401 values of x ranging from -31 to 31. The maximum value obtained by the function is at $t=0$ tapering off to $t=5$. The tail area for the mode increases with time.

Solving the same equation (2.1.15), with the same boundary conditions but using the trimodal initial condition (4.2.1.11) is now given in figure 4.3.2, the MATLAB® code is saved as diffusion_Mode3, (appendix A2).

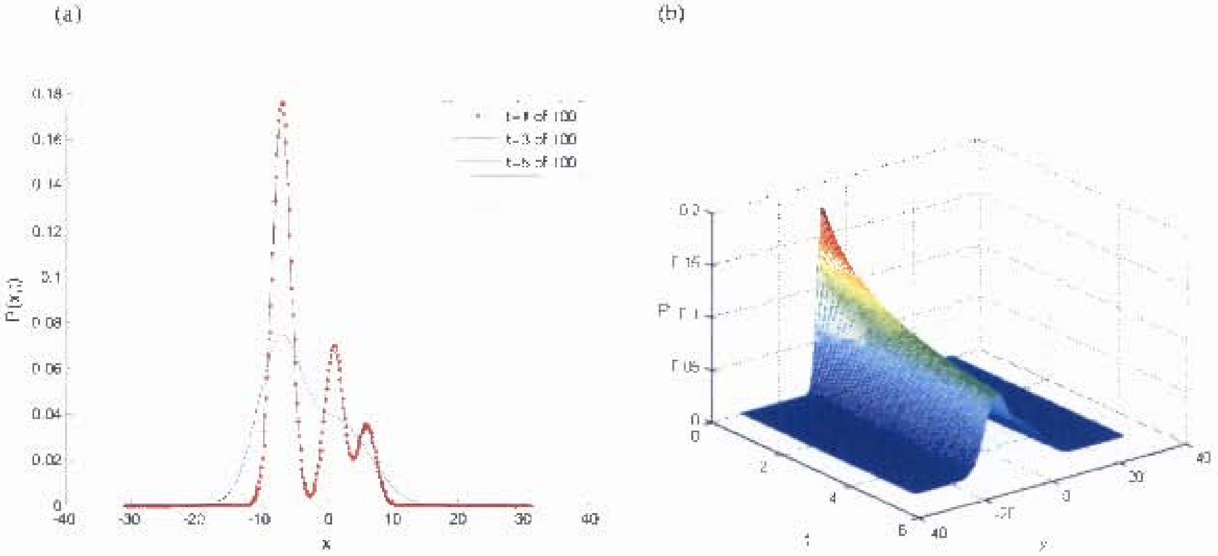

Figure 4.3.2 Solution profile of Fick's 2nd Law for (a) the probability density as a function of x and in (b) the probability density as a function of x and t. The three modes merge with increasing tail area with time.

Now we shift our attention to the Fokker-Planck equation (4.2.2.2), using the same boundary conditions and trimodal initial condition (4.2.1.11), as above. For $\gamma = 0.2$ see figure 4.3.3. The MATLAB® code is saved as fpc_Mode3, (appendix B1).

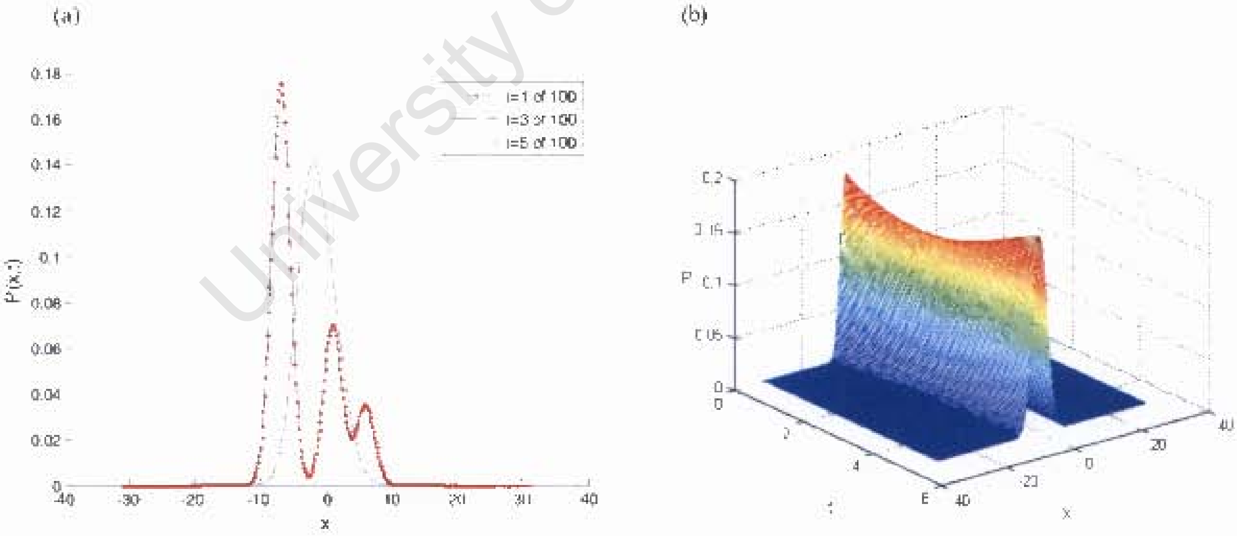

Figure 4.3.3 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. The three modes merge quite quickly into one mode with time.

We compare the solution plots of Fick's 2nd law (figure 4.3.2) and the Fokker-Plank equation ($\gamma = 0.2$). Both equations have the same boundary and initial conditions. The diffusion equation peaks at $t = 0$, but decays along its x trajectory (about $x \approx -7.5$) with the smaller two modes traversing across x, to the maximum value at $x \approx -7.5$, with time. The final solution at $t = 5$ has less area in the tails than at the initial time $t = 0$. The Fokker-Planck equation behaves differently. The maximum value of the function, like for the diffusion equation, is at $t = 0$, but it is the dominant mode that now traverses towards the other two smaller modes. Also, whereas the tail area increased with time for the diffusion equation, the Fokker-Planck equation has decreasing tail area with time.

Now we solve the Fokker-Planck equation for a range of γ, *i.e.*, $\gamma = 0.0002$, 0.1, 0.276, 0.4, 0.8, 1, and 6.

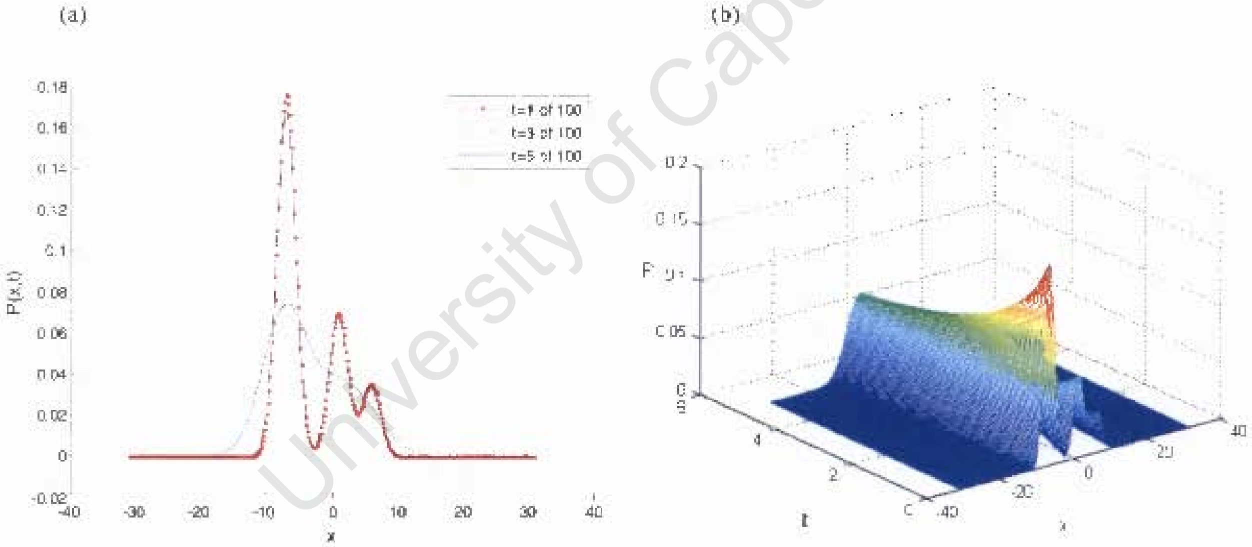

Figure 4.3.4 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. For an arbitrary chosen value of $\gamma = 0.0002$. The three modes merge slowly with increasing tail area with time, exactly like Fick's 2nd law, see figure 4.3.2

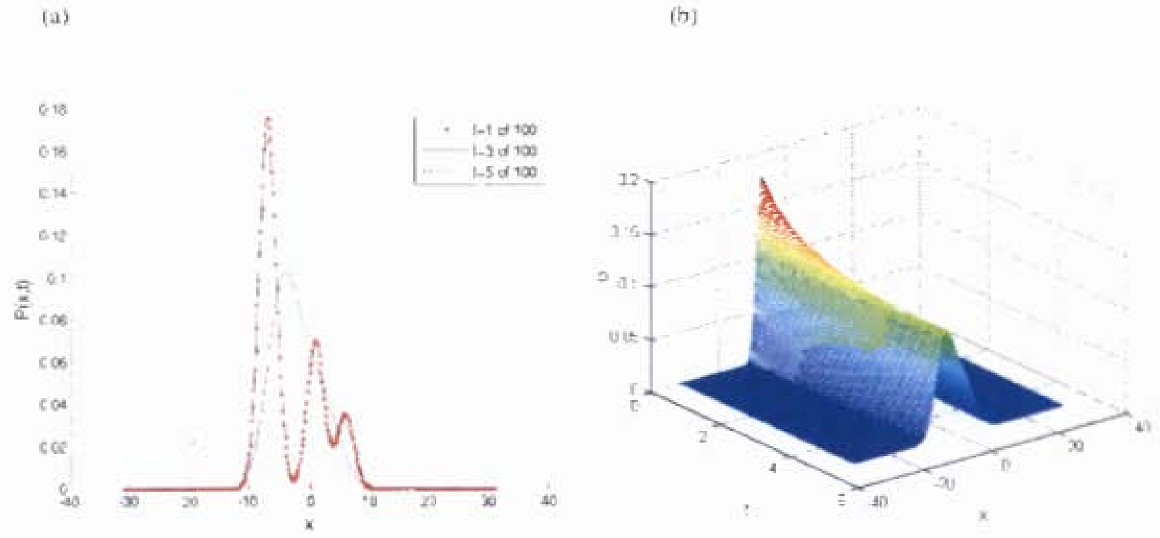

Figure 4.3.5 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. For $\gamma = 0.1$, here the maximum value obtained by the function is at $t = 0$ tapering off to $t = 5$. The three modes merge slowly with tail area remaining constant with time.

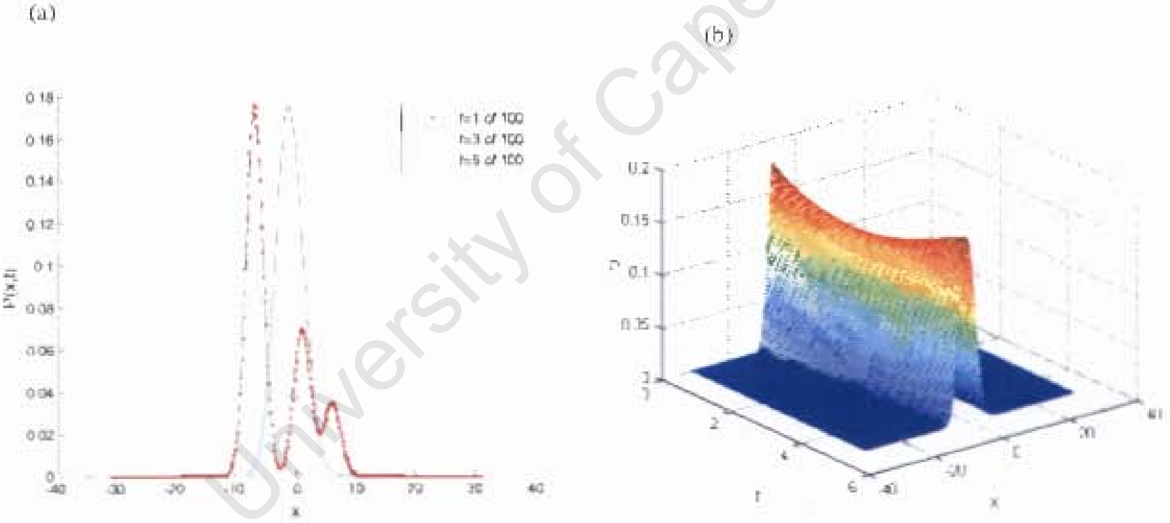

Figure 4.3.6 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. For $\gamma = 0.276$, here the maximum value remains constant with time. The three modes merge slowly with time.

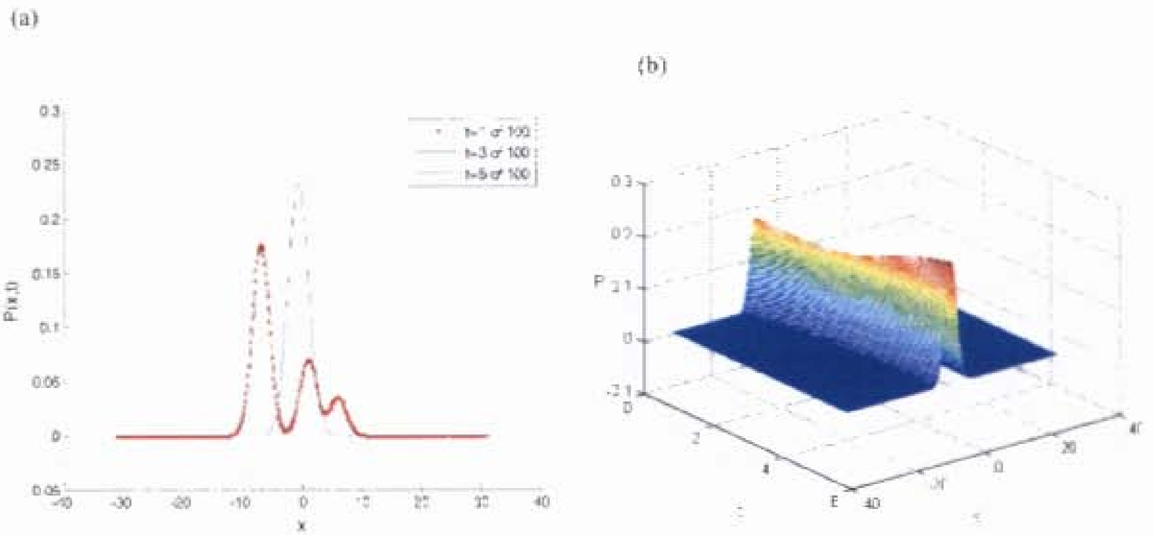

Figure 4.3.7 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. For $\gamma = 0.4$, here the maximum value is at $t = 5$. The three modes merge slowly with time.

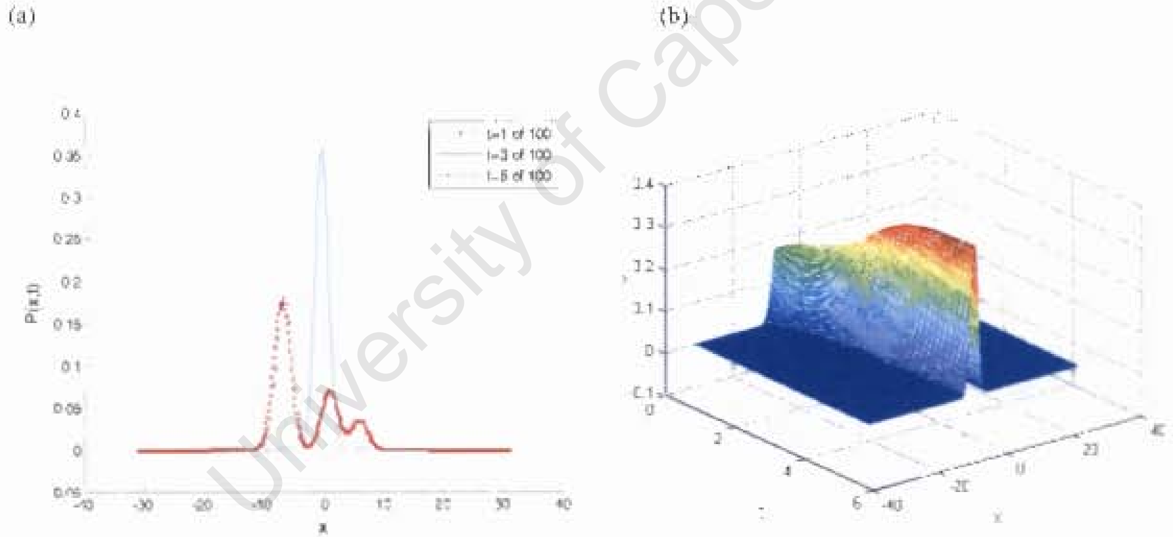

Figure 4.3.8 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. For $\gamma = 0.8$, here the maximum value is at $t = 5$. The three modes at $t = 0$ merge more quickly with time.

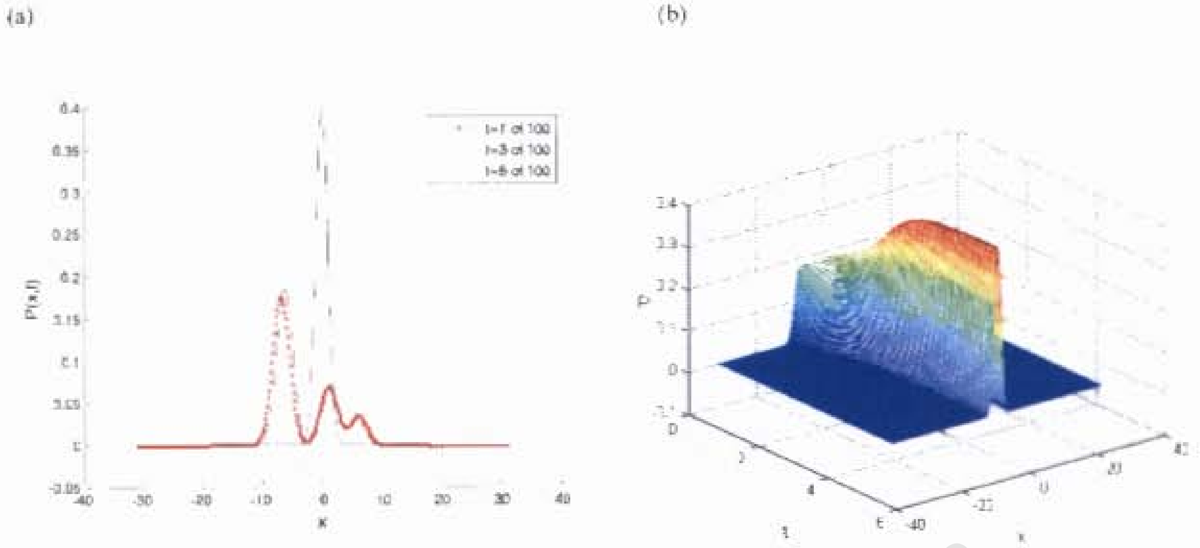

Figure 4.3.9 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. For $\gamma = 1$, again a maximum value at $t = 5$. The three modes at $t = 0$ merge quickly with time.

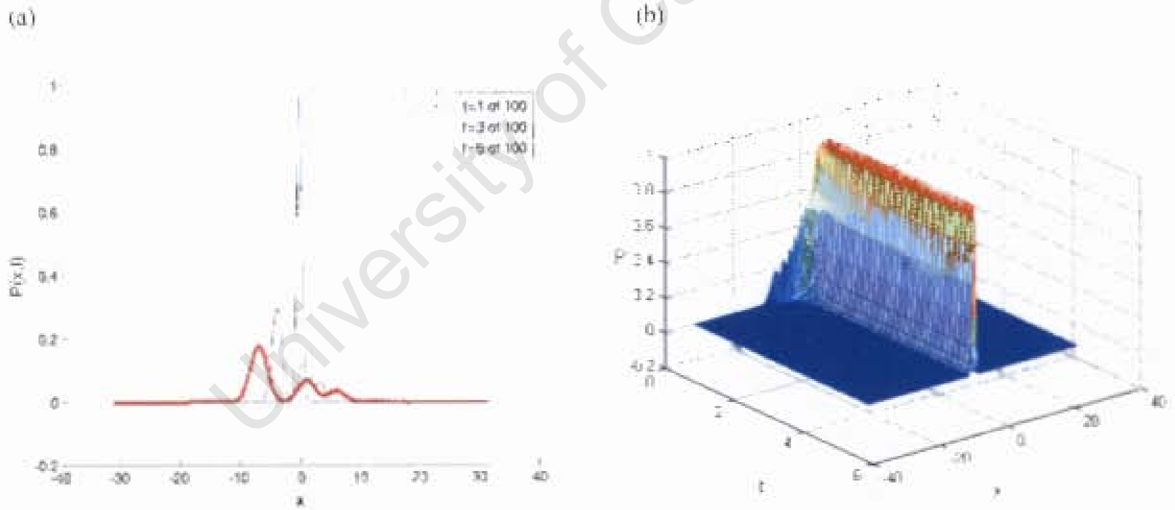

Figure 4.3.10 Solution profile of the Fokker-Planck equation 4.2.2.2 (a) the probability density as a function of x and in (b) the probability density as a function of x and t. For $\gamma = 6$, again a maximum value at $t = 5$ with a minimum way below at $t = 0$. The three modes merge quickly with time.

Analysing the above plots for the diffusion equation (2.1.4) and the Fokker-Planck equation (4.2.2.2), for $\gamma = 0.002$, 0.1, 0.276, 0.4, 0.8, 1, and 6 we find the following:

I. for very small values of γ, (figure 4.3.4, $\gamma = 0.0002$), the solution to the Fokker-Planck equation is similar to the diffusion equation (figure 4.3.2), as expected.

II. for increasing values of γ, the following takes place:
   a) the maximum value of the function shifts from $t = 0$ to $t = 5$;
   b) the three modes at $t = 0$ merge to one mode at $t = 5$;
   c) the area in the tails decreases at $t = 0$ to $t = 5$ and the modes become more peaked; and
   d) the maximum value of the function traverses from $-x$ to $x = 0$. The modes merge at $x = 0$.

III. for a special value of γ ($\gamma \approx 0.276$), figure 4.3.6, the maximum value remains constant with changing time but shifts position from $-x$ to $x = 0$;

IV. for large values of γ, the modes quickly merge at $x = 0$ which becomes the 'spine' of the function.

Chapter 5

Application to a Physical System

5.1 Calculating the Diffusion Coefficients

As an application to a physical system we consider the simple one dimensional case of a vacancy diffusing by a hopping mechanism under an applied stress, using data obtained by Härting *et al* in 'Near Surface Stress Determination in Kr-implanted Polycrystalline Titanium by the X-Ray $\sin^2 \Psi$-Method' [18]. Using this data we estimated the stress and gradient. From the work of Herzig *et al* [43] we used the vacancy migration enthalpy for titanium to find the diffusion coefficients, and by the Einstein relation the mobility. In [18] the point defects were created by ion implantation with 180 keV Kr^+ ions in polycrystalline titanium samples at doses of 1×10^{15} to 1×10^{16} ions cm^{-2} at room temperature (300K). The titanium samples were disks with a diameter 25 mm and a thickness of 0.33 mm, cut from rolled titanium sheet of 99.6% purity. The objective was to determine the effect of the total dose of krypton ions on the pre-existing stress state in titanium. The titanium samples were characterised by Rutherford backscattering spectroscopy, positron annihilation lifetime spectroscopy and X-ray diffraction. The results obtained, using the $\sin^2 \Psi$-method for x-ray stress determination, are plotted in figure 5.1.1, which shows a near surface tensile stress of 1.6 GPa in the top 75 nm and a compressive stress of 40 MPa deeper in the titanium.

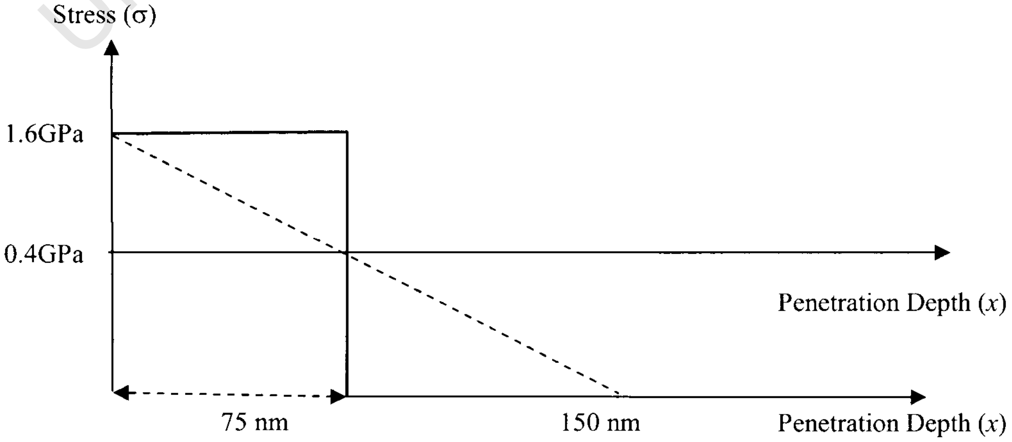

Figure 5.1.1 An approximate stress distribution found in rolled Ti [18]: a tensile stress of 1.6 GPa in the top 75 nm and a compressive stress of 40 MPa deeper in the titanium. The stress gradient is found by extrapolation to a penetration depth of 150 nm.

From this data, plotted in figure 5.1.1 we calculated the stress gradient to be,

$$\frac{d\sigma}{dx} = \frac{\Delta\sigma}{l} = -\frac{(1.6+0.4)}{150} = -0.013 \text{ GPa/nm}. \tag{5.1.1}$$

The vacancy migration enthalpy for titanium is taken from work done by Herzig *et al* [43], who obtained a migration enthalpy value of 0.7 eV. Substituting this value into equation (2.1.3) with a prefactor $D_0 = 1.7\times10^{-4}$ cm^{2}s^{-1}, at room temperature, gave $D = 2.983\times10^{-16}$ cm^{2}s^{-1}. From the Einstein relation and the calculated stress gradient estimated we obtained $\mu F = 9.366\times10^{20}$ cms^{-1}. Substituting these coefficients into our Fokker-Planck equation below

$$\frac{dP(x,t)}{dt} = \mu F\frac{dP(x,t)}{dx} + D\frac{d^2P(x,t)}{dx^2}, \tag{5.1.2}$$

we obtained

$$\frac{dP(x,t)}{dt} = 9.366\times10^{20}(\text{cms}^{-1})\frac{dP(x,t)}{dx} + 2.983\times10^{-16}(\text{cm}^2\text{s}^{-1})\frac{d^2P(x,t)}{dx^2}. \tag{5.1.3}$$

5.2 The Initial Condition

The initial condition is obtained from the vacancy profile from modelling the point defects created by ion implantation of 180 keV Kr$^+$ ions in polycrystalline titanium samples using TRIM [45]. A mean depth of 45nm and a straggle of 25nm for the vacancies produced were obtained as shown in figure 5.2.1.

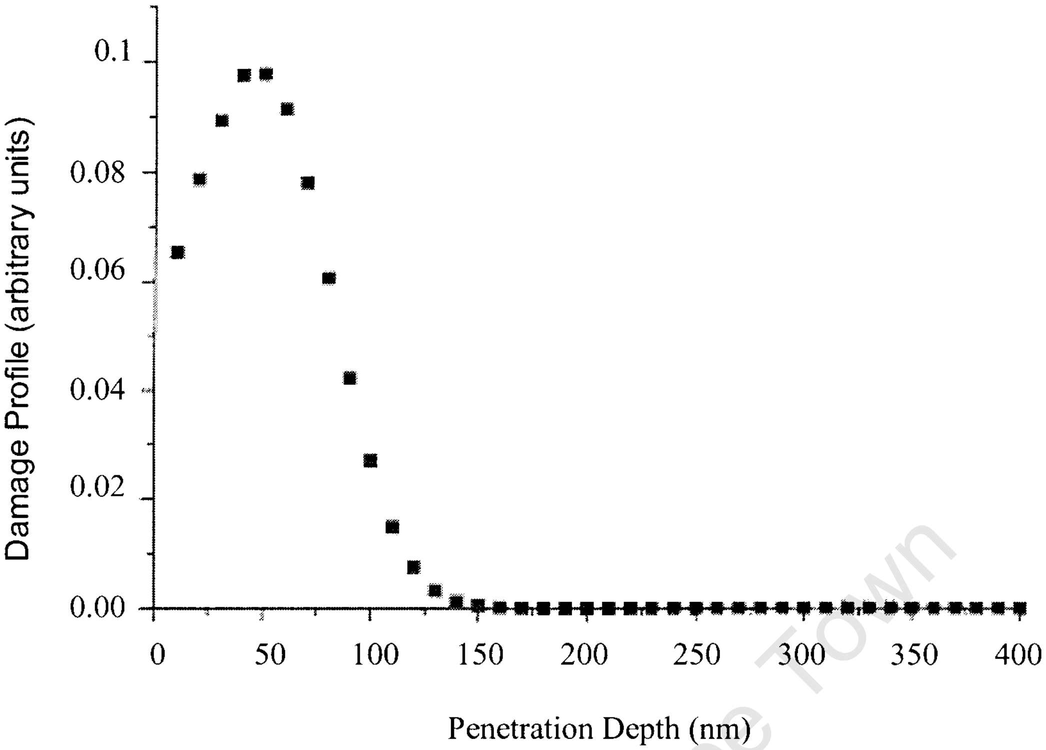

Figure 5.2.1 The vacancy profile gained from modelling the point defects created by implantation of 180 keV Kr$^+$ ions in polycrystalline titanium using TRIM.

The initial condition is thus gaussian with a mean of 45 nm and standard deviation of 25 nm *i.e.*

$$P(x,t=0)=\frac{1}{25\sqrt{2\pi}}e^{-(\frac{1}{2})[\frac{x-45}{25}]^2}\ \text{nm}^{-1}, \qquad (5.2.1)$$

as shown in figure 5.2.2 below.

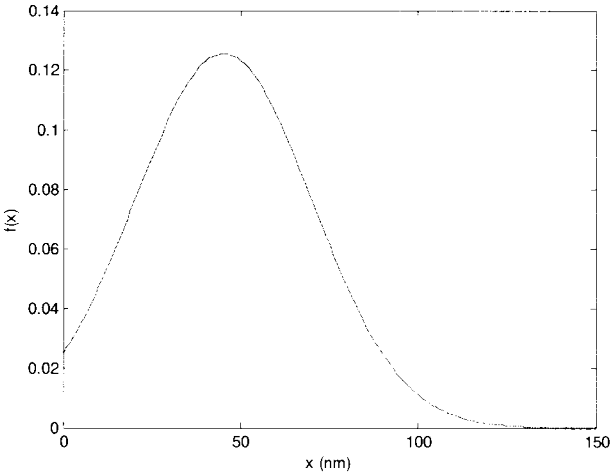

Figure 5.2.2 A plot of the initial condition, function (5.2.1).

5.3 Discussion of the Solution Profile

We can set $\mu F \approx 10^{27}$nm and $D = 10^{-16}$ in our Fokker-Planck equation (5.1.3). Then using a suitable scale for $\frac{dP(x,t)}{dx}$, with Dirichlet boundary conditions of $P(x=0,t) \equiv 0$, as in section 4.2.2 and initial condition of equation (5.2.1), we rewrite (4.2.2.2) in the form of (4.2.1) and model the Fokker-Planck equation (5.1.3) using the MATLAB® program, fpe_Physical.m. The solution profile of its density functions as a function of x and t is given in figures 5.2.3 (a) and (b).

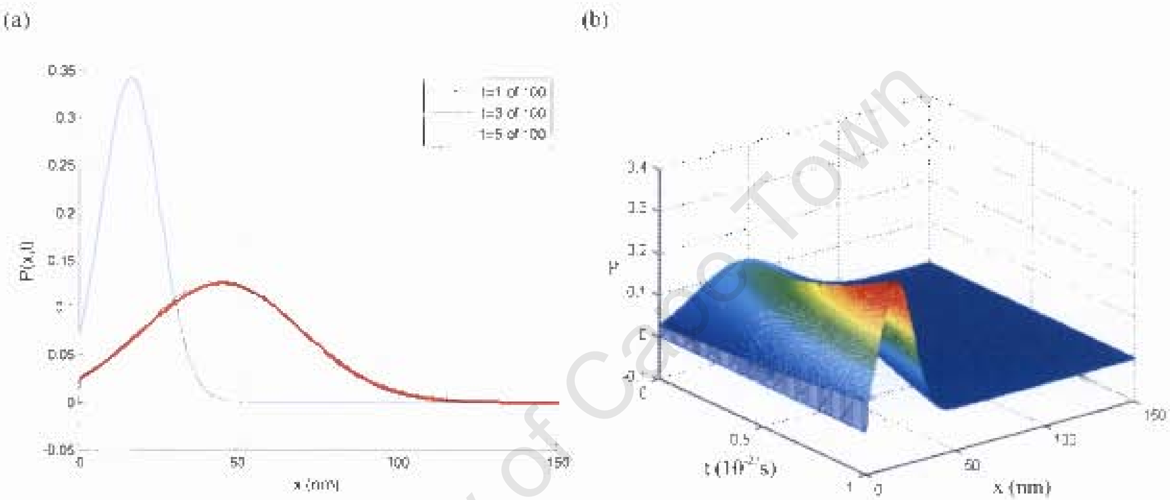

Figure 5.2.3 Solution profile of equation (5.1.3) (a) the probability density as a function of x and in (b) as a function of t and x. The dominant term is the drift.

Clearly the dominant term is the drift as we have decreasing tail area and a shift of the peak towards the surface, *i.e.* at $x = 0$ with $\Sigma P \equiv 1$. The effect of the diffusion term dominating would be to deepen the maximum of the distribution [46], whereas the drift causes the distribution to narrow.

Chapter 6

Application to a Non Physical System

6.1 Cross-Fertilising Economics and Physics

The aim here is to setup up a Fokker-Planck equation describing incremental changes in foreign exchange (FX) prices. The purpose of chapter 6 is to show that the same approach, namely a Fokker-Planck equation, can be applied to non material systems provided the Markov property, given by equation (3.1.12), is satisfied. In so doing we are able to quantify the deterministic as well as the random influences on the statistics of that system. However, unlike using the hopping model as a first approximation to setup the master equation for vacancy diffusion, here the Fokker-Planck equation is directly derived from the FX data.

The method used to formulate a Fokker-Planck equation directly from the FX data is a new idea developed by Joachim Peinke *et al* [19,20,23] and is based on the following two ideas.

First, there is an analogy between the short time dynamics of FX price changes and fully developed hydrodynamic turbulence, as proposed by Ghashghaie *et al* [21]. This is clearly seen in figures 6.1.1(a) and (b). In figure 6.1.1(a) the standardised probability density is derived from price increments for different changes in time and is almost identical to the standardised probability density of velocity increments for different Kolmogorov scales given in figure 6.1.1(b). Turbulence is the puzzling blend of order and disorder that occurs in fluid flows [36]. Periods of smooth laminar flow are often followed with irregular bursts of chaotic flow that dissipate energy. The analogy to FX data would be periods of stable prices followed by sudden extreme fluctuations, *i.e.*, the energy flow in fluids is analogous to the flow of information in financial markets. In both systems there is a cascade like flow from large scale energy pumped into fluid flow dissipated on smaller scales to that of information passed on to the short term investors by those taking long term positions in financial markets [36].

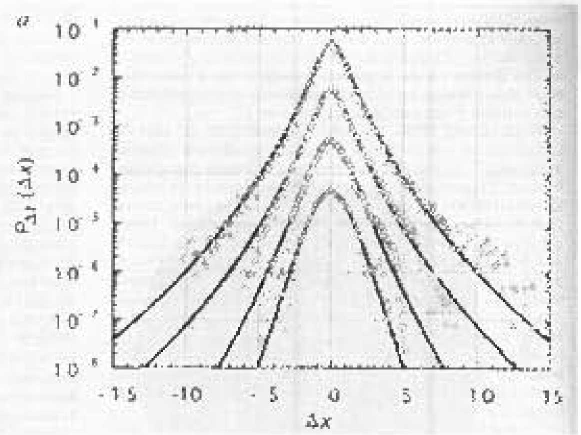

Figure 6.1.1(a) Price fluctuations in a financial market. Data points consist of standardised probability density $P(\Delta x, \Delta t)$ of price increments $\Delta x = x(t) - x(t + \Delta t)$ for Δt 640s, 5 120s, 40 960s and 163 840s from top to bottom [21].

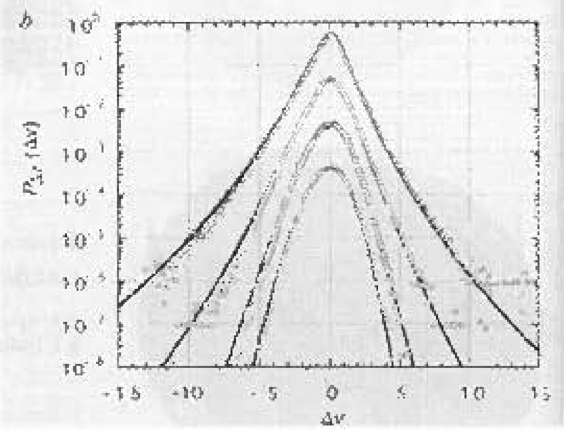

Figure 6.1.1(b) Velocity changes in turbulent flow. Data points consist of standardised probability density $P(\Delta v, \Delta t)$ of velocity increments for a turbulent flow with scales $\Delta r = 3{,}3\eta, 18{,}5\eta, 138\eta 325\eta$; η is the Kolmogorov scale [21].

Second, one has to establish that the behaviour of traders and the trading mechanisms results in a Markovian process for price increments,

$$\Delta x = x(t + \Delta t) - x(t), \tag{6.1.1}$$

for different time delays, Δt. Here $x(t)$ refers to the price of the foreign exchange bid with a physical time-scale for t. The merit of using Δx over x to describe the stochastic behaviour of price fluctuations is based on the simple linear relationship of equation (6.1.1). This means that price changes are additive:

$$\Delta x(t, \Delta t_1 + \Delta t_2) = \Delta x(t - \Delta t_1, t_2) + \Delta x(t, \Delta t_1). \tag{6.1.2}$$

We continue much like in section 3.1. First we defined the probability density that the FX price increment (the stochastic variable) will have a value Δx_1 at delay time Δt_1, *i.e.* $P(\Delta x_1, \Delta t_1)$. Similarly the joint probability density function is

$$P(\Delta x_2 \Delta t_2, \Delta x_1 \Delta t_1) \tag{6.1.3}$$

and the conditional probability density function is

$$P(\Delta x_2 \Delta t_2 | \Delta x_1 \Delta t_1) = \frac{P(\Delta x_2 \Delta t_2, \Delta x_1 \Delta t_1)}{P(\Delta x_1 \Delta t_1)}. \tag{6.1.4}$$

The conditional probability density is interpreted as follows. The probability density function for price increment Δx_2 at delay time Δt_2 given Δx_1 at delay time Δt_1 is equal to the joint probability of Δx_1 and Δx_2 for Δt_1 and Δt_2 at the same time, *t*. For a Markovian process it is necessary that $\Delta t_2 < \Delta t_1$ in equation (6.1.4).

One eventually arrives at the Chapman-Kolmogorov equation (see section 3.1 and figure 3.1.1)

$$P(\Delta x_2 \Delta t_2 | \Delta x_1 \Delta t_1) = \int P(\Delta x_2 \Delta t_2 | \Delta x_i \Delta t_i) P(\Delta x_i \Delta t_i | \Delta x_1 \Delta t_1) d(\Delta x_i), \tag{6.1.5}$$

where $\Delta t_2 < \Delta t_i < \Delta t_1$. This equation can be interpreted as follows. Given the initial change in price, Δx_1, at time Δt_1, this is the probability that, at a change in time Δt_2 the change in price will be Δx_2. This is equal to the probability that a change in price is Δx_2 at a change in time Δt_2 when the change in price was Δx_i at change in time Δt_i times the probability that the change in price is Δx_i at a change in time Δt_i when the change in price was Δx_1 at change in time Δt_1, for all possible Δx_i.

The validity of the Chapman-Kolmogorov equation (6.1.5) for different time delays $\Delta t_2 < \Delta t_1$ and hence Markov property existence, can be evaluated directly from the data by calculating the conditional probability density function (6.1.4) and comparing it to equation (6.1.5).

The Chapman-Kolmogorov equation (6.1.5) stated in differential form is the Fokker-Planck equation

$$\frac{dP(\Delta x\tau)}{d\tau} = -D^{(1)}(\Delta x\tau)\frac{\partial P(\Delta x\tau)}{\partial(\Delta x)} + D^{(2)}(\Delta x\tau)\frac{\partial^2 P(\Delta x\tau)}{\partial(\Delta x^2)}. \tag{6.1.6}$$

For convenience, we used a logarithmic time scale $\tau = \mathrm{Ln}(\frac{t_1}{\Delta t})$. This means that increasing τ is because of a decreasing interval, $\tau = 0 \Rightarrow \Delta t = t_1$. The drift, $D^{(1)}(\Delta x \tau)$, and diffusion coefficient, $D^{(2)}(\Delta x \tau)$, are then estimated directly from the time series as moments $M^{(k)}$ of the transitional probability distributions:

$$D^{(k)}(\Delta x, \tau) = \frac{1}{k!} \lim_{\Delta \tau \to 0} M^{(k)}, \qquad (6.1.7a)$$

$$M^{(k)} = \frac{1}{\Delta \tau} \int (\Delta x' - \Delta x)^k P(\Delta x', \tau + \Delta \tau | \Delta x, \tau) d(\Delta x'). \qquad (6.1.7b)$$

But first a word of caution, in physics the drift and diffusion coefficients have a very precise and definite meaning to them. They have definite units of measurements and can be calculated from first principals, such as from Newtons' laws of motion. However, when dealing with a non physical system like the financial markets, one cannot simply transfer their meaning except in terms of the evolution of a system as for large ensembles, where the details of the microscopic interactions are not all known. In such physical systems we use D and μ or $D^{(1)}$ and $D^{(2)}$, which have the same meaning. The assumptions we impose on both physical and non physical systems are also not easily transferred between the two. In the hopping model, particle interaction did not take place, however in economics the most disturbing and necessary action is the behaviour of an individual being affected by others, the herding phenomenon, which is represented by interacting gases and the stochastic random walk in a physical system. So unless we are able to fully qualify the drift and diffusion coefficients in its context we run the risk of believing 'to measure is to understand'. Just by measuring the drift and diffusion coefficients in this chapter we are only able to comment about the comparison of the magnitude of the drift coefficients for different financial instruments and indexes, which could possibly allow us to draw conclusions about the similarity of factors effecting transactions of the different financial instruments. This is further evidence for the need to start from a 'physical' model when formulating the Fokker-Planck equation. In other words we should first have developed the transition probabilities for a master equation.

6.2 Data Processing

The data set, $x(t)$, consist of 1 995 retail bid prices for South African rand (ZAR) – U.S. dollar exchange rates from 3 March 2005 to 8 March 2005 recorded every minute [47]. The data is plotted in figure 6.2.1. FX data recorded every minute is considered as high frequency or high resolution data, however, daily averages as well as stock indexes may be used as proven by Ivanova *et al* [22]. Price changes are generally modelled using one of three models [23]:

relative changes

$$r(t,\Delta t) := \frac{x(t+\Delta t)}{x(t)} \qquad (6.2.1)$$

or logarithmic-returns

$$l(t,\Delta t) := \ln\frac{x(t+\Delta t)}{x(t)}, \qquad (6.2.2)$$

or by increments

$$\Delta x := x(t+\Delta t) - x(t)\,. \qquad (6.2.3)$$

From the work done by Joachim Peinke *et al* [23] stochastic equivalence is found for all three models. The probability densities of changes for the three models can be described with the same model, with the statistics not being significantly different. Thus no type is preferred over the other. For this study incremental changes in the FX price is used.

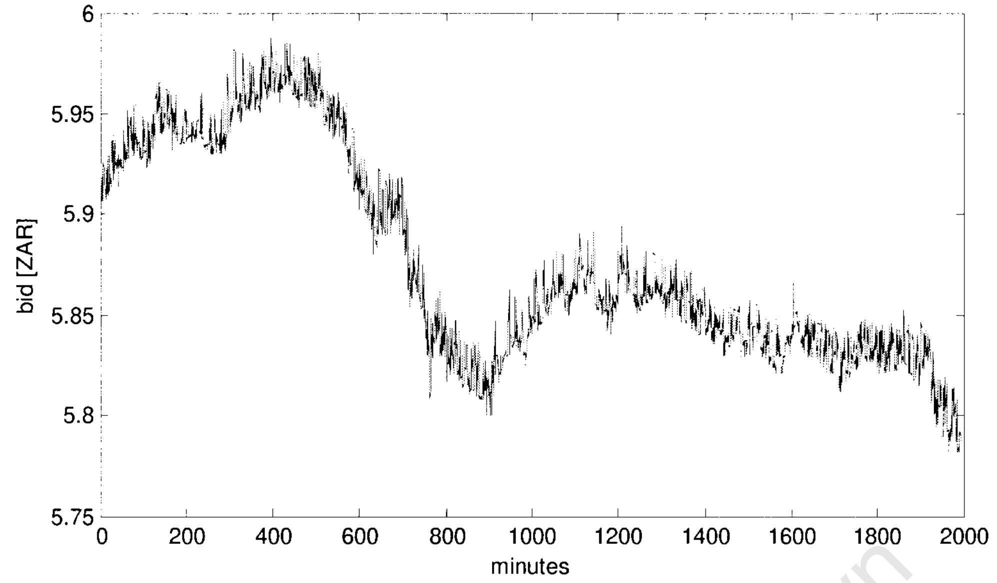

Figure 6.2.1 U.S.$/ZAR bid exchange rates from 14h41, 03 March 2005 to 15h03, 08 March 2005.

By plotting the spectral analyses of the time series $x(t)$ in figure 6.2.2, we see that noise starts to enter for higher frequencies, *i.e.* at frequencies higher than 0.005 cycles/min.

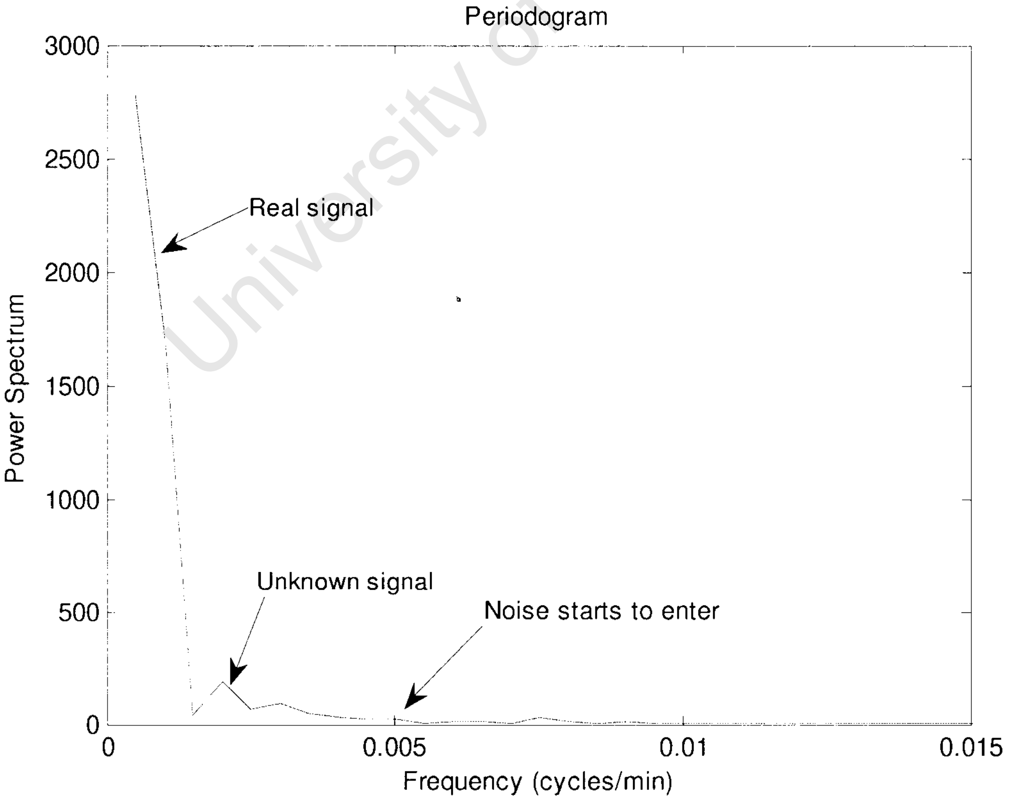

Figure 6.2.2 A periodogram of $x(t)$ showing white noise for frequencies above 0.005 cycles/min.

Applying a low-pass filter in a form of a Gaussian centred at $t = 3$ minutes with a width of 5 minutes we plot the smooth signal as a solid line, $x(t)$, and the original data as points, see figure 6.2.3.

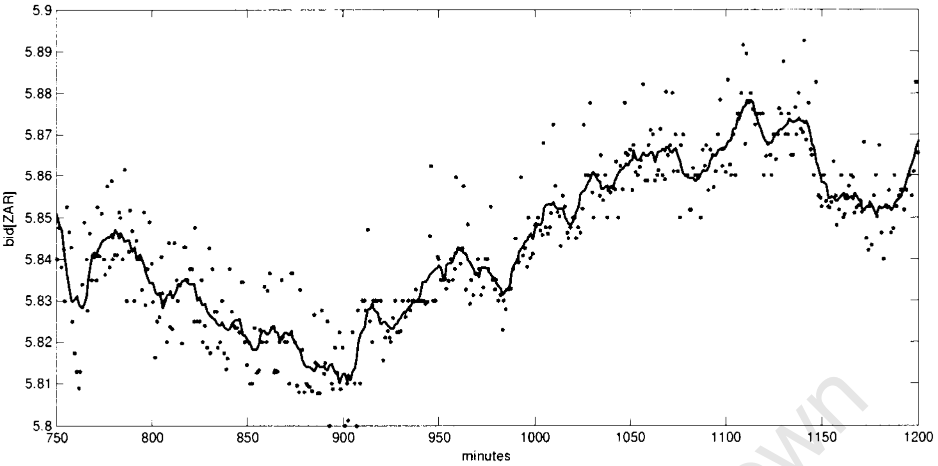

Figure 6.2.3 U.S.$/ZAR bid exchange rates as from 14h38, 03 March 2005 to 12h27, 08 March 2005 with the solid line as the smooth signal and the original data as points.

The original time series can be resolved into the 'real' signal and extracted noise *i.e.*

$$\text{Noise}\,(\Delta x\Delta t) = \text{original signal}\,(\Delta x\Delta t) - \text{smooth signal}\,(\Delta x\Delta t).$$

By plotting the autocorrelation function, figure 6.2.4, of the extracted noise we see the noise contains non-zero values for delays less than 5 minutes.

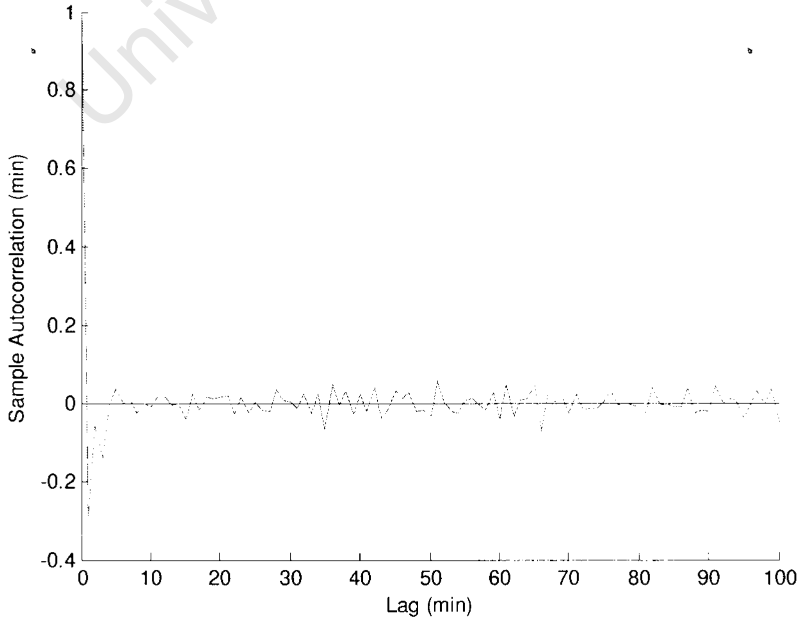

Figure 6.2.4 The autocorrelation function of the extracted noise.

6.3 The Markov Property

The study proved statistical dependence between Δx_2 and Δx_1 and hence the validity of a transition from $\Delta x_1 \Delta t_1$ to $\Delta x_2 \Delta t_2$, *i.e.* equation (6.1.5), by evaluating the transitional probability density function (6.1.4). A contour plot of equation (6.1.4) for $\Delta t_2 = 6\,\text{min} < \Delta t_1 = 8\,\text{min}$ is constructed in figure 6.3.1. The striking feature is the gradient equalling almost one, i.e., the tilted form of the plot which is clear evidence of correlation between the two time series. If no correlation existed one would find that

$$P(\Delta x_2 \Delta t_2 \,|\, \Delta x_1 \Delta t_1) = P(\Delta x_2 \Delta t_2)\,, \tag{6.3.1}$$

i.e., the contour plot would have concentric circles around $\Delta x = 0$. Correlation between scales is a reasonable expectation, in that if the price increased in period Δt_1 then it will most likely increase in the smaller period Δt_2 which is nested in the larger period, Δt_1. The degree of correlation is given by the closeness of the contour lines.

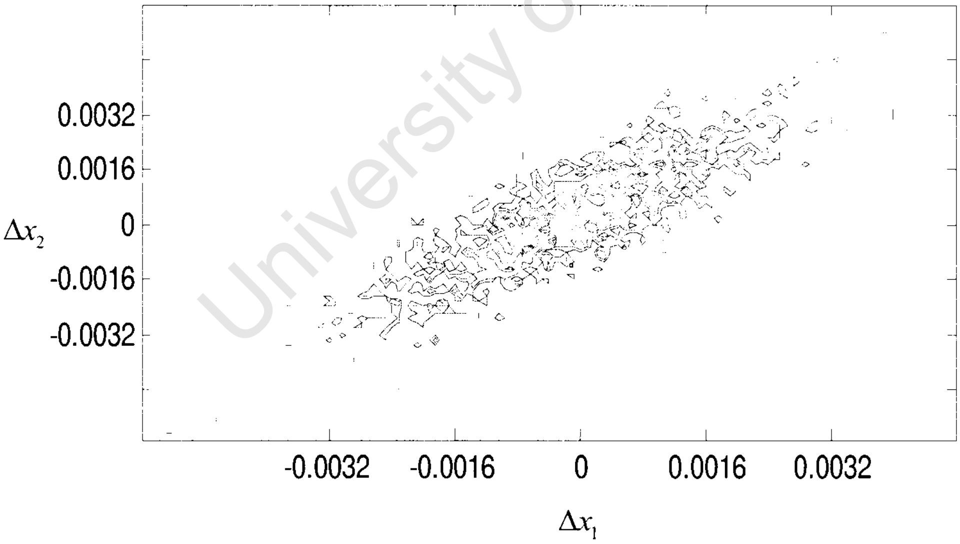

Figure 6.3.1 Contour plots of the transitional pdf
$P(\Delta x_2 \Delta t_2 \,|\, \Delta x_1 \Delta t_1) = \dfrac{P(\Delta x_2 \Delta t_2 \cap \Delta x_1 \Delta t_1)}{P(\Delta x_1 \Delta t_1)}$ for $\Delta t_2 = 6\,\text{min}$ and $\Delta t_1 = 8\,\text{min}$

At larger scales one cannot say whether the Markov property holds or not because there is no information. Having confirmed the Markov property we proceed to calculate the diffusion coefficients.

6.4 Calculating the Drift and Diffusion Coefficients

The drift and diffusion coefficients $D^{(1)}(\Delta x,\tau)$ and $D^{(2)}(\Delta x,\tau)$, can be estimated from the transitional probability plots as moments $M^{(k)}$ for different small changes in Δt. Thus from equation (6.1.7b) we first calculated $P(\Delta x',\tau+\Delta\tau|\Delta x,\tau)$ for different $d(\Delta x')$ and τ. We then multiplied by $(\Delta x'-\Delta x)^k$ and summed over $d(\Delta x')$. We continue in this fashion for different Δt from 44 minutes to 4 minutes producing both moments M^1 and M^2 per period, Δt. By plotting the moments and exercising equation (6.1.7a), (intrapolating to $\tau=0$) we obtained $D^{(1)}(\Delta x,\tau)=-0.817$ and $D^{(2)}(\Delta x,\tau)=0.45$, see figures 6.4.1 and 6.4.2. The Fokker-Planck equation is thus

$$\frac{dP(\Delta x\tau)}{d\tau}=|-0.817|\frac{\partial P(\Delta x\tau)}{\partial(\Delta x)}+|0.45|\frac{\partial^2 P(\Delta x\tau)}{\partial(\Delta x^2)}. \tag{6.4.1}$$

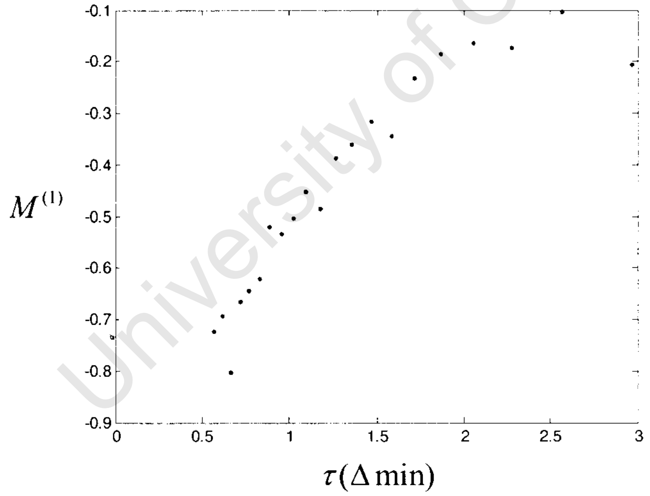

Figure 6.4.1 The drift $D^{(1)}(\Delta x,\tau)$ is estimated as moments of the transitional probability for small changes in Δt from 44 minutes to 4minutes and by taking $\lim_{\Delta\tau\to 0} M^{(1)}$ to get $D^{(1)}(\Delta x,\tau)=-0.817$.

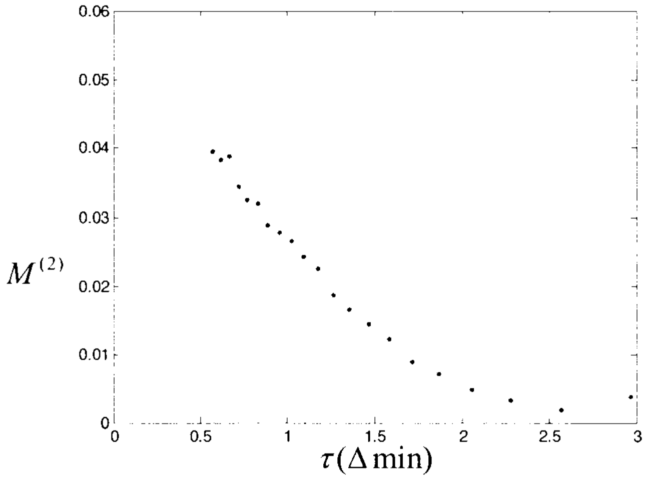

Figure 6.4.2 The diffusion coefficient $D^{(2)}(\Delta x,\tau)$ is estimated as moments of the transitional probability for small changes in Δt from 44 minutes to 4minutes and by taking $\lim_{\Delta\tau\to 0} M^{(2)}$ to get $D^{(2)}(\Delta x,\tau)=0.45$.

The derivation of $D^{(1)}(\Delta x,\tau)$ and $D^{(2)}(\Delta x,\tau)$ limits us to a technical analyses of the magnitude of these coefficients. The diffusive term, $D^{(2)}(\Delta x,\tau)$, causes the spreading out of the distribution of price changes in reciprocal time, because of our use of a logarithmic time scale $\tau = \mathrm{Ln}(\frac{t_1}{\Delta t})$. Thus in real time, the distribution of price changes converges to a steady change in prices. The drift term, $D^{(1)}(\Delta x,\tau)$, measures the rate of increase of US dollar prices and is in the direction of increasing Δx, *i.e.* an 'uphill force'. This was indeed the case for ZAR- U.S. dollar prices in 2005. After an initial gain in price for U.S. dollars (loss in ZAR terms) in the first quarter the ZAR began to steadily gain in the next quarter. See appendix C1, for ZAR- U.S. dollar daily prices for 2005.

The magnitude of the coefficients may also tell us about the factors affecting transactions for different financial instruments and indexes. Thus different financial instruments having the same coefficients may have similar variables affecting their price.

We are unable to fully qualify these coefficients in terms of macro and micro economic variables and financial indicators which make up the underlying complex financial system driving price changes. A more wholesome and rigorous approach would be starting from a physical system as in chapters 3 and 5. This would allow us the possibility of describing price change dynamics in a universal theoretical framework with the confidence derived from the success of the tools and methodologies practised in physics.

Chapter 7

Conclusion

6.1 Conclusion

There are many variants to the diffusion equation but no correct and precise form for inhomogeneous media exist, only a general form, provided the diffusing particles are independent of each other. But, whatever the form of the diffusion equation, the mobility of the diffusing particle is the coefficient of $\Delta V(x)$ and the diffusion coefficient D is the coefficient of the second derivative, having the form of equation (2.2.8). Another feature of the correct diffusion equation would be the satisfaction of the Einstein relation and under what conditions this relation, between μ and D, would divorce. Of interest also, but not covered in this study, would be what other relations, besides the Einstein relation, would connect these two terms? However, when having a diffusing system with low reactants, it becomes misleading to talk about the mean change in concentration. Instead the discrete number of particles becomes more important than the average concentration, especially when drift diffusion takes place in solids. It has been found in the literature that jump processes and their associated master equation are more wholesome and mathematically rigorous in modelling both the deterministic motion and fluctuations which arise out of the individual jumps. Also of importance in the literature is starting from a physical model when formulating Fokker-Planck equations. The physical model chosen was a particle hopping to next nearest sites with each jump or transition, occurring with a certain probability, giving a stochastic process.

The master equation gave an integro-differential equation for the time evolution of this probability through integration over the microscopic jumps between states. However, it is only in rare cases that the master equation can be solved and in other cases a suitable approximation is needed, resulting in the formation of a solvable Fokker-Planck equation. Many methods are used in literature to expand the master equation all described by van Kampen as ‘ad hoc prescriptions for cutting off higher moments of the fluctuations’. This study made use of the systematic Ω-expansion, by introducing a system size parameter Ω, as used by van Kampen, which was chosen so that it appeared in the master equation in the transition probability function, $W(x|x')$. This makes the Ω-expansion dependant on a physical model describing the fluctuating system. The expansion in its lowest form produced a macroscopic equation demonstrating how a deterministic equation emerged from a stochastic description. The stationary solution (4.1.11) obtained for the Fokker-Plank equation (3.6.9) in section (4.1) demonstrated this importance of starting from a physical model, not only so that a correct translation between the microscopic model and the derived mesoscopic diffusion equation can take place, but also because it has serious implications for numerical modelling of diffusive systems.

As an application to a physical system we considered the simple one dimensional case of a point defect created by implantation of 180 keV Kr^+ ions in polycrystalline titanium samples diffusing by a hopping mechanism. From the results obtained we were able to compute the stress gradient and from the literature value of migration enthalpy for vacancies in titanium we were able to compute the coefficients for our Fokker-Planck equation (5.1.3).

As an application to a non physical system we considered computing a Fokker-Planck equation describing incremental changes in foreign exchange (FX) prices. It was found that the cascade-like process of FX price changes obeying a Markov process enabled us to apply a Fokker-Planck approach to describe the evolution of the probability density functions of these price changes. In this non material system no assumptions were made or models proposed for the underlying stochastic processes, such as the hopping model for the drift-diffusion of a vacancy. Instead the Fokker-Planck equation was completely determined by the drift and diffusion coefficients, which were directly calculated from the actual data. It was found that correlation does indeed exist between scales validating the conditional probability density functions and hence the Markov property. However this formulation of the Fokker-Planck equation limits our comments to the comparison of the magnitude of the drift coefficients for different financial instruments and indexes, which could possibly allow us to draw conclusions about the similarity of factors effecting transactions of the different financial instruments. The Fokker-Planck equation derived was unable to qualify the deterministic and the random influences on the statistics of this system. It is illustrative of the necessity to start from a physical model, to deduce the mechanics of the individual 'particle' forming the system, in other words, the necessity to find the ‘atomic constants’ for our non physical system. Indeed, having a diffusing system with low reactants is analogous to a complex system such as the financial markets where relevant quantities such as price fluctuations are hidden by the very complex evolution of the macro economy.

Finally, a case can be made for further study in the new field of econophyics which would involve setting up master equations and their transition probability functions $W(x|x')$ for economic systems exhibiting macro economic activity, but due to small microscopic degrees of freedom, describing 'statistical equations of economics'.

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Appendix

A1 MATLAB® code for solving the homogeneous diffusion equation using initial condition (4.2.1.10).

```
% diffusion_Model1.m
%
% Solves the one-dimensional homogeneous diffusion equation
%(Fick's 2nd law)using pdepe routine.
%
%
% Lloyd A Corker
% University of Cape Town
% Department of Physics
% lcorker@Uwc.ac.za
% 2005 February
%
%
%---------------------------------------------------------------------
function P = diffusion(x,t)

% This solves the diffusion equation on the interval -31=<x>=31
% from time t = 0 to t = 5. For values of change in t and change
% in x there will be 100 values of t ranging from 0 to 5 and 401
% values of x ranging from -31 to 31.
x = linspace(-31,31,401);
t = linspace(0,5,100);

% m is a paramter which describes the geometry of the problem. In
% this case we set it to linear.
m = 0;
sol = pdepe(m,@diffpde,@diffic,@diffbc,x,t);

%the first solution in P
P = sol(:,:,1);

%---------------------------------------------------------------------
%Plots Solutions
```

```
%---------------
%Plots the solution as a 3D mesh
m1 = figure;
mesh(x,t,P);
xlabel('x','FontSize',12);
ylabel('t','FontSize',12);
zlabel('P','FontSize',12,'Rotation',0);

%Plots the solution profile for various time.
p1 = figure;
hold on;

plot(x,P(1,:),'Color',[1 0 0],...
  'LineStyle',':',...
  'Marker','.',...
  'MarkerSize',3);
plot(x,P(3,:),'K--');
plot(x,P(end,:));
xlabel('x','FontSize',12)
ylabel('P(x,t)','FontSize',12)
legend('t=1 of 100','t=3 of 100','t=5 of 100')



%--------------------------------------------------------------------
% subfunctions
%-------------
function [c,f,s] = diffpde(x,t,P,DPDx)
c = 1;
f = DPDx;
s = 0;

%----------------------------------
% Sets the initial condition at t=0
%----------------------------------
function P0 = diffic(x)
P0 = ((5/8) * exp(-(-7-x)^2/4)) /((4*pi)^(1/2));%Mode 1

%--------------------------------------
% Sets the Dirichlet boundary conditons
```

```
%---------------------------------------
function [pa,qa,pb,qb] = diffbc(xa,Pa,xb,Pb,t)
pa = Pa;
qa = 0;
pb = Pb;
qb = 0;
%/////////////////////////////////\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
```

A2 MATLAB® code for solving the homogeneous diffusion equation using initial condition (4.2.1.11).

```
% diffusion_Mode3.m
%
% Solves the one-dimensional homogeneous diffusion equation
%(Fick's 2nd law)using pdepe routine.
%
%
% Lloyd A Corker
% University of Cape Town
% Department of Physics
% lcorker@Uwc.ac.za
% 2005 February
%
%
%--------------------------------------------------------------------
function P = diffusion(x,t)

% This solves the diffusion equation on the interval -31=<x>=31
% from time t = 0 to t = 5. For values of change in t and change
% in x there will be 100 values of t ranging from 0 to 5 and 401
% values of x ranging from -31 to 31.
x = linspace(-31,31,401);
t = linspace(0,5,100);

% m is a paramter which describes the geometry of the problem. In
%this case we set it to linear.
m = 0;
sol = pdepe(m,@diffpde,@diffic,@diffbc,x,t);
```

```
%the first solution in P
P = sol(:,:,1);

%-------------------------------------------------------------------
%Plots Solutions
%---------------
%Plots the solution as a 3D mesh
m1 = figure;
mesh(x,t,P);
xlabel('x','FontSize',12);
ylabel('t','FontSize',12);
zlabel('P','FontSize',12,'Rotation',0);

%Plots the solution profile for various time.
p1 = figure;
hold on;

plot(x,P(1,:),'Color',[1 0 0],...
  'LineStyle',':',...
  'Marker','.',...
  'MarkerSize',3);
plot(x,P(3,:),'K--');
plot(x,P(end,:));
xlabel('x','FontSize',12)
ylabel('P(x,t)','FontSize',12)
legend('t=1 of 100','t=3 of 100','t=5 of 100')

%-------------------------------------------------------------------
% subfunctions
%-------------
function [c,f,s] = diffpde(x,t,P,DPDx)
c = 1;
f = DPDx;
s = 0;

%----------------------------------
% Sets the initial condition at t=0
%----------------------------------
```

```
function P0 = diffic(x)
P0 = ((5/8) * exp(-(-7-x)^2/4)+ (2/8) * exp(-(1-x)^2/4)+ (1/8) *
exp(-(6-x)^2/4)) /((4*pi)^(1/2));%Mode 3

%--------------------------------------
% Sets the Dirichlet boundary conditons
%--------------------------------------
function [pa,qa,pb,qb] = diffbc(xa,Pa,xb,Pb,t)
pa = Pa;
qa = 0;
pb = Pb;
qb = 0;
%////////////////////////////////\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
```

B1 MATLAB® code for solving the Fokker-Planck equation using initial condition (4.2.1.11).

```
% fpe_Mode3.m
%
% solves the one-dimensional Fokker-Planck equation
% using pdepe routine or an initail condition with 3 modes.
%
%
% Lloyd A Corker
% University of Cape Town
% Department of Physics
% lcorker@Uwc.ac.za
% 2005 February
%
%
%--------------------------------------------------------------------
function P = fpe(x,t,w)

% This solves the Fokker-Planck equation on the interval -31=<x>=31
% from time t = 0 to t = 5. For values of change in t and change
% in x there will be 101 values of t ranging from 0 to 5 and 401
% values of x ranging from -31 to 31.
x = linspace(-31,31,401);
t = linspace(0,5,100);
```

```
% m is a paramter which describes the geometry of the problem. In
% this case we set it to linear.
m = 0;
sol = pdepe(m,@fpe,@fpeic,@fpebc,x,t);

%the first solution in P:
P = sol(:,:,1);

%------------------------------------------------------------------
%Plots Solutions
%---------------
%Plots the solution as a 3D mesh
m1 = figure;
mesh(x,t,P);
xlabel('x','FontSize',12);
ylabel('t','FontSize',12);
zlabel('P','FontSize',12,'Rotation',0);

%Plots the solution profile for various time.
p1 = figure;
hold on;

plot(x,P(1,:),'Color',[1 0 0],...
  'LineStyle',':',...
  'Marker','.',...
  'MarkerSize',3);
plot(x,P(3,:),'K--');
plot(x,P(end,:));
xlabel('x','FontSize',12)
ylabel('P(x,t)','FontSize',12)
legend('t=1 of 100','t=3 of 100','t=5 of 100')



%--------------------------------------------------------------------
% subfunctions
%-------------
function [c,f,s] = fpe(x,t,P,DPDx)
w = 0.4; % This is the drift term γ
```

```
c = 1;
f = DPDx;
s = w*x*DPDx+w*P;


%-----------------------------------------------------------------
% Sets the initial condition at t=0
%----------------------------------
function P0 = fpeic(x)
P0 = ((5/8) * exp(-(-7-x)^2/4)+ (2/8) * exp(-(1-x)^2/4)+ (1/8) *
exp(-(6-x)^2/4)) /((4*pi)^(1/2));%Mode 3


%--------------------------------------
% Sets the Dirichlet boundary conditons
%--------------------------------------
function [pa,qa,pb,qb] = fpebc(xa,Pa,xb,Pb,t)
pa = Pa;
qa = 0;
pb = Pb;
qb = 0;
%/////////////////////////////////////\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
```

B2 MATLAB® code for solving the Fokker-Planck equation using initial condition (5.2.1) for the physical system in chapter 5.

```
% fpe_physical.m
%
% solves the one-dimensional Fokker-Planck equation
% using pdepe toolbox.
%
%
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% University of Cape Town
% Department of Physics
% MSc
% lcorker@Uwc.ac.za
% 2005 February
%
%
%-------------------------------------------------------------
function [P] = fpe(x,t,d)
%
```
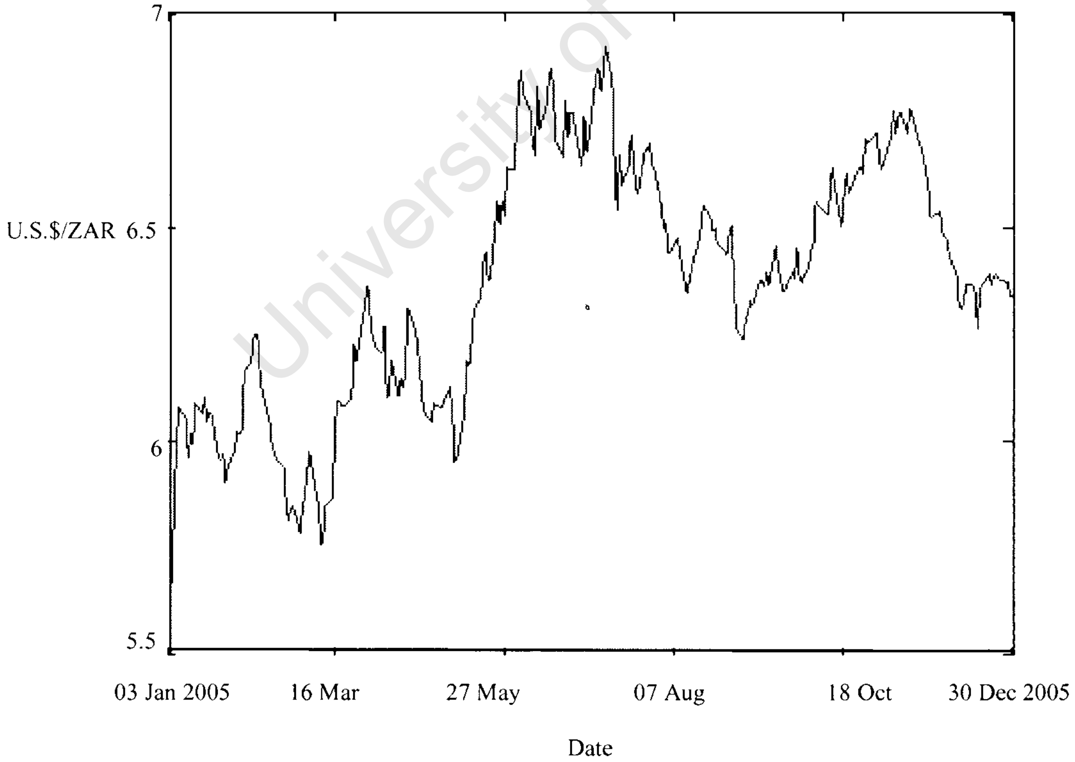

```
% sets the geometry to linear
m = 0;

% This solves the Fokker-Planck equation on the interval 0=<x>=150
% from time t = 0 to t = 1. For values of change in t and change
% in x there will be 100 values of t ranging from 0 to 1 and 401
% values of x ranging from 0 to 150.
x = linspace(0,150,401);
t = linspace(0,1,100);

sol = pdepe(m,@fpex,@fpeicx,@fpebcx,x,t);

%the first solution in P:
P = sol(:,:,1);

%-------------------------------------------------------------------
%Plots the solution as a 3D mesh:
mesh(x,t,P);
xlabel('x','FontSize',12)
ylabel('t','FontSize',12)
zlabel('P','FontSize',12,'Rotation',0)



%Plots the solution profile:
p1 = figure;
hold on;

plot(x,P(1,:),'Color',[1 0 0],...
  'LineStyle',':',...
  'Marker','.',...
  'MarkerSize',3);
plot(x,P(3,:),'K--');
plot(x,P(end,:));
xlabel('x','FontSize',12)
ylabel('P(x,t)','FontSize',12)
legend('t=1 of 100','t=3 of 100','t=5 of 100')

%------------------------------------------------------------------
% subfunctions:
%------------------------------------------------------------------
function [c,f,s] = fpex(x,t,P,DPDx)
```

```
g = 1;
c = 1;
f = 0*DPDx;
s = g*x*DPDx+g*P;


%-----------------------------------------------------------------
% ic - initial cond. at t=0
function P0 = fpeicx(x)
P0 = ((1/25)*(2*pi)^1/2) * exp(-(1/2)*((x-45) /25)^(2));


%-----------------------------------------------------------------
% bc - boundary cond.
function [pa,qa,pb,qb] = fpebcx(xa,Pa,xb,Pb,t)
pa = Pa;
qa = 0;
pb = Pb;
qb = 0;
%////////////////////////////////////\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
```

C1 ZAR- U.S. dollar daily prices for 2005.



After an initial gain in price for U.S. dollars in the first quarter the ZAR began to steadily gain in the next quarter of 2005.