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A SEMICLASSICAL APPROACH TO

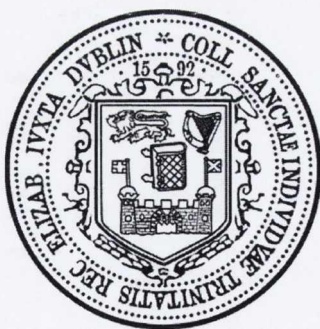
QUANTUM BROWNIAN MOTION

IN

WIGNER'S PHASE SPACE

BY
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Declaration

This Thesis is submitted to the University of Dublin, Trinity College, in fulfilment of the requirements for the degree of Doctor of Philosophy (Ph.D.).

I, the undersigned, declare that this work has not previously been submitted to this or any other university and unless otherwise stated is entirely my own work. Trinity College may lend or copy this Thesis upon request.



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Abstract

In this thesis, the recent semiclassical approach to quantum Brownian motion of Coffey *et al.* [Phys. Chem. Chem. Phys. **9**, 3361 (2007)] is studied in detail. This approach is based on a semiclassical extension of Wigner's method of obtaining corrections to the classical equilibrium Maxwell-Boltzmann distribution, yielding a master equation for the reduced Wigner function in quasi-phase space valid in the weak coupling and high temperature limits. In the non-inertial or high damping limit, this master equation reduces to a quantum Smoluchowski equation (QSE), where the drift coefficient remains as in the classical case, while the diffusion coefficient is altered to include the quantum parameter and derivatives of the potential.

The QSE is applied to both the linear and nonlinear dynamics of a point Josephson junction, allowing one to treat quantum effects in the zero capacitance limit using the methods of solution already developed for the classical Smoluchowski equation, namely continued fractions. A simple comparison of the predictions of the QSE with those of another form of the QSE, in which the drift as well as the diffusion coefficient is altered, is also presented. In the dc characteristics of the junction, the latter equation predicts unphysical results such as a negative resistance for zero voltage and negative differential resistance. The QSE is also applied to the Brownian dynamics of a quantum particle in a double well potential and a ratchet potential. In the former, quantum effects in the linear dynamic susceptibility are in agreement with predictions of quantum reaction rate theory in the high damping limit, constituting a novel result. In the latter, quantum effects in the Shapiro steps of the nonlinear response of the Brownian ratchet to an ac stimulus mimic the nonlinear response of the Josephson junction, with pronounced quantum effects for small stimulus amplitude.

Finally, a comparison of the longest relaxation time predicted by the semiclassical master equation of Coffey *et al.* and the quantum master equation of Diósi [Physica A **199**, 517 (1993)] (a density operator evolution equation of Lindblad form) with the analytical predictions of quantum reaction rate theory is presented. While good agreement with the Coffey *et al.* equation is obtained, the results of the Diósi equation fail to predict even qualitatively the analytical results, suggesting that mere positivity of the density operator does not in itself guarantee solutions which are consistent with the predictions of quantum reaction rate theory.

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Chapter 1

Introduction

The theory of Brownian motion in a potential is encountered in diverse areas of physics and chemistry and continues to find new and more demanding applications. In this chapter we briefly review the broad subject of quantum dissipative systems, in particular the classical and quantum theory of the Brownian motion. We then introduce the necessary formalism and theoretical concepts of Wigner's phase space representation of quantum mechanics, thereby setting the stage for the semiclassical approach to the theory of quantum Brownian motion of Coffey *et al.* introduced in Chapter 2.

1.1 Quantum dissipative systems

The theory of quantum dissipative systems or open quantum systems plays a major role in many applications of quantum physics since perfect isolation of quantum systems is not possible in practice. Indeed any empirical test of the statistical predictions on a quantum system requires one to couple the previously isolated system to a measuring apparatus, which generally leads to non-negligible influences on the observable being measured. In other words, in order to effect the occurrence of chance events (realisations) a quantum system must be subject to interactions with its surroundings¹. Thus, a theory of open quantum systems is a much sought-after goal for many communities, for example Nuclear Magnetic Resonance [1], quantum optics [2–8], condensed matter physics [9–14], mathematical physics [15–19], and condensed phase chemical physics [20–27].

Broadly speaking, the theory of quantum dissipation can be divided into three main classes. The first class considers a complete quantum system comprising a system coupled to a dissipative bath and then proceeds to project the dynamics of the system onto a reduced system subspace, e.g. Redfield theory [1], the path integral approach of Feynman and Vernon [9], and the projection operator approach of Nakajima and Zwanzig [23, 24]. This approach has been popular since the work of Boltzmann [28], which of course was purely classical. The second approach begins with a set of linear equations of motion for the reduced density matrix before determining their exact form in order that they describe real physical motion, e.g. the semigroup approach developed by mathematical physicists [15]. The third approach, which may be viewed as intermediate between the two above, envisages the heat bath as exerting a fluctuating force on the system and is often used in the quantum theory of the laser. In particular within this approach one may speak of three further approaches, namely the noise operator method pursued by M. Lax and W. H. Louisell [3], the density matrix techniques by M. Sargent, M. O. Scully and W. E. Lamb [4], and the phase space method by G. S. Agarwal [5], H. Haken [6], H. Risken [7] and C. W. Gardiner [8].

While many of the above quantum mechanical approaches, for example, the functional integral approach [9], have the disadvantage that they can be relatively difficult to visualise in terms of the classical representation as averages of dynamical quantities over probability distributions, a notable exception is the phase space method, where such a visualisation is provided by Wigner's phase space representation of quantum mechanics in terms of *quasi*-probability distributions of the canonical variables. For example, starting

¹This phenomenon is crucial to the foundation of quantum mechanics and is known as *decoherence*

from the phase space representation of the Schrödinger equation of motion for the density operator (i.e. the Wigner transform of the Liouville von-Neumann equation) Agarwal [3] developed a theory of Brownian motion of a quantum harmonic oscillator², obtaining an equation of motion for the reduced phase space distribution similar to the classical Fokker-Planck equation [7]. Furthermore, the Wigner representation allows quantum-mechanical expectation values involving the density matrix to be calculated just as classical ones and so is eminently suited to the study of the semiclassical limit or classical correspondence of quantum systems. For example, using the Wigner phase space representation, an excellent comparison of several of the approaches mentioned above is presented in Ref. [29], where, considering the Markovian dynamics of a damped harmonic oscillator, the density evolution operator from each theory is transformed into a Wigner phase space distribution allowing a transparent investigation of the quantum-classical correspondence via comparison with the Fokker-Planck equation.

Recently, Coffey *et al.* [30, 31] have introduced a semiclassical master equation for the reduced Wigner function in the phase space of positions x and momenta p . This master equation, which essentially comprises the Wigner-Moyal equation coupled to a classical heat bath, describes the dissipative dynamics of a quantum Brownian particle in the weak coupling and high temperature limits. The most important advantage of quantum master equations in phase space, is that one may invoke the methods of solution of statistical mechanics, allowing one to calculate such observables as the average drift velocity, relaxation time, dynamic susceptibility, linear and nonlinear response, etc. Thus, the solution of the semiclassical phase space master equation of Coffey *et al.* is the main objective of this thesis. In particular, using the methods of classical statistical mechanics, evaluation of observables in the more tractable regime of the noninertial limit, whereby the master equation of Coffey *et al.* reduces to a quantum Smoluchowski equation, greatly simplifying its solution, embodies the principal results of this thesis. Furthermore, a rigorous comparison of the various quantum kinetic models of dissipation, notably the Caldeira-Leggett master equation [10], the master equation of Diósi [32, 33], and the master equation of Vacchini [34], with the semiclassical master equation of Coffey *et al.* is currently lacking and an attempt at such a comparison is made by considering the dynamics of a quantum Brownian particle in a cosine potential and evaluating the dynamic structure factor and longest relaxation time. Let us now review the necessary theory and essential concepts for a description of quantum Brownian motion.

²A ubiquitous model in physics and one of the most important individual topics in quantum mechanics. We shall meet it in § 1.7 and its damped (Brownian) version in § 2.6

1.2 The theory of Brownian motion

The fundamental theory of Brownian motion has been well established since the seminal works of Einstein [35], Langevin [36] and Smoluchowski [37] and is essential to our understanding of classical dissipative dynamics in a thermal environment. The extension of the theory of Brownian motion to the realm of quantum mechanics is infinitely fascinating. Quantum dissipative dynamics, which are inherently statistical in nature, have been studied in fields as diverse as solid-state physics, chemical physics, biophysics, quantum optics, nuclear and particle physics, comprising myriad theoretical approaches, ranging from the functional integral approach to the more tractable approaches using semiclassical Fokker-Planck-like equations and quasiclassical Langevin equations [2–14].

The question of quantum Brownian motion, i.e. how a distinguished *Brownian* quantum particle experiences friction, diffusion, and thermalization due to the interaction with an unobserved surrounding liquid or gas, has long been of interest. Starting with the work of Caldeira and Leggett [10] the majority of studies on this problem treat the environment in a phenomenological way, usually by linearly coupling the Brownian particle position to a continuous thermal bath of harmonic oscillators, whose spectral density is then chosen so as to reproduce the desired relaxation and diffusion constants. Using the Feynman-Vernon path integral approach [9], these linear models can even be solved exactly for some cases [11, 38–40]. However, as is well known, these non-Markovian dynamical solutions also have limitations. Firstly, they usually have to assume that the Brownian particle and the environment are initially in a product state, leading to an unphysical initial transient dynamics due to the re-adjustment of the energies once the coupling is switched on [41]. Secondly, the generic assumption of a linear coupling with the unbounded position operator, leading to spatial correlations over any length scale, can be justified at best for a restricted class of initial states. It will be valid if the Brownian particle state is close to a classical state, but may lead to unphysically large decoherence rates if the Brownian state is characterized by macroscopically large coherence lengths [42].

In the light of the foregoing, one may consider two classes of quantum Brownian motion (i) where one is interested in timescales such that the Markov assumption is permissible and (ii) where the motional states considered are close to a classical state in the sense that the coherence scales are not macroscopic. The latter is the regime of the Caldeira-Leggett model for free quantum Brownian motion, obtained from the path integral approach in a high-temperature limit containing the damping parameter γ as a phenomenological parameter [10]. As we shall see, the collision kernel of that equation written in

the quasi-phase space of Wigner's function corresponds exactly to the collision kernel of the Klein-Kramers equation governing the classical Brownian motion. However, it is the former regime that is of principal concern in this thesis. At this juncture it is fitting to review the essential theory of classical Brownian motion, following closely the excellent exposition of the topic by Kubo, Toda and Hashitsume [43].

We begin by considering the simplest possible idealisation of Brownian motion, namely the diffusion equation in one dimension due to Einstein [35]

$$\frac{\partial}{\partial t} P(x, t) = D \frac{\partial^2}{\partial x^2} P(x, t), \quad (1.1)$$

where $D = (\zeta\beta)^{-1}$ is the Einstein relation between the diffusion coefficient D and the friction coefficient ζ , and $\beta = (kT)^{-1}$ is the inverse thermal energy. $P(x, t)$ is the configuration space probability distribution so that the probability of finding a particle between x and $x + dx$ at time t is simply $P(x, t)dx$. The fundamental solution for the initial conditions

$$P(x, t_0 | x_0, t_0) = \delta(x - x_0) \quad (1.2)$$

is the transition probability³ $P(x, t | x_0, t_0)$ (also known as the Green function or propagator) given by

$$P(x, t | x_0, t_0) = \frac{1}{\sqrt{4\pi D |t - t_0|}} \exp\left(\frac{-(x - x_0)^2}{4D |t - t_0|}\right), \quad (1.3)$$

which is a Gaussian distribution of variance $\sigma^2 = 2D |t - t_0|$. If boundaries and/or sources exist then appropriate boundary conditions must be imposed. Notice that the probability of finding a particle at x at time t , when it is certainly located at x_0 at time t_0 , is independent of the knowledge of where the particle was before t_0 . In other words, its entire history previous to the time t_0 is contained in the information that the particle was located at x_0 at time t_0 alone, expressed by⁴

$$P(x, t | x_0, t_0; x', t') = P(x, t | x_0, t_0), \quad (t' < t_0),$$

and hence

$$P(x_2, t_2; x_1, t_1 | x_0, t_0) = P(x_2, t_2 | x_1, t_1) P(x_1, t_1 | x_0, t_0), \quad (t_0 < t_1 < t_2). \quad (1.4)$$

³The conditional probability $P(x, t | x_0, t_0)$ is equal to the probability that the process takes on the value x at time t under the condition that the process took the value x_0 at some prior time t_0 . Consequently it is often referred to as the *transition probability* or *propagator*

⁴Here $P(x', t'; x_0, t_0)$ denotes the joint probability distribution.

That is to say the current state of the particle depends only on its immediate past state, i.e. we have a *Markov* process. Hence, the evolution of the process in the time interval (t_0, t_2) can be constructed from evolution in the two intervals (t_0, t_1) and (t_1, t_2) where t_1 is an arbitrary point between t_0 and t_2 . Therefore integrating over all possible values (realisations) of x_1 at t_1 gives

$$P(x_2, t_2 | x_0, t_0) = \int P(x_2, t_2 | x_1, t_1) P(x_1, t_1 | x_0, t_0) dx_1. \quad (1.5)$$

This is the Chapman-Kolmogorov equation relating the transition probabilities of a Markov process. A stochastic process satisfying Eqs. (1.4) and (1.5) is called Markovian. That the Brownian motion as defined by (1.1) is Markovian is a direct consequence of the fact that the evolution equation is first order with respect to time.

Now, considering a specific detailed kinetic model of collisions of hard spheres, Smoluchowski was able to obtain the time evolution equation of the Brownian particle subjected to an external force $-dV(x)/dx$, namely

$$\frac{\partial}{\partial t} P(x, t) = \frac{\partial}{\partial x} \left\{ \frac{P}{\zeta} \frac{\partial V(x)}{\partial x} + \frac{\partial}{\partial x} D P(x, t) \right\}, \quad (1.6)$$

now known as the Smoluchowski equation. For a detailed account of Smoluchowski's method of derivation see Mazo [37]. We note that Einstein was able to write down Eq. (1.6) by simply inserting his diffusion term into the continuity equation for the concentration of particles in configuration space. Both the Smoluchowski equation and the diffusion equation (1.1) are a special single variable form of a class of equations (probability density diffusion equations) known as Fokker-Planck equations [7]. While several generalisations of Fokker-Planck equations exist, here we consider only its generalisation for Markovian stochastic processes. For a Markov process, the probability density $P(x, t)$ at time t is related to the probability density $P(x_0, t_0)$ at time t_0 viz.

$$P(x, t) = \int P(x, t | x_0, t_0) P(x_0, t_0) dx_0. \quad (1.7)$$

This equation is readily obtained from the definition of the marginal probability $P(x, t) = \int P(x, t; x_0, t_0) dx_0$ and Bayes' theorem⁵. From Eq. (1.7) one may derive an expression for the differential $\partial P(x, t)/\partial t$ (see Ref. [7] for three detailed derivations), namely

$$\frac{\partial}{\partial t} P(x, t) = \sum_{\nu=1}^{\infty} \left(-\frac{\partial}{\partial x} \right)^{\nu} D^{(\nu)}(x, t) P(x, t), \quad (1.8)$$

⁵Bayes' theorem states that the joint probability is equal to the product of the conditional and marginal probabilities viz. $P(x, t; x_0, t_0) = P(x, t | x_0, t_0) P(x_0, t_0)$

where the differential operator acts on both $D^{(\nu)}(x, t)$ and $P(x, t)$ and ν is the order of the expansion. Equation (1.8) is called the *Kramers-Moyal* expansion [44, 45]. If x is a random variable obeying a Langevin equation with Gaussian δ -correlated noise then all coefficients $D^{(\nu)}$ with $\nu \geq 3$ vanish and Eq. (1.8) reduces to the classical Smoluchowski equation (1.6), with $D^{(1)} = -\zeta^{-1} \partial V / \partial x$ and $D^{(2)} = (\zeta \beta)^{-1}$. We note that for the special case of δ -initial conditions $P(x, t_0) = \delta(x - x_0)$ the transition probability $P(x, t | x_0, t_0)$ is the distribution $P(x, t)$. Thus, the transition probability must also obey (1.8), where the initial condition of $P(x, t | x_0, t_0)$ is given by Eq. (1.2).

Now, as both Einstein and Smoluchowski were well aware, both of the above treatments of Brownian motion, ignore the effects of the inertia of the Brownian particles. This amounts to assuming that equilibrium of the momenta has been attained, i.e. the friction is so high that the particles are always in thermal equilibrium in the momentum space and the distribution function is therefore independent of the initial momentum distribution. Consequently Eqs. (1.1) and (1.6) are said to be valid in the *high damping* or more accurately the *noninertial* limit. Physically, the number of collisions between the Brownian particle and the surrounding heat bath of oscillators is so high that after only a very short transient time (greater than the inertial time m/ζ) the molecular momenta have completely randomised and so their distribution corresponds to the Maxwell equilibrium distribution of the momenta, and is independent of initial conditions. In order to include the inertia of particles, one must consider the complete phase space probability distribution $P(x, p, t)$, which evolves according to a two variable Fokker-Planck equation, namely the Klein-Kramers equation

$$\frac{\partial}{\partial t} P(x, p, t) + \frac{p}{m} \frac{\partial P}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial P}{\partial p} = \gamma \frac{\partial}{\partial p} \left(pP + \frac{m}{\beta} \frac{\partial P}{\partial p} \right), \quad (1.9)$$

where we have introduced the damping parameter $\gamma = \zeta/m$. The Klein-Kramers equation is usually solved by expanding the momentum part of the joint phase space distribution $P(x, p, t)$ in orthogonal Hermite polynomials of order n , namely $\exp(-p^2/4) H_n(p/\sqrt{2})$, where $n = 0, 1, 2, \dots$, leading to a partial differential recurrence relation in n for the separation coefficients $\phi_n(x, t)$ in configuration space x known as Brinkman's hierarchy [46]. Expansion of the distribution function in Hermite polynomials is equivalent to taking the Fourier transform over the momentum distribution, i.e., calculating the characteristic function of the momentum [47]. As we shall see in § 2.5, Brinkman's hierarchy provides a rigorous method of obtaining the noninertial limit of phase space master equations.

Before leaving the classical description of Brownian motion, we must finally mention a fundamental theorem of statistical mechanics known as Liouville's theorem, which de-

scribes the dynamical evolution of a conservative or closed system of N particles moving in three dimensions viz.

$$\frac{\partial}{\partial t}\rho + \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial x_i} - \frac{\partial H}{\partial x_i} \frac{\partial \rho}{\partial p_i} \right) = 0. \quad (1.10)$$

Here ρ is a distribution function in the phase space of canonical variables q and p representing the statistical ensemble of phase points with Hamiltonian H . It is a purely dynamical theorem and is entirely equivalent to Hamilton's equations, yielding two important properties of phase space, namely that phase space is incompressible and consequently that the volume of any phase space region is conserved in time (for an excellent account of Liouville's theorem see [48]).

The Liouville equation (1.10) describes the complete *closed* system of phase points accounting for all degrees of freedom of the N particles. It is thus completely intractable and hence requires modification. The first and best known modification is due to Boltzmann [28], who obtained a time evolution equation for the density of molecules in phase space provided that only encounters between two molecules are ever of any importance [49, 50]. Boltzmann's idea was to replace the entire system of $3N$ degrees of freedom by a single system of 3 degrees of freedom interchanging energy with the rest of the system. In other words, to consider a single particle coupled to a heat bath, where the effects of all other particles (the heat bath) on the single particle are represented by their collisions with the single particle. This reduction of the number of degrees of freedom results in the famous Boltzmann integro-differential equation for the evolution of the single particle or *reduced* distribution. This equation can be further reduced in the particular case, whereby in a collision, the positions are unchanged and their velocities altered by such small amounts that they can be treated as infinitesimal, so that the Boltzmann equation reduces to a linear, partial-differential equation for the single-particle distribution. For the particular case of mechanical particles, i.e. $H = p^2/2m + V(x)$, this is the Klein-Kramers equation (1.9).

The concept of *reduced* system dynamics is critical to non-equilibrium statistical mechanics and *a fortiori* to quantum dissipative systems. We shall meet this concept again in Chapter 2, where the closed system dynamics, as governed by the Wigner phase space representation of the Liouville-von Neumann equation, are reduced and specialised to Markovian, high-temperature, quantum Brownian motion by coupling to a semiclassical dissipative bath. However, before considering any such reduction of the closed system dynamics of a quantum particle, we must first consider the dynamics of closed quantum systems, the starting point of which is the Liouville-von Neumann equation.

1.3 The Liouville-von Neumann equation

As briefly mentioned above, in classical statistical mechanics, a statistical ensemble is represented by a distribution function in the phase space of canonical variables describing the system, the time evolution of which is governed by the Liouville equation (1.10). In quantum mechanics such a distribution function is replaced by a density operator $\hat{\rho}(t)$, often referred to as the statistical operator. It is straightforward to derive an equation of motion for the density operator starting from the Schrödinger equation. Following Breuer and Petruccione [51], the Schrödinger equation for the time evolution of the *pure* state vector $|\psi(t)\rangle$ is

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle. \quad (1.11)$$

Introducing a unitary⁶ time evolution operator $\hat{U}(t, t_0)$ which transforms the state $|\psi(t_0)\rangle$ at some initial time t_0 to the state $|\psi(t)\rangle$, we may represent the solution of (1.11) as

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle. \quad (1.12)$$

Substituting Eq. (1.12) into (1.11), we have the time evolution of the unitary operator

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H}(t) \hat{U}(t, t_0), \quad (1.13)$$

subject to the initial condition $\hat{U}(t_0, t_0) = \hat{I}$, where $\hat{I}$ is the identity operator. Now, we wish to consider a system in a mixed state, where the corresponding quantum statistical ensemble is characterized by the density operator $\hat{\rho}(t)$. Let us assume that at some initial time t_0 the state of the system is

$$\hat{\rho}(t_0) = \sum_i w_i |\psi_i(t_0)\rangle \langle \psi_i(t_0)| \quad (1.14)$$

where w_i are the respective positive weights of the statistical mixture and the normalized state vectors $|\psi_i(t_0)\rangle$ evolve according to the Schrödinger equation (1.12). The state of the system at time t will therefore be given by

$$\hat{\rho}(t) = \hat{U}(t, t_0) \hat{\rho}(t_0) \hat{U}^\dagger(t, t_0) \quad (1.15)$$

where $\hat{U}^\dagger(t, t_0)$ is the complex transpose⁷ of $\hat{U}(t, t_0)$. Differentiating Eq. (1.15) w.r.t. time we have

⁶A square matrix A with complex entries is unitary if $A^{-1} = A^{*T} = A^\dagger$

⁷A square matrix A with complex entries is Hermitian if $A = A^{*T} = A^\dagger$

$$\begin{aligned}
\frac{\partial}{\partial t} \hat{\rho}(t) &= \frac{\partial}{\partial t} [\hat{U}(t, t_0) \hat{\rho}(t_0) \hat{U}^\dagger(t, t_0)] \\
&= \frac{\partial}{\partial t} [\hat{U}(t, t_0)] \hat{\rho}(t_0) \hat{U}^\dagger(t, t_0) + \hat{U}(t, t_0) \hat{\rho}(t_0) \frac{\partial}{\partial t} [\hat{U}^\dagger(t, t_0)] \quad (1.16)
\end{aligned}$$

Using Eq. (1.13) and its complex transpose $\partial_t \hat{U}^\dagger(t, t_0) = i\hat{U}^\dagger(t, t_0) \hat{H}(t)/\hbar$ we have

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \hat{\rho}(t) &= \hat{H}(t) \hat{U}(t, t_0) \hat{\rho}(t_0) \hat{U}^\dagger(t, t_0) - \hat{U}(t, t_0) \hat{\rho}(t_0) \hat{U}^\dagger(t, t_0) \hat{H}(t) \\
&= (\hat{H}(t) \hat{\rho}(t) - \hat{\rho}(t) \hat{H}(t)) \quad (1.17)
\end{aligned}$$

or simply

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] \quad (1.18)$$

where $[\cdot, \cdot]$ denotes the commutator of two operators. This equation governs the time evolution of the density operator of a mixed state for a closed system and is known as the Liouville-von Neumann equation. Knowledge of the density operator as governed by Eq. (1.18) constitutes a knowledge of the complete quantum system accounting for all degrees of freedom of the closed system.

This thesis is principally concerned with a semiclassical extension of the non-dissipative quantum dynamics of the closed system embodied by the Liouville-von Neumann equation to the dissipative dynamics of the open system. However, as we shall see in Chapter 2, the semiclassical master equation of Coffey *et al.* [30, 31] is proposed, not in the Hilbert space of the density operator $\hat{\rho}$, but the more classically meaningful phase space of positions and momenta, namely Wigner's *quasi*-phase space.

1.4 Wigner's phase space

In 1932, prompted by the symmetries of the Heisenberg-Weyl group of translations, E. P. Wigner [52] introduced his famous phase space distribution function of a quantum state described by the density operator $\hat{\rho}$ in the form of the overlap integral

$$W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle x + y/2 | \hat{\rho} | x - y/2 \rangle e^{-ipy/\hbar} dy, \quad (1.19)$$

in order to study quantum corrections to thermodynamic equilibrium, i.e. to the Maxwell-Boltzmann distribution of classical statistical mechanics. In the case of a pure state $|\psi\rangle$, the density operator is simply the outer product $\hat{\rho} = |\psi\rangle\langle\psi|$ and the Wigner function reduces to

$$W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \psi^*(x - y/2) \psi(x + y/2) e^{-ipy/\hbar} dy \quad (1.20)$$

where $\psi(x)$ is the position representation (wave function) of the state $|\psi\rangle$. Hence the Wigner function is the Fourier transform of the shifted position wave functions of the state $|\psi\rangle$.

The Wigner function has most of the attributes of a *true* phase space distribution function [53] (for illuminating discussions see the chapters by Baker and Feynman in Ref. [54]). It is real but not everywhere positive, i.e. it may exhibit negative basins, so that it must be regarded as a joint *quasi*-probability distribution. Notwithstanding this, one of the crucial properties of the Wigner function is that upon integration over the momentum or position one obtains the correct probability distribution of the position and momentum respectively. In other words, the 'true' probability distributions of the position $|\psi(x)|^2$ and momentum $|\Phi(p)|^2$ are contained in the marginal distributions of the Wigner function, namely [55]

$$\int_{-\infty}^{\infty} W(x, p) dp = |\psi(x)|^2 \quad \text{and} \quad \int_{-\infty}^{\infty} W(x, p) dx = |\Phi(p)|^2,$$

or for a mixed state

$$\int_{-\infty}^{\infty} W(x, p) dp = \langle x | \hat{\rho} | x \rangle \quad \text{and} \quad \int_{-\infty}^{\infty} W(x, p) dx = \langle p | \hat{\rho} | p \rangle,$$

where $\Phi(p) = \int_{-\infty}^{\infty} \psi(x) e^{-ipx} dx$ is the wave function of the momentum. Hence, the Wigner function allows one to calculate quantum mechanical expectation values using the concepts of classical statistical mechanics [53–55]. This result is quite intuitive, since the only thing inhibiting the coexistence of a well defined position and momentum in the Hilbert space of Schrödinger's wave mechanics is the Fourier transform of their respective wave functions. The Wigner function itself encodes this very Fourier transform, thus creating a quasi-phase space of positions and momenta.

Wigner's representation of quantum mechanics (also known as the Moyal quantization [45]) may be formally defined [45, 56] as a means of associating a *c*-number (or classically meaningful) function in the classical phase space of positions x and momenta p with every operator that is a function of the position and momentum operators $(\hat{x}, \hat{p})$ in Hilbert space. It is, in effect, the inverse of Weyl's rule [57] for associating quantum mechanical operators with corresponding classical quantities, and formally represents (as emphasized by Moyal) quantum mechanics as a statistical theory on classical phase space [45]. The Wigner function is but one of an infinite number of possible phase space

distributions that allow the calculation of quantum mechanical expectation values using the concepts of classical statistical mechanics [58].

1.5 Time evolution of the Wigner function

The time evolution of the Wigner function for the density operator Eq. (1.19) may be calculated directly from the Liouville-von Neumann equation (see Eq. (1.18) of § 1.3)

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)].$$

Taking the Wigner transform of both sides (i.e. taking matrix elements of both sides with the bra and ket vectors $\langle x + y/2|$ and $|x - y/2\rangle$, multiplying by $e^{-ipy/\hbar}$ and taking the integral $(2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dy$) we find (see Appendix 1.B for details)

$$\frac{\partial}{\partial t} W(x, p, t) = \frac{-p}{m} \frac{\partial W}{\partial x} + \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \sum_{r=1}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1} W}{\partial p^{2r+1}}. \quad (1.21)$$

This equation is known as the Wigner-Moyal equation and governs the time evolution of the phase space distribution function or Wigner function of the density operator $\hat{\rho}$. The time evolution of the Wigner function for a pure state $|\psi\rangle$ is formally identical to Eq. (1.21) and may be derived completely analogously starting from the definition (1.20) and considering the Schrödinger equation (1.11). The details of this calculation are presented in Appendix 1.A. Clearly, in the limit of $\hbar \rightarrow 0$ Eq. (1.21) reduces to the classical Liouville equation (1.10).

For a potential expressible as a polynomial, the quantum corrections terminate with the highest nonzero derivative of the potential. Hence, it is clear that for a potential containing no third- or higher-order derivatives (such as the harmonic oscillator) one obtains the classical Liouville equation. However, a subtle difference exists, as one must pay particular attention to the possible initial conditions because not all $W(x, p, t)$ are now permissible [59]. As we shall see in § 1.6, in order to solve this equation for an arbitrary well-behaved potential $V(x)$ one must resort to a perturbation solution in Planck's constant $\hbar$.

Now, as accomplished by Moyal [45], the Wigner function may also be interpreted in the familiar language of probability theory as the inverse Fourier transform of a characteristic function (moment generating function), whence observables may be calculated by parametric differentiation with respect to the transform variables. Moyal demonstrated

that the Wigner function is the correct joint distribution if one stipulates the Weyl correspondence between operators in Hilbert space and their corresponding c -number functions on Wigner's phase space, namely [54]

$$\hat{A}\hat{B} = A(x, p) \exp(i\hbar\hat{T}/2)B(x, p),$$

where $\hat{T}$ is the differential operator [56]

$$\hat{T} = \left(\frac{\overleftarrow{\partial}}{\partial x} \frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p} \frac{\overrightarrow{\partial}}{\partial x} \right), \quad (1.22)$$

and the arrows indicate the direction of operation of the derivative. The main transforms are summarised in Table 1.1 (note that in general, the Wigner transform of a product of two operators is not the same as the product of the two transforms, i.e. $(\hat{A}\hat{B})_W \neq (A)_W(B)_W$).

Using this prescription for the Wigner transform, we now demonstrate the usefulness of this correspondence rule by obtaining the time evolution of the Wigner function as follows. We simply take the transform of the Liouville-von Neumann equation using Table 1.1. Thus, the time evolution of the Wigner function $W(x, p, t) = (\hat{\rho})_W$ in phase space is

$$\frac{\partial}{\partial t} W(x, p, t) = \frac{2}{\hbar} H(x, p) \sin(\hbar\hat{T}/2) W(x, p, t), \quad (1.23)$$

where $H(x, p) = (\hat{H})_W$. We can easily expand the sine function in a Taylor series viz.

$$\sin(\hbar\hat{T}/2) = \frac{1}{2}\hbar\hat{T} - \frac{1}{6}(\hbar\hat{T}/2)^3 + \dots \quad (1.24)$$

Considering the Hamiltonian $H(x, p) = p^2/2m + V(x)$, we have from the first term in the expansion (1.24)

Hilbert Space	Phase Space
$\hat{A}(t)$	$A(x, p, t) = \int \langle x + y/2 \hat{A}(t) x - y/2 \rangle e^{-ipy/\hbar} dy$
$\langle x + y/2 \hat{A}(t) x - y/2 \rangle = \int A(x, p, t) e^{ipy/\hbar} dp$	$A(x, p, t)$
$\hat{A}\hat{B}$	$A(x, p) \exp(i\hbar\hat{T}/2)B(x, p)$
$[\hat{A}, \hat{B}]$	$2iA(x, p) \sin(\hbar\hat{T}/2)B(x, p)$
$\{\hat{A}, \hat{B}\}$	$2A(x, p) \cos(\hbar\hat{T}/2)B(x, p)$

Table 1.1: Wigner transforms in the phase space of positions x and momenta p .

$$\begin{aligned}
\frac{\partial}{\partial t} W(x, p, t) &= H(x, p) \hat{T} W(x, p, t) \\
&= \frac{\partial}{\partial x} \left[\frac{p^2}{2m} + V(x) \right] \frac{\partial W}{\partial p} - \frac{\partial}{\partial p} \left[\frac{p^2}{2m} + V(x) \right] \frac{\partial W}{\partial x} \\
&= \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} - \frac{p}{m} \frac{\partial W}{\partial x}
\end{aligned}$$

Including the next term in the expansion (1.24) yields

$$\begin{aligned}
\frac{\partial}{\partial t} W(x, p, t) &= -\frac{2}{6\hbar} H(x, p) (\hbar \hat{T}/2)^3 W(x, p, t) \\
&= -\frac{\hbar^2}{24} \left[\frac{\partial^3}{\partial x^3} \left[\frac{p^2}{2m} + V(x) \right] \frac{\partial^3 W}{\partial p^3} + \dots - \frac{\partial^3}{\partial p^3} \left[\frac{p^2}{2m} + V(x) \right] \frac{\partial^3 W}{\partial x^3} \right] \\
&= -\frac{\hbar^2}{24} \frac{\partial^3 V}{\partial x^3} \frac{\partial^3 W}{\partial p^3}
\end{aligned}$$

Note that only the first term in the $\hat{T}^3$ acting upon H and W remains. Continuing on in this manner one finds the result

$$\frac{\partial}{\partial t} W(x, p, t) = \frac{-p}{m} \frac{\partial W}{\partial x} + \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \sum_{r=1}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1} W}{\partial p^{2r+1}} \quad (1.25)$$

This is exactly the Wigner-Moyal equation as obtained by much more strenuous means in Appendices 1.A and 1.B. This equation may be solved at high temperatures by means of perturbation theory in $\hbar$ [52]. Having been obtained via a high-temperature perturbation expansion, the resulting Wigner function is thus eminently suited to the study of quantum corrections to classical distributions, i.e. the semiclassical limit.

1.6 Stationary solution of the closed system

In order to find the stationary solution of the Wigner-Moyal equation (1.21) for an arbitrary well-behaved potential $V(x)$, one must resort to a perturbation solution in Planck's constant $\hbar$. This problem was first discussed in the context of quantum corrections to classical thermodynamic equilibrium by Wigner [52]. He solved the closed (equilibrium) equation for relatively high temperatures using perturbation expansions in Planck's constant so yielding the Wigner stationary distribution $W_{st}(x, p)$. The ultimate objective of his investigation [60] was to obtain quantum corrections (due to high-temperature tunnelling near the top of the potential barrier) to classical reaction rate or transition state theory (TST). This theory is based on the assumption that thermodynamic equilibrium prevails everywhere in the potential well under consideration so that the closed equation applies, i.e.

the Brownian motion is ignored. The Wigner results, which take the form of the classical TST rate $\Gamma_{\text{TST}}^{\text{cl}}$ multiplied by a temperature and potential dependent quantum correction factor Ξ , causing an *effective lowering* of the potential barrier (so increasing the reaction rate), are limited to relatively high temperatures. This is so because in calculating the quantum corrected reaction rate, the potential is replaced by that of a harmonic oscillator near the bottom of a well while near the top it is replaced by that of an inverted harmonic oscillator [60].

Now, the solution of equation (1.25) can in general be developed in a power series in $\hbar^2$ [52]

$$W_{st}(x, p) = W_0(x, p) + \hbar^2 W_2(x, p) + \hbar^4 W_4(x, p) + \dots$$

where $W_0 = e^{-\beta(p^2/2m + V(x))}$ is the classical stationary distribution, i.e. the Maxwell-Boltzmann distribution. Following Wigner, the perturbed functions $W_{2r}(x, p)$ can be evaluated explicitly in terms of the derivatives of $V(x)$ to any desired power of r . We expand the functions $W_2(x, p)$ and $W_4(x, p)$ as follows

$$W_2 = e^{-\beta(p^2/2m + V(x))} [f_0(x) + pf_1(x)],$$

and

$$W_4 = e^{-\beta(p^2/2m + V(x))} [g_0(x) + pg_1(x) + p^2g_2(x)].$$

Substituting into (1.25) with the time derivative equal to zero and ignoring all terms of higher order than $\hbar^4$ (see [31] for details) we find the stationary solution

$$\begin{aligned} W_{st}(x, p) = & e^{-\beta(p^2/2m + V(x))} \left\{ 1 + \Lambda \left(\frac{\beta p^2}{m} V'' - 3V'' + \beta V'^2 \right) \right. \\ & + 3\Lambda^2 \left[\frac{p^4}{m^2} \left(\frac{(\beta V'')^2}{6} - \frac{\beta V''''}{10} \right) \right. \\ & + \frac{p^2}{m} \left(V'''' - \frac{2\beta V'''V'}{5} + \frac{V''(\beta V')^2}{3} - \frac{9\beta V''^2}{5} \right) \\ & \left. \left. + \frac{\beta^2 V'^4}{6} + \frac{5V''^2}{2} - \frac{9\beta V''V'^2}{5} + 2V'''V' - \frac{3V''''}{2\beta} \right] \right\}, \quad (1.26) \end{aligned}$$

where we have introduced the characteristic quantum parameter $\Lambda = \hbar^2 \beta^2 / (24m)$. This equation was first given by Wigner [52] and is known as the Wigner stationary solution. One may infer from the form of the first and second order perturbation solutions $W_2(x, p)$ and $W_4(x, p)$ that, generally in the $2n$ th order of perturbation theory, quantum corrections

to the classical stationary distribution will occur in the form of spatial derivatives of the potential of highest order $2n$. Thus, quantum effects give rise to non-Gaussian behaviour of the momentum distribution and in general the equilibrium phase space distribution function is no longer separable in the position and momentum variables. The above equations are written explicitly to $o(\hbar^4)$. In like manner, higher order quantum correction terms to the Wigner stationary distribution $W_{st}(x, p)$ may be calculated. Thus, $W_{st}(x, p)$ can be given, in principle to any desired degree r of $\hbar^{2r}$.

1.7 The quantum harmonic oscillator

In classical mechanics a harmonic oscillator is a particle constrained to move along an axis and subject to a restoring force proportional to a point located on that axis. The corresponding quantum harmonic oscillator is a particle of mass m moving in one dimension with the Hamiltonian

$$\hat{H} = \frac{1}{2m}(\hat{p}^2 + m^2\omega_0^2\hat{x}^2), \quad (1.27)$$

and constitutes one of the most important individual dynamical systems in quantum mechanics, since its Hamiltonian enters in all problems involving quantised oscillations: from the theory of molecular crystalline vibrations to quantum Electrodynamics and quantum Field Theory. It also serves as an excellent illustration of the formalism of quantum mechanics and to this end is employed here to illustrate the power of Wigner's phase space representation.

Now, the pure state harmonic oscillator is a particularly simple quantum system whose time-independent Schrödinger equation

$$\hat{H}\psi = E\psi, \quad (1.28)$$

can be solved rigorously (see Ch. XII of Messiah [61]) yielding the well-known eigenfunctions (e.g. see Eq. (2.41) of Atkins and Friedman [62])

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega_0}{\pi\hbar} \right)^{1/4} H_n(x\sqrt{m\omega_0/\hbar}) e^{-m\omega_0 x^2/2\hbar}, \quad (1.29)$$

corresponding to the energy eigenvalues $E_n = (n + 1/2)\hbar\omega_0$, where $H_n(z)$ are the Hermite polynomials and $n = 0, 1, 2, \dots$. Hence, one may obtain the Wigner functions of a harmonic oscillator in a pure state simply by taking the Wigner transform of Eq. (1.29), viz.

$$\begin{aligned}
W_n(x, p) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \psi_n^*(x - y/2) \psi_n(x + y/2) e^{-ipy/\hbar} dy \\
&= \frac{(-1)^n}{\pi\hbar} e^{-(p^2 + m^2\omega_0^2 x^2)/(m\omega_0\hbar)} L_n(2(p^2 + m^2\omega_0^2 x^2)/(m\omega_0\hbar)), \quad (1.30)
\end{aligned}$$

where $L_n(z)$ are Laguerre's polynomials (see § 2.4 of [53] for details). However, Wigner's phase space representation of quantum mechanics (whilst essentially born out of Schrödinger's wave mechanics) is an independent and equivalent representation and may be utilised without complete recourse to wave mechanics. One may take the Wigner transform of the time-independent Schrödinger equation (1.28) and proceed to solve the resulting phase space equation for the distribution function, yielding the pure state Wigner functions Eq. (1.30). Following Zachos, Fairlie and Curtright [54], this calculation is presented in Appendix 1.C.

We now calculate the Wigner function of an ensemble of oscillators. Consider a harmonic oscillator in thermodynamic equilibrium with a heat reservoir at temperature T . Its dynamical state is then no longer a pure state but a statistical mixture represented by the stationary density operator of a canonical ensemble [61]

$$\hat{\rho}_{st} = \frac{\hat{\rho}}{Z} = \frac{e^{-\beta\hat{H}}}{\text{Tr}\{e^{-\beta\hat{H}}\}}, \quad (1.31)$$

in conformity with the Boltzmann law. Equivalently, from Eq. (1.14) one may also write

$$\hat{\rho}_{st} = \sum_{n=0}^{\infty} w_n |\psi_n\rangle \langle \psi_n| / \sum_{n=0}^{\infty} w_n, \quad (1.32)$$

where $w_n = \exp(-\beta E_n)$ and E_n are the eigenvalues of the oscillator. Hence we have

$$\sum_{n=0}^{\infty} w_n = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega_0} = e^{-\beta\hbar\omega_0/2} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega_0})^n,$$

which after evaluation of the geometric series on the right becomes

$$\sum_{n=0}^{\infty} w_n = e^{-\beta\hbar\omega_0/2} / (1 - e^{-\beta\hbar\omega_0}).$$

Hence, the canonical quantum density operator is

$$\hat{\rho}_{st} = (1 - e^{-\beta\hbar\omega_0}) \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_0} |\psi_n\rangle \langle \psi_n|, \quad (1.33)$$

where the pure states $|\psi_n\rangle$ are given by the eigenfunctions (1.29). Taking the Wigner transform (1.19) of Eq. (1.33) yields the Wigner distribution for a mixed state

$$W_{st}(x, p) = (1 - e^{-\beta\hbar\omega_0}) \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_0} W_n(x, p), \quad (1.34)$$

where the pure state Wigner functions $W_n(x, p)$ are given by the Laguerre polynomials, viz. Eq. (1.30). Evaluating the summation and using the properties of the Laguerre polynomials, the stationary Wigner function can be presented in the simple exact form [53, 58, 59]

$$W_{st}(x, p) = Z^{-1} \exp \left\{ -\frac{1}{2} \left(\frac{x^2}{\langle x^2 \rangle} + \frac{p^2}{\langle p^2 \rangle} \right) \right\}, \quad (1.35)$$

which represents a centred 2D Gaussian distribution where the mean squared displacement (second moment in the position) is

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x^2 W_{st}(x, p) dp dx = \frac{\hbar}{2m\omega} \coth \frac{\beta\hbar\omega}{2}, \quad (1.36)$$

the mean squared momentum (second moment in the momentum) is

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p^2 W_{st}(x, p) dp dx = \frac{m\hbar\omega}{2} \coth \frac{\beta\hbar\omega}{2}, \quad (1.37)$$

and the normalisation factor is

$$\begin{aligned} Z &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left\{ -\frac{1}{2} \left(\frac{x^2}{\langle x^2 \rangle} + \frac{p^2}{\langle p^2 \rangle} \right) \right\} dp dx \\ &= \pi \hbar \coth \frac{\beta\hbar\omega}{2}. \end{aligned} \quad (1.38)$$

However, one may again obtain Eq. (1.35) independently of Eq. (1.34) by taking the Wigner transform of the Bloch equation [63] for the temperature-dependence of the density operator and solving the resulting phase space equation for the Wigner distribution. Following the work of Oppenheim and Ross [64] and Hillery *et al.* [53], this calculation is presented in Appendix 1.D.

Finally, we remark that the Wigner distribution for a mixed state may again be written in the Gaussian form

$$W(x, p) = \frac{\omega}{2\pi\sigma} \exp \left(-\frac{p^2/m + m\omega^2 x^2}{2\sigma} \right),$$

where the standard deviation σ , is the mean thermal energy of the harmonic oscillator

$$\sigma = \frac{\hbar\omega}{2} \coth \frac{\beta\hbar\omega}{2}.$$

1.A Time evolution of the Wigner function: Pure state

A most intuitive derivation of the time evolution of the Wigner probability distribution for a pure state is presented by Hillery *et al.* [53]. We begin with the Wigner function $W(x, p, t)$ for a pure state

$$W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \psi^*(x - y/2) \psi(x + y/2) e^{-ipy/\hbar} dy. \quad (1.39)$$

Taking the derivative of $W(x, p, t)$ w.r.t. t and using the product rule $(uv)' = uv' + u'v$ we have

$$\frac{\partial}{\partial t} W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left[\psi^*(x - y/2) \frac{\partial \psi(x + y/2)}{\partial t} + \frac{\partial \psi^*(x - y/2)}{\partial t} \psi(x + y/2) \right] e^{-ipy/\hbar} dy. \quad (1.40)$$

Since the wave function $\psi(x, t)$ must evolve according to the Schrödinger equation (1.11), we can make the substitution

$$\frac{\partial \psi(x, t)}{\partial t} = \left[\frac{i\hbar}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{i\hbar} V(x) \right] \psi(x, t),$$

whose complex conjugate is simply

$$\frac{\partial \psi^*(x, t)}{\partial t} = - \left[\frac{i\hbar}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{i\hbar} V(x) \right] \psi^*(x, t).$$

We thus have

$$\begin{aligned} \frac{\partial}{\partial t} W(x, p, t) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\{ \psi^*(x - y/2) \left[\frac{i\hbar}{2m} \frac{\partial^2 \psi}{\partial (x + y/2)^2} + \frac{V(x + y/2)}{i\hbar} \psi \right] \right. \\ &\quad \left. - \left[\frac{i\hbar}{2m} \frac{\partial^2 \psi^*}{\partial (x - y/2)^2} + \frac{V(x - y/2)}{i\hbar} \psi^* \right] \psi(x + y/2) \right\} e^{-ipy/\hbar} dy \end{aligned} \quad (1.41)$$

Since the Schrödinger equation is a linear partial-differential equation, the time evolution of $W(x, p, t)$ may be decomposed into two parts so that we may consider the contributions from the kinetic energy T and potential energy U terms separately. We first calculate the contribution from the kinetic energy

$$\begin{aligned} T &= \frac{i\hbar}{2m} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\{ \psi^*(x - y/2) \frac{\partial^2 \psi(x + y/2)}{\partial (x + y/2)^2} \right. \\ &\quad \left. - \frac{\partial^2 \psi^*(x - y/2)}{\partial (x - y/2)^2} \psi(x + y/2) \right\} e^{-ipy/\hbar} dy. \end{aligned} \quad (1.42)$$

From the chain rule of ordinary derivatives we have $\frac{\partial^2 \psi(x \pm y/2)}{\partial (x \pm y/2)^2} = 4 \frac{\partial^2 \psi(x \pm y/2)}{\partial y^2}$ so that

$$T = \frac{i\hbar}{m} \frac{2}{2\pi\hbar} \int_{-\infty}^{\infty} \left[\psi^*(x - y/2) \frac{\partial^2 \psi(x + y/2)}{\partial y^2} - \frac{\partial^2 \psi^*(x - y/2)}{\partial y^2} \psi(x + y/2) \right] e^{-ipy/\hbar} dy \quad (1.43)$$

Performing a single partial integration w.r.t. y , and noting that the boundary terms do not contribute and the two cross terms will cancel, we obtain

$$T = \frac{-i\hbar - ip}{m} \frac{2}{2\pi\hbar} \int_{-\infty}^{\infty} \left[\psi^*(x - y/2) \frac{\partial \psi(x + y/2)}{\partial y} - \frac{\partial \psi^*(x - y/2)}{\partial y} \psi(x + y/2) \right] e^{-ipy/\hbar} dy \quad (1.44)$$

Switching back to ∂_x we have from the chain rule $\frac{\partial \psi(x \pm y/2)}{\partial y} = \pm \frac{1}{2} \frac{\partial \psi(x \pm y/2)}{\partial x}$ so that

$$T = \frac{-p}{m} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left[\psi^*(x - y/2) \frac{\partial \psi(x + y/2)}{\partial x} + \frac{\partial \psi^*(x - y/2)}{\partial x} \psi(x + y/2) \right] e^{-ipy/\hbar} dy \quad (1.45)$$

The remaining integral is simply the derivative $\partial_x W(x, p, t)$. Thus we have

$$T = -\frac{p}{m} \frac{\partial W}{\partial x}. \quad (1.46)$$

Next, we calculate the contribution of the potential energy. From Eq. (1.41) we have

$$U = \frac{-i}{\hbar} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} [V(x + y/2) - V(x - y/2)] \psi^*(x - y/2) \psi(x + y/2) e^{-ipy/\hbar} dy \quad (1.47)$$

Expanding the potential $V(x)$ in a Taylor series we have

$$V(x \pm y/2) = \sum_{r=0}^{\infty} \frac{V^r(x)}{r!} \left(\frac{\pm y}{2}\right)^r = V(x) \pm \frac{y}{2} V'(x) + \frac{y^2}{8} V''(x) \pm \dots$$

Upon taking the difference we notice that only odd terms remain, so that

$$V(x + y/2) - V(x - y/2) = 2 \sum_{r=0}^{\infty} \frac{V^{2r+1}(x)}{(2r+1)!} \left(\frac{y}{2}\right)^{2r+1} \quad (1.48)$$

We can write the powers of $y/2$ as derivatives of the exponential viz.

$$\left(\frac{y}{2}\right)^{2r+1} = \left(\frac{i\hbar}{2}\right)^{2r+1} \frac{\partial^{2r+1}}{\partial p^{2r+1}} \quad (1.49)$$

Substituting Eqs. (1.48) and (1.49) into Eq. (1.47) we have

$$U = \frac{-i}{\hbar} i\hbar \sum_{r=0}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1}}{\partial p^{2r+1}} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \psi^*(x-y/2) \psi(x+y/2) e^{-ipy/\hbar} dy \quad (1.50)$$

The remaining integral is simply the Wigner distribution. Hence

$$U = \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \sum_{r=1}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1}}{\partial p^{2r+1}} W. \quad (1.51)$$

Combining the contributions from the kinetic energy and the potential energy we have the time evolution of the Wigner function as

$$\frac{\partial}{\partial t} W = \frac{-p}{m} \frac{\partial W}{\partial x} + \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \sum_{r=1}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1}}{\partial p^{2r+1}} W. \quad (1.52)$$

This equation, which excludes dissipation, i.e. represents a *closed system*, may be solved by perturbation theory to any order in $(\hbar)^{2r}$, to yield quantum corrections to the classical Maxwell-Boltzmann distribution.

1.B Time evolution of the Wigner function: Mixed state

Taking the matrix elements of both sides of the Liouville-von Neumann equation (1.18) with the bra and ket vectors $\langle x+y/2|$ and $|x-y/2\rangle$ we arrive at

$$\frac{\partial}{\partial t} \langle x+y/2|\hat{\rho}|x-y/2\rangle = -\frac{i}{\hbar} \langle x+y/2| [\hat{H}, \hat{\rho}] |x-y/2\rangle.$$

Considering the Hamiltonian operator $\hat{H} = \hat{p}^2/2m + V(\hat{x})$ and taking the Wigner transform of both sides, the time evolution of the Wigner function reads

$$\frac{\partial}{\partial t} W = T + U,$$

where the contribution from the kinetic term is

$$T = -\frac{1}{2m} \frac{i}{\hbar} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle x+y/2|\hat{p}^2\hat{\rho} - \hat{\rho}\hat{p}^2|x-y/2\rangle e^{-ipy/\hbar} dy, \quad (1.53)$$

and the contribution from the potential term is

$$U = -\frac{i}{\hbar} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle x+y/2|V(\hat{x})\hat{\rho} - \hat{\rho}V(\hat{x})|x-y/2\rangle e^{-ipy/\hbar} dy. \quad (1.54)$$

Following Schleich [55], we introduce a more compact notation for the kinetic term

$$T = -\frac{1}{2m} \frac{i}{\hbar} \tilde{F}_t(\hat{\rho}), \quad (1.55)$$

where $\tilde{F}_t(\hat{\rho})$ is the Fourier transform

$$\tilde{F}_t(\hat{\rho}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} f_t(y) e^{-ipy/\hbar} dy, \quad (1.56)$$

of the matrix elements

$$f_t(y) = \langle x + y/2 | \hat{p}^2 \hat{\rho} - \hat{\rho} \hat{p}^2 | x - y/2 \rangle. \quad (1.57)$$

Similarly, we rewrite the potential energy term as

$$U = -\frac{i}{\hbar} \tilde{F}_u(\hat{\rho}), \quad (1.58)$$

where $\tilde{F}_u(\hat{\rho})$ is the Fourier transform

$$\tilde{F}_u(\hat{\rho}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} f_u(y) e^{-ipy/\hbar} dy, \quad (1.59)$$

of the matrix elements

$$f_u(y) = \langle x + y/2 | V(\hat{x}) \hat{\rho} - \hat{\rho} V(\hat{x}) | x - y/2 \rangle. \quad (1.60)$$

In order to rewrite Eq. (1.53) in phase space we require the completeness relation⁸ (see VIII.57 of [61])

$$\int_{-\infty}^{\infty} |\psi\rangle \langle \psi| d\psi = 1. \quad (1.61)$$

Inserting this into Eq. (1.57) we have

$$f_t(y) = \int \langle x + y/2 | \hat{p}^2 | \psi \rangle \langle \psi | \hat{\rho} | x - y/2 \rangle - \langle x + y/2 | \hat{\rho} | \psi \rangle \langle \psi | \hat{p}^2 | x - y/2 \rangle d\psi \quad (1.62)$$

From the fundamental property of the momentum operator

$$\langle x | \hat{p}^2 | \psi \rangle = -\hbar^2 \frac{\partial^2}{\partial x^2} \langle x | \psi \rangle, \quad (1.63)$$

we have the relations

$$\langle x + y/2 | \hat{p}^2 | \psi \rangle = -\hbar^2 \frac{\partial^2}{\partial (x + y/2)^2} \langle x + y/2 | \psi \rangle,$$

⁸This is often called the closure relation and is equivalently written $\sum_n |n\rangle \langle n| = 1$ (see Eq. (1.42) of [62])

$$\langle \psi | \hat{p}^2 | x - y/2 \rangle = -\hbar^2 \frac{\partial^2}{\partial (x - y/2)^2} \langle \psi | x - y/2 \rangle.$$

Substituting the above relations into Eq. (1.62) we have

$$f_t(y) = -\hbar^2 \int \frac{\partial^2}{\partial (x + y/2)^2} \langle x + y/2 | \psi \rangle \langle \psi | \hat{\rho} | x - y/2 \rangle - \langle x + y/2 | \hat{\rho} | \psi \rangle \frac{\partial^2}{\partial (x - y/2)^2} \langle \psi | x - y/2 \rangle d\psi \quad (1.64)$$

Removing the completeness relation we find

$$f_t(y) = -\hbar^2 \left[\frac{\partial^2}{\partial (x + y/2)^2} - \frac{\partial^2}{\partial (x - y/2)^2} \right] \langle x + y/2 | \hat{\rho} | x - y/2 \rangle. \quad (1.65)$$

Now, the partial derivatives can be rewritten as follows. Noting that the derivatives in Eq. (1.65) act on a function of $u = x + y/2$ and $v = x - y/2$, the chain rule⁹ of partial derivatives yields

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial u} \frac{\partial u}{\partial x} + \frac{\partial}{\partial v} \frac{\partial v}{\partial x} \quad \text{and} \quad \frac{\partial}{\partial y} = \frac{\partial}{\partial u} \frac{\partial u}{\partial y} + \frac{\partial}{\partial v} \frac{\partial v}{\partial y}.$$

Evaluating $\partial_x u$, $\partial_x v$, $\partial_y u$ and $\partial_y v$, and rearranging we find

$$\frac{\partial}{\partial u} = \frac{1}{2} \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \quad \text{and} \quad \frac{\partial}{\partial v} = \frac{1}{2} \frac{\partial}{\partial x} - \frac{\partial}{\partial y}.$$

Hence, for the second order derivatives we have

$$\frac{\partial^2}{\partial u^2} = \frac{1}{4} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x \partial y} + \frac{\partial^2}{\partial y^2} \quad \text{and} \quad \frac{\partial^2}{\partial v^2} = \frac{1}{4} \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x \partial y} + \frac{\partial^2}{\partial y^2}.$$

Equation (1.65) now reduces to

$$f_t(y) = -2\hbar^2 \frac{\partial^2}{\partial x \partial y} \langle x + y/2 | \hat{\rho} | x - y/2 \rangle. \quad (1.66)$$

Substituting back into Eq. (1.56) we have

$$\tilde{F}_t(\hat{\rho}) = \frac{-2\hbar^2}{2\pi\hbar} \frac{\partial}{\partial x} \int_{-\infty}^{\infty} \frac{\partial}{\partial y} \langle x + y/2 | \hat{\rho} | x - y/2 \rangle e^{-ipy/\hbar} dy. \quad (1.67)$$

Performing a single partial integration w.r.t. y (and noting that boundary terms do not contribute) we find

$$\tilde{F}_t(\hat{\rho}) = \frac{2\hbar^2}{2\pi\hbar} \frac{-ip}{\hbar} \frac{\partial}{\partial x} \int_{-\infty}^{\infty} \langle x + y/2 | \hat{\rho} | x - y/2 \rangle e^{-ipy/\hbar} dy. \quad (1.68)$$

⁹If $z = f(u, v)$ is differentiable and $u = g(x, y)$ and $v = h(x, y)$ have continuous first partial derivatives, then $\partial_x z = \partial_u z \partial_x u + \partial_v z \partial_x v$ and $\partial_y z = \partial_u z \partial_y u + \partial_v z \partial_y v$.

Finally, substituting into Eq. (1.55) we have the contribution from the kinetic term

$$T = -\frac{p}{m} \frac{\partial}{\partial x} W. \quad (1.69)$$

For the potential energy term we insert the completeness relation (1.61) into Eq. (1.60) giving

$$f_u(y) = \int \langle x+y/2 | V(\hat{x}) | \psi \rangle \langle \psi | \hat{p} | x-y/2 \rangle - \langle x+y/2 | \hat{p} | \psi \rangle \langle \psi | V(\hat{x}) | x-y/2 \rangle d\psi \quad (1.70)$$

From the fundamental relation of the position operator (see Eq. (III.60) of [61])

$$\langle x' | V(x) | \psi \rangle = V(x') \langle x' | \psi \rangle, \quad (1.71)$$

we have the relations

$$\langle x+y/2 | V(\hat{x}) | \psi \rangle = V(x+y/2) \langle x+y/2 | \psi \rangle,$$

$$\langle \psi | V(\hat{x}) | x-y/2 \rangle = V(x-y/2) \langle \psi | x-y/2 \rangle.$$

Substituting the above relations into Eq. (1.70) we have

$$f_u(y) = \int V(x+y/2) \langle x+y/2 | \psi \rangle \langle \psi | \hat{p} | x-y/2 \rangle - \langle x+y/2 | \hat{p} | \psi \rangle V(x-y/2) \langle \psi | x-y/2 \rangle d\psi \quad (1.72)$$

Removing the completeness relation we find

$$f_u(y) = [V(x+y/2) - V(x-y/2)] \langle x+y/2 | \hat{p} | x-y/2 \rangle. \quad (1.73)$$

We now expand the potential in a Taylor series (see Appendix 1.A, Eqs. (1.48) and (1.49)) yielding

$$f_u(y) = i\hbar \sum_{r=0}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1}}{\partial p^{2r+1}} \langle x+y/2 | \hat{p} | x-y/2 \rangle. \quad (1.74)$$

Finally, substituting Eq. (1.74) back into Eqs. (1.59) and (1.58), we have the contribution from the potential term

$$U = \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \sum_{r=1}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1}}{\partial p^{2r+1}} W \quad (1.75)$$

1.C Solution of the harmonic oscillator: Pure state

Considering the time-independent Schrödinger equation $\hat{H}\psi = E\psi$ and using the Wigner transform (see Table 1.1)

$$(\hat{A}\hat{B})_W = A(x, p) \exp(i\hbar\hat{T}/2)B(x, p),$$

we readily obtain the time-independent eigenvalue equation for the Wigner function of a pure state as

$$H(x, p)e^{i\hbar\hat{T}/2}W(x, p) = EW(x, p). \quad (1.76)$$

Now, since the exponential contains derivative operators it may be evaluated in practice through the translation of function arguments (Bopp shifts) [54]

$$A(x, p) \exp(i\hbar\hat{T}/2)B(x, p) = A(x + i\hbar\vec{\partial}_p/2, p - i\hbar\vec{\partial}_x/2)B(x, p).$$

Thus, setting $m = 1$ and $\omega_0 = 1$ for the phase space Hamiltonian of the harmonic oscillator $H(x, p) = (p^2 + x^2)/2$, Eq. (1.76) becomes

$$\left[\left(x + \frac{i\hbar}{2}\partial_p \right)^2 + \left(p - \frac{i\hbar}{2}\partial_x \right)^2 - 2E \right] W(x, p) = 0. \quad (1.77)$$

Equating the imaginary coefficients we obtain the PDE

$$(x\partial_p - p\partial_x)W(x, p) = 0, \quad (1.78)$$

while equating the real coefficients we obtain the PDE

$$\left[x^2 + p^2 - \frac{\hbar^2}{4}(\partial_p^2 + \partial_x^2) - 2E \right] W(x, p) = 0. \quad (1.79)$$

Now Eq. (1.78) restricts $W(x, p)$ to depend only upon one variable in phase space namely,

$$z = 4H/\hbar = 2(x^2 + p^2)/\hbar. \quad (1.80)$$

Using the chain rule we have

$$\partial_x W(z) = \partial_z W \partial_x z \quad \text{and} \quad \partial_p W(z) = \partial_z W \partial_p z.$$

One must be careful when forming the sum of the second derivatives $\partial_p^2 + \partial_x^2$ since

$$\begin{aligned}
\partial_p^2 + \partial_x^2 &= \frac{\partial}{\partial z} \left(\frac{16x^2}{\hbar^2} \frac{\partial W}{\partial z} \right) + \frac{\partial}{\partial z} \left(\frac{16p^2}{\hbar^2} \frac{\partial W}{\partial z} \right) \\
&= \frac{8}{\hbar} \frac{\partial}{\partial z} \left(\frac{2(x^2 + p^2)}{\hbar} \frac{\partial W}{\partial z} \right) = \frac{8}{\hbar} \frac{\partial}{\partial z} \left(z \frac{\partial W}{\partial z} \right)
\end{aligned} \tag{1.81}$$

Substituting this into Eq. (1.79) we obtain the ODE

$$\left(\frac{z}{4} - z \partial_z^2 - \partial_z - \frac{E}{\hbar} \right) W(z) = 0. \tag{1.82}$$

If we now substitute $W(z) = e^{-z/2} L(z)$ into Eq. (1.82) we obtain a differential equation for $L(z)$, namely

$$\left(z \partial_z^2 + (1 - z) \partial_z + \frac{E}{\hbar} - \frac{1}{2} \right) L(z) = 0. \tag{1.83}$$

This is simply Laguerre's differential equation $xy'' + (1 - x)y' + ny = 0$, the solution of which is the set of Laguerre polynomials [65]

$$L_n(x) = \frac{1}{n!} e^x \partial_x^n (e^{-x} x^n),$$

where $n = 0, 1, 2, \dots$. Comparing with Eq. (1.83) we have the energy eigenvalues $E_n = (n + 1/2)\hbar$ with the Wigner functions given by

$$W_n(x, p) = \frac{(-1)^n}{\pi \hbar} e^{-2H/\hbar} L_n(4H/\hbar), \tag{1.84}$$

with $L_0(z) = 1$, $L_1(z) = 1 - z$, $L_2(z) = z^2/2 - 2z + 1$, etc.

1.D Solution of the harmonic oscillator: Mixed state

The un-normalised equilibrium density operator of a canonical ensemble is

$$\hat{\rho} = e^{-\beta \hat{H}}. \tag{1.85}$$

Differentiating both sides w.r.t. β yields the the well-known Bloch equation [63]

$$\frac{\partial}{\partial \beta} \hat{\rho} = -\hat{\rho} \hat{H} = -\hat{H} \hat{\rho}, \tag{1.86}$$

subject to the initial condition $\hat{\rho}|_{\beta=0} = \hat{I}$. The latter relation arises simply from the fact that any function of the Hamiltonian operator commutes with the Hamiltonian itself. Consequently we may write [64]

$$\frac{\partial}{\partial \beta} \hat{\rho} = -\frac{1}{2} \{ \hat{H}, \hat{\rho} \}, \quad (1.87)$$

where $\{.,.\}$ denotes the anti-commutator. Taking the Wigner transform of Eq. (1.87) (see Table 1.1) we have

$$\frac{\partial}{\partial \beta} W(x, p) = -H(x, p) \cos(\hbar \hat{T}/2) W(x, p). \quad (1.88)$$

This is simply the Bloch equation in Wigner's phase space. In identical manner to § 1.5, we expand the cosine in a Taylor series so that for the Hamiltonian of the harmonic oscillator

$$H(x, p) = p^2/2m + m\omega_0^2 x^2/2,$$

Eq. (1.88) simplifies to

$$\frac{\partial}{\partial \beta} W(x, p) = \left[\frac{-p^2}{2m} - m\omega_0^2 x^2/2 + \frac{\hbar^2}{8} \left(\frac{1}{m} \frac{\partial^2}{\partial x^2} + m\omega_0^2 \frac{\partial^2}{\partial p^2} \right) \right] W(x, p). \quad (1.89)$$

To solve Eq. (1.89) we make the ansatz [53]

$$W(x, p) = e^{-A(\beta)H(x, p) + B(\beta)}, \quad (1.90)$$

where $A(0) = B(0) = 0$. Substituting this into (1.89) we have

$$H(x, p) \left[1 - \frac{dA}{d\beta} - \left(\frac{\hbar\omega_0 A}{2} \right)^2 \right] + \frac{dB}{d\beta} + \left(\frac{\hbar\omega_0}{2} \right)^2 A = 0.$$

Now, since $H(x, p)$ is arbitrary, when $H(x, p) = 0$ we have the differential equation

$$\frac{dB}{d\beta} + \left(\frac{\hbar\omega_0}{2} \right)^2 A = 0,$$

and hence the differential equation

$$\frac{dA}{d\beta} + \left(\frac{\hbar\omega_0}{2} \right)^2 A^2 - 1 = 0.$$

The solution of the above coupled differential equations is

$$A(\beta) = \frac{2}{\hbar\omega_0} \tanh \left(\frac{\beta\hbar\omega_0}{2} \right) \quad \text{and} \quad B(\beta) = -\ln \cosh \left(\frac{\beta\hbar\omega_0}{2} \right).$$

Thus, we have from Eq. (1.90)

$$W(x, p) = \text{sech} \left(\frac{\beta\hbar\omega_0}{2} \right) e^{-2H(x, p) \tanh(\beta\hbar\omega_0/2)/\hbar\omega_0}. \quad (1.91)$$

In order to obtain the normalised distribution we divide Eq. (1.91) by its average

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W(x, p) dx dp = \pi \hbar [\sinh(\beta \hbar \omega_0 / 2)]^{-1},$$

yielding the normalised Wigner distribution

$$W_{st}(x, p) = (\pi \hbar)^{-1} \tanh\left(\frac{\beta \hbar \omega_0}{2}\right) \exp\left(-\frac{p^2/m + m\omega_0^2 x^2}{\hbar \omega_0 \coth(\beta \hbar \omega_0 / 2)}\right). \quad (1.92)$$

This is exactly Eq. (1.35).

Chapter 2

A semiclassical master equation

In this chapter it is shown how Wigner's method of obtaining quantum corrections to the classical equilibrium Maxwell-Boltzmann distribution may be extended to the dissipative non-equilibrium dynamics governing the quantum Brownian motion in an external potential $V(x)$, as recently accomplished by Coffey *et al.* Such an extension yields a semiclassical Markovian master equation for the Wigner distribution function $W(x, p, t)$ in phase space (x, p) , containing quantum correction terms up to any order in $\hbar^2$ valid in the weak coupling and high temperature limit. In the high dissipation limit, the master equation reduces to a semiclassical Smoluchowski equation describing noninertial quantum diffusion in configuration space. For a quantum harmonic oscillator, the method yields an evolution equation coinciding in all respects with that of Agarwal [5].

2.1 Markovian dynamics: The Kramers-Moyal expansion

The extension of Wigner's method of obtaining quantum corrections to the classical equilibrium Maxwell-Boltzmann distribution (see § 1.6) to the dissipative non-equilibrium dynamics governing the quantum Brownian motion in an external potential $V(x)$ has recently been accomplished by Coffey *et al* [30, 31]. The purpose of this chapter is to give a detailed exposition of the derivation of their semiclassical master equation for Wigner's function, paying particular attention to the assumptions made and their range of validity.

In addition, the noninertial or high damping limit of the master equation is treated in § 2.3, leading to a so-called quantum Smoluchowski equation. One may derive this equation from the complete phase space master equation by considering either of two equivalent and complementary approaches. The first approach consists of simply applying the *equilibrium Ansatz*, as applied by Coffey *et al.* to the phase space master equation of the open system, to the corresponding configuration space master equation of the open system. That is, one postulates the Wigner equilibrium distribution in configuration space as the stationary solution of the open system in configuration space. One may then determine the coefficients of the Kramers-Moyal expansion in configuration space just as for phase space.

The second approach is the powerful method of Brinkman [46], whereby a hierarchy of partial-differential recurrence relations for the configuration space coefficients is constructed by expanding the distribution function in a set of orthonormal Weber functions (harmonic oscillator or orthogonal Hermite polynomials). Upon taking the noninertial limit, this infinite hierarchy reduces to a closed set of equations, which after some careful manipulation produces the quantum Smoluchowski equation. This will serve as an introduction to the application of the quantum Smoluchowski equation to the noninertial quantum Brownian motion of a particle in a tilted cosine potential, a double-well potential and ratchet potential, as considered in Chapters 3 & 4, 5, and 6 respectively.

Now, as we have seen in § 1.4, the Wigner representation [52] or *phase space formulation of quantum mechanics* in terms of quasi-probability distributions of the canonical variables, also known as the Moyal quantization [45], allows quantum mechanical expectation values involving the density operator to be calculated just as classical ones and is eminently suited to the calculation of quantum corrections to these. In addition to this classical-like representation of expectation values, a further advantage of the semiclassical approach is that the classical definitions of work and heat remain valid allowing direct extension of fluctuation-dissipation theorems to quantum systems, yielding important in-

sights in the semiclassical limit [66], since the Wigner representation contains only those features common to both quantum and classical statistical mechanics and formally represents quantum mechanics as a statistical theory on classical phase space.

Consequently, Wigner's phase space is useful in diverse branches of physics (see, e.g., [54, 67]). In particular it may be applied to *open* quantum systems [72], providing a useful tool for the calculation of quantum corrections to classical models of dissipation such as Brownian motion (see, for example, [5, 68–71]). In this context, the one-dimensional quantum Brownian motion of a particle moving in a potential is usually studied by regarding the Brownian particle as bi-linearly coupled to a bath of harmonic oscillators in thermal equilibrium at temperature T . The dynamics of the particle are described by a master equation for the time evolution of the Wigner distribution $W(x, p, t)$ in the phase space (x, p) of positions and momenta of the particle. This equation is a partial-differential equation in phase space akin to the classical Fokker-Planck equation so that operators are not involved. By using existing powerful computational techniques developed for the Fokker-Planck equation [7], quantum effects on diffusive transport properties can then in principle be estimated for arbitrary potentials and in a wide range of dissipation parameters (see, e.g. [73–75]).

For a quantum Brownian particle moving along the x -axis under the influence of a potential $V(x)$, the canonical variables are the position x and the momentum p of the particle. The corresponding *reduced* (single-particle) joint quasi-probability distribution function¹ in phase space, namely the Wigner function $W(x, p, t)$, represents the projection of all the other degrees of freedom of the system, comprised of the quantum Brownian particle and its heat bath, onto the phase space (x, p) of that particle. The master equation for the time evolution of the reduced Wigner distribution $W(x, p, t)$ in the phase space of positions x and momenta p is thus

$$\frac{\partial W}{\partial t} + \hat{M}_W W = \hat{M}_D W, \quad (2.1)$$

where

¹The time evolution for the Wigner function of the closed system describes the evolution of the system as a whole accounting for all degrees of freedom of the system. Upon including coupling to a heat bath we no longer consider the evolution of the system (plus reservoir) as a whole accounting for all degrees of freedom of the specific bath (such an evolution equation would be completely intractable), but rather just the influence of the bath on the system. Thus we want not the total Wigner function but the so-called *reduced* or *single particle* Wigner function describing the effects of the heat bath on a single particle.

$$\hat{M}_W W = \frac{p}{m} \frac{\partial W}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} - \sum_{r=1}^{\infty} \frac{(i\hbar/2)^{2r}}{(2r+1)!} \frac{\partial^{2r+1} V}{\partial x^{2r+1}} \frac{\partial^{2r+1} W}{\partial p^{2r+1}}, \quad (2.2)$$

and $\hat{M}_D$ is the collision kernel operator. The left-hand side is simply the Wigner-Moyal equation (or quantum analogue of the classical Liouville equation), so that setting the right-hand side equal to zero, Eq. (2.1) constitutes the evolution equation for the Wigner distribution function in the phase space of the *closed* system [cf. Eq. (1.21)], as originally given by Wigner [52]. As presented in § 1.6, he solved that equation via perturbation theory in Λ in order to obtain semiclassical corrections to the Maxwell-Boltzmann distribution. Hence, classical transition state theory is modified because quantum effects, due to high temperature tunnelling near the top of the barrier, lower the effective barrier heights [60].

Now, the right-hand side of Eq. (2.1) contains the collision kernel $\hat{M}_D$, responsible for the bath-particle interaction of the *open* system, various forms of which have been discussed in detail in Ref. [76]. On specialising to the quantum Brownian motion in the high temperature and weak coupling limits, the collision operator $\hat{M}_D$ can be represented just as in the classical theory by a Kramers-Moyal expansion truncated at the second term (see § 1.2). In other words, one considers the correlation time characterising the heat bath to be so short that one can regard the stochastic process originating in the bath as Markovian (a detailed discussion of the validity of this approximation is given by Grabert [71] and Weiss [72]), thus allowing one to use the Kramers-Moyal expansion. In the case of two random variables x_1 and x_2 the Kramers-Moyal expansion of the time derivative of the joint distribution is [7]

$$\frac{\partial}{\partial t} W(x_1, x_2, t) = \sum_{\nu=1}^{\infty} \frac{(-\partial)^{\nu}}{\partial x_{j_1} \dots \partial x_{j_{\nu}}} D_{j_1, \dots, j_{\nu}}^{(\nu)}(x_1, x_2, t) W(x_1, x_2, t), \quad (2.3)$$

where ν is the order of the expansion, $D_{j_1, \dots, j_{\nu}}^{(\nu)}(x_1, x_2, t)$ are the coefficients and the index $j_{\nu} = 1, 2$ is written using the Einstein summation convention². Restricting the noise originating in the heat bath to Gaussian δ -correlated noise, the above expansion may be truncated at the second term $\nu = 2$ (remember Isserlis's (Wick's) theorem is necessary for the truncation of the Kramers-Moyal expansion as then one may express all n -tuple averages in terms of averages of the second moment). Hence, using equation (2.3), for the position and momentum random variables $x_1 = x$, $x_2 = p$, the collision kernel of Eq. (2.1) becomes

²This is convenient to write but tricky to read, e.g. for $\nu = 1$, $\partial_{x_{j_1}} D_{j_1}^{(1)} \equiv \sum_{j_1=1}^2 \partial_{x_{j_1}} D_{j_1}^{(1)} = \partial_{x_1} D_1^{(1)} + \partial_{x_2} D_2^{(1)}$. Similarly for $\nu = 2$, $\partial_{x_{j_1}} \partial_{x_{j_2}} D_{j_1, j_2}^{(2)} \equiv \sum_{j_1=1}^2 \sum_{j_2=1}^2 \partial_{x_{j_1}} \partial_{x_{j_2}} D_{j_1, j_2}^{(2)} = \partial_{x_1} \partial_{x_1} D_{11}^{(2)} + \partial_{x_1} \partial_{x_2} D_{12}^{(2)} + \partial_{x_2} \partial_{x_1} D_{21}^{(2)} + \partial_{x_2} \partial_{x_2} D_{22}^{(2)}$

$$\hat{M}_D W = \frac{\partial}{\partial p} \left[D_p p W + D_{pp} \frac{\partial W}{\partial p} + D_{xp} \frac{\partial W}{\partial x} \right] + D_{xx} \frac{\partial^2 W}{\partial x^2}, \quad (2.4)$$

where the coefficients $D_p, D_{xx}, D_{xp}, D_{pp}$ are coordinate-, momentum- and time-dependent parameters to be determined. For example, in the classical Brownian motion, a solution of Eq. (2.4) is the Maxwell-Boltzmann equilibrium distribution for the positions and momenta $P(x, p) = \exp[-\beta(p^2/2m + V(x))]$, viz. $\hat{M}_D P(x, p) = 0$, where

$$D_p = \gamma, \quad D_{pp} = \gamma \frac{m}{\beta}, \quad D_{xp} = D_{xx} = 0. \quad (2.5)$$

Equation (2.4) with the coefficients (2.5) is exactly the collision kernel of the Klein-Kramers equation (1.9) for the classical phase space probability distribution $P(x, p, t)$. As briefly alluded to in § 1.2, the semiclassical master equation (2.1) with the classical collision kernel of Brownian motion, Eq. (2.4) with (2.5), was first given by Caldeira and Leggett [10]. The collision kernel (2.4) is quite general, being subject only to the restriction of Markovian dynamics within a white noise environment. As we shall see in Chapter 7, the quantum master equations of Diósi [32, 33] and Vacchini [34] to leading order in the quantum parameter, derived from independent quantum kinetic models, both necessarily contain a collision kernel of the form (2.4). The exact form of the coefficients when altered by the inclusion of quantum effects continues to be a point of much interest. We now continue with the semiclassical approach of Coffey *et al.* and determine the coefficients explicitly.

2.2 Equilibrium Ansatz and the Kramers-Moyal coefficients

The phrase *equilibrium Ansatz* shall mean the following: If the interactions between the particle and the heat bath are small enough to allow one to use the weak coupling limit and if the correlation time characterizing the bath is so short that one can regard the stochastic process originating in the bath as Markovian, the equilibrium distribution of the closed system may be used as the first approximation to the equilibrium distribution of the open system. We now employ this Ansatz to determine the coefficients of the Kramers-Moyal expansion (2.4).

Imposing the Wigner distribution of the closed system as the first approximation to the equilibrium distribution of the open system, the diffusion coefficients appearing in the operator $\hat{M}_D$ may be calculated to any order of perturbation theory in $\hbar^2$ in a manner anal-

ogous to Wigner's perturbation solution of the closed equation (see § 1.6). This approach is based on an extension of the *Ansatz* that the Boltzmann distribution is the equilibrium solution of the classical Smoluchowski equation. This simple heuristic idea was originally used by Einstein [35], Smoluchowski [37], and others in order to calculate the drift and diffusion coefficients. By extending this idea, the drift and diffusion coefficients in Eq. (2.4) can be directly evaluated from *a knowledge of the stationary phase space quantum distribution only*. As we have already seen, the stationary solution to first order in Λ (cf. Eq. (1.26) for $o(\Lambda^2)$ terms) is the Wigner stationary distribution

$$W_{st}(x, p) = e^{-\beta[p^2/(2m) + V(x)]} \left[1 + \Lambda \left(\frac{\beta p^2}{m} V'' - 3V'' + \beta V'^2 \right) \right]. \quad (2.6)$$

This distribution corresponds to the canonical density operator $\hat{\rho}_{st} = e^{-\beta \hat{H}}/Z$ and describes the system in thermal equilibrium without coupling to the thermal bath, i.e. it pertains to the closed system. Hence, $W_{st}(x, p)$ renders the left-hand side of (2.1) [to $o(\Lambda)$] zero so that our task simplifies to solving $\hat{M}_D W_{st} = 0$, for the coefficients $D_p, D_{pp}, D_{xp}, D_{xx}$. Assuming frequency-independent damping, which is valid for a wide range of parameters in both weak and strong damping limits [71, 72], the coefficients become time-independent

$$D_{p,\dots,xx}(x, p, t) \rightarrow D_{p,\dots,xx}(x, p).$$

While the approximation of frequency-independent damping, which underlies the classical Brownian motion, may restrict the applicability of the collision kernel (so simplifying matters considerably), it is justifiable here since one merely wishes to understand how quantum effects treated in semiclassical fashion alter the classical Brownian motion in a potential. Recalling Wigner's approach to obtaining a high-temperature stationary solution of the Wigner-Moyal equation (see § 1.6), the Kramers-Moyal coefficients are expanded as

$$\begin{aligned} D_p &= \gamma + \hbar^2 d_2^p(x, p) + \hbar^4 d_4^p(x, p) + \dots, \\ D_{pp} &= \frac{\gamma m}{\beta} + \hbar^2 d_2^{pp}(x, p) + \hbar^4 d_4^{pp}(x, p) + \dots, \\ D_{xp} &= \hbar^2 d_2^{xp}(x, p) + \hbar^4 d_4^{xp}(x, p) + \dots, \\ D_{xx} &= \hbar^2 d_2^{xx}(x, p) + \hbar^4 d_4^{xx}(x, p) + \dots, \end{aligned} \quad (2.7)$$

i.e. in the form of the classical coefficients of Brownian motion Eq. (2.5) perturbed by a power series in $\hbar^2$. Substituting Eq. (2.6) into the collision kernel (2.4) with the above coefficients one finds after some algebra the coefficients

$$D_p = \gamma, \quad D_{pp} = \gamma \frac{m}{\beta} (1 + 2\Lambda V''), \quad D_{xp} = D_{xx} = 0,$$

so that the collision kernel to first order in Λ is

$$\hat{M}_D W = \gamma \frac{\partial}{\partial p} \left[pW + \frac{m}{\beta} (1 + 2\Lambda V'') \frac{\partial W}{\partial p} \right]. \quad (2.8)$$

Hence, unlike the classical theory, the coefficients of the truncated Kramers-Moyal expansion become functions of the derivatives of the potential. Equation (2.4) with Eq. (2.8) is the semiclassical master equation in phase space to first order in Λ and describes the relaxation of $W(x, p, t)$ to the stationary state $W_{st}(x, p)$ in the long time limit. Including second order terms, i.e. substituting Eq. (1.26) into the collision kernel (2.4) and evaluating the coefficients, one finds the explicit form of the semiclassical master equation (2.1) to $\mathcal{O}(\Lambda^2)$, namely [30, 31]

$$\begin{aligned} \frac{\partial W}{\partial t} &+ \frac{p}{m} \frac{\partial W}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \frac{\hbar^2}{24} \frac{\partial^3 V}{\partial x^3} \frac{\partial^3 W}{\partial p^3} - \frac{\hbar^4}{1920} \frac{\partial^5 V}{\partial x^5} \frac{\partial^5 W}{\partial p^5} \\ &= \gamma \frac{\partial}{\partial p} \left[pW + \frac{m}{\beta} \left\{ 1 + 2\Lambda V'' - \frac{2}{5} \Lambda^2 \left[6V''''V' + 2(V'')^2 \right. \right. \right. \\ &\quad \left. \left. \left. + 3V'''' \left(\frac{p^2}{m} - \frac{5}{\beta} \right) \right] \right\} \frac{\partial W}{\partial p} \right]. \end{aligned} \quad (2.9)$$

This is the semiclassical master equation of Coffey *et al.* The semiclassical master equation (2.9) is only valid in the weak coupling and high temperature approximation, viz.

$$T \gg T_0 = \hbar\zeta/(2\pi mk). \quad (2.10)$$

As we shall see in Chapter 3, where the above master equation (2.9) is applied to the dynamics of a point Josephson junction in the zero-capacitance limit, this condition is valid in a wide range of model parameters. For parameter ranges, where such an approximation is invalid (e.g. throughout the very-low-temperature region where non-Markovian effects are substantial), other methods should be used [72].

The *equilibrium Ansatz* has been successfully used before, e.g. both by Gross and Lebowitz [77] in their formulation of quantum kinetic models of impulsive collisions, and by Redfield [1] in calculating the matrix elements of the relaxation operator in the context of his theory of relaxation processes. However, in general in open quantum systems [72], the equilibrium phase space distribution may depend on the damping and hence may deviate from the canonical distribution $W_{st}(x, p)$, insofar as the canonical distribution describes the thermal equilibrium of the system in the weak coupling and high temperature limits only. A detailed discussion of this problem is given by Geva *et al.* [78]. The

damping-independent stationary distribution will reproduce the correct quantum results only with the condition embodied in Eq. (2.10). Furthermore, as the equilibrium distribution of the open system may depend on the bath-particle interaction [78], the imposition of the Wigner distribution of the closed system as the equilibrium distribution is tantamount to neglecting terms of $o(\gamma^2)$, which is ultimately the meaning of the term *weak interaction* in the present context. This has been formally demonstrated for the harmonic oscillator [79].

Finally, calculation of diffusion coefficients using the *equilibrium Ansatz* has been successfully applied in the quantum Brownian motion of particles [74, 75] and spins [80]. For spins, which have no classical analogue and, in general, non-separable Hamiltonians, the representation space [81] is the space of polar and azimuthal angles, (ϑ, φ) , which constitute the canonical variables. Thus, the classical equilibrium distribution, assumed in order to calculate diffusion coefficients in the Fokker-Planck equation for the distribution of spin orientations, is the Boltzmann distribution of orientations. In the quantum spin case, however, the stationary Wigner distribution must be determined from first principles for each particular case of the spin Hamiltonian operator [80, 81].

2.3 The quantum Smoluchowski equation (QSE)

In general, in both the classical and quantum cases it is impossible to write a partial-differential equation in configuration space describing the evolution of the probability distribution $P(x, t)$ [7]. The sole exception, however, is in the noninertial limit (i.e. in the limit of very high dissipation (VHD) to the heat bath), where the description of the quantum dynamics of a Brownian particle can be considerably simplified just as in the classical theory of Brownian motion, where the governing kinetic equation is the Smoluchowski equation (1.6).

Following arguments used by Kramers [44] to derive the classical Smoluchowski equation from the Klein-Kramers equation (1.9), Coffey *et al.* recently obtained a QSE by integrating the phase space master equation (2.9) over a straight line in phase space and then proceeding to the noninertial (over-damped) limit by assuming that the equilibrium distribution of the momenta has set in. The resulting QSE for the time evolution of the *quasi*-probability distribution $P(x, t)$ is of essentially the same form as the classical Smoluchowski equation and characterises the motion of a quantum Brownian particle in the noninertial limit.

Now, the quasi-probability distribution in configuration space $P(x, t)$ is simply a marginal

distribution of the Wigner phase space distribution viz.

$$P(x, t) = \int_{-\infty}^{\infty} W(x, p, t) dp \quad (2.11)$$

Hence, following Coffey *et al.*, a simple way of obtaining the noninertial limit of the semiclassical master equation (2.9) is to integrate this equation over the momentum p in the manner of Klein and Kramers [7, 44]. For example, including terms up to $o(\Lambda^2)$ the explicit form of the phase space diffusion coefficient D_{pp} of the master equation (2.9) is

$$D_{pp}(x, p) = \gamma \frac{m}{\beta} \left\{ 1 + \frac{\hbar^2 \beta^2}{12m} V'' - \frac{\hbar^4 \beta^4}{1440m^2} \left[6V'''V' + 2V''^2 + 3V'''' \left(\frac{p^2}{m} - \frac{5}{\beta} \right) \right] \right\} \quad (2.12)$$

Therefore the configuration space diffusion coefficient is

$$D(x) = \int_{-\infty}^{\infty} e^{-\beta p^2/2m} D_{pp}(x, p) dp / \int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp \quad (2.13)$$

$$= \frac{\gamma}{720m\beta} \left\{ 720m^2 + 60\hbar^2 m \beta^2 V'' - \hbar^4 \beta^4 (V''^2 - 3V'V''' + 6V''''/\beta) \right\} \quad (2.14)$$

Thus, integration of the phase space master equation (2.9) over the momenta [30, 75], exactly as for the classical Smoluchowski equation [44, 82], leads to the QSE for the quasi-probability distribution $P(x, t)$ in configuration space (x), namely

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{P(x, t)}{\zeta} \frac{\partial V(x)}{\partial x} + \frac{\partial}{\partial x} [D(x)P(x, t)] \right\}, \quad (2.15)$$

where

$$D(x) = \frac{1}{\zeta\beta} \left\{ 1 + 2\Lambda V''(x) - \frac{4\Lambda^2}{5} \left[(V''(x))^2 + 3V'(x)V^{(3)}(x) - 3\beta^{-1}V^{(4)}(x) \right] \right\} \quad (2.16)$$

is the quantum diffusion coefficient in configuration space and depends on the derivatives of the potential and the characteristic quantum perturbation parameter $\Lambda = \hbar^2 \beta^2 / (24m)$, $\zeta = \gamma m$ is the friction coefficient, γ is the damping parameter characterising the bath-particle interaction and of course $(\zeta\beta)^{-1}$ is the classical diffusion coefficient determined by Einstein.

The quantum Smoluchowski equation (2.15) resembles the classical Smoluchowski equation, however, unlike that equation the diffusion coefficient $D(x)$ depends on the derivatives of the potential and the characteristic quantum parameter, Λ , while the drift coefficient remains the same. Equation (2.15) reduces to the classical Smoluchowski equation for the configuration space distribution function $P(x, t)$ when the quantum parameter

$\Lambda = 0$. Furthermore, just as the classical case, the QSE describes the long time (or low frequency) relaxation behavior of a system [44, 82]. It holds (just as its classical counterpart) if the energy loss per cycle of particles on the escape trajectory is much greater than the thermal energy. The quantum Smoluchowski equation (again just as its classical counterpart) relies on the assumption that the momentum part of the phase space distribution has reached equilibrium long before the configuration part.

Recall from § 1.4 that the marginal distributions of the Wigner function are

$$\int_{-\infty}^{\infty} W(x, p) dp = \langle x | \hat{\rho} | x \rangle \quad \text{and} \quad \int_{-\infty}^{\infty} W(x, p) dx = \langle p | \hat{\rho} | p \rangle.$$

Hence from Eq. (2.11), the quasi-probability distribution $P(x, t)$ is simply the trace of the density operator $\hat{\rho}$, i.e. $P(x, t) = \langle x | \hat{\rho} | x \rangle$. Thus, one may calculate quantum mechanical expectation values just as classical ones, via the Weyl correspondence [57],

$$\langle \hat{A} \rangle = \text{Tr} \{ \hat{\rho} \hat{A} \} = \int A(x) P(x, t) dx, \quad (2.17)$$

so allowing one to study the influence of thermal as well as quantum mechanical fluctuations.

One must also remark that the dynamics of a quantum system described by the semiclassical Smoluchowski Eq. (2.15) may be equivalently described using a quantum analogue of the Langevin equation with multiplicative noise. The Langevin equation corresponding to Eq. (2.15) in the Stratonovich interpretation [7, 82] reads

$$\dot{x}(t) = -\frac{1}{\zeta} \frac{\partial}{\partial x} \left\{ V[x(t)] + \frac{\zeta}{2} D[x(t)] \right\} + \sqrt{\frac{\beta}{\zeta}} D[x(t)] \lambda(t), \quad (2.18)$$

where the diffusion coefficient $D(x)$ is given by Eq. (2.16), the dot denotes the time derivative and $\lambda(t)$ is a random force with the Gaussian white noise properties

$$\overline{\lambda(t)} = 0, \quad \overline{\lambda(t)\lambda(t')} = (2\zeta/\beta)\delta(t-t').$$

Here, the overbar means the statistical average over the realizations of the random force. Equation (2.18) may be used as an approximate description of the kinetics of a quantum Brownian particle in the noninertial limit. One may average Eq. (2.18) over its realisations in configuration space to obtain the averaged equation of motion

$$\ddot{x} = -\zeta^{-1} \overline{\partial_x V(x)}, \quad (2.19)$$

and so the drift coefficient, coinciding with its classical counterpart.

2.4 Equilibrium Ansatz in configuration space

The explicit form of the diffusion coefficient (2.16) has been obtained from the phase space master equation (2.9) by direct integration. A much simpler, albeit indirect, method of determining $D(x)$, avoiding the time-dependent phase space master equation entirely, is to postulate *a priori* to any order of perturbation theory in $\hbar^2$ the Smoluchowski equation with a position dependent diffusion coefficient. This coefficient is then calculated in terms of the derivatives of the potential by imposing as the stationary solution the Wigner equilibrium configuration space distribution, just as for the phase space master equation in § 2.2.

In order to determine the explicit form of the diffusion coefficient $D(x)$, we first recall that the stationary distribution function in configuration space $P_{st}(x)$ must be a stationary solution of the QSE, Eq. (2.15). Now, $P_{st}(x)$ can be evaluated directly from the stationary Wigner distribution function $W_{st}(x, p)$ since

$$P_{st}(x) = \int_{-\infty}^{\infty} W_{st}(x, p) dp. \quad (2.20)$$

Substituting Eq. (1.26) into (2.20) and evaluating the integral one finds the explicit equation for the Wigner stationary distribution in configuration space $P_{st}(x)$ to second order in $\hbar^2$ [31]

$$\begin{aligned} P_{st}(x) = e^{-\beta V} \left\{ 1 + \Lambda \left[\beta (V')^2 - 2V'' \right] + \frac{\Lambda^2}{10} \left[36V''^2 \right. \right. \\ \left. \left. + 48V'''V' - 44\beta V''V'^2 + 5\beta^2 V'^4 - 24V''''/\beta \right] \right\}. \end{aligned} \quad (2.21)$$

According to the *equilibrium Ansatz*, the stationary distribution $P_{st}(x)$ must be the *stationary* solution of the postulated quantum Smoluchowski equation

$$\frac{\partial}{\partial x} \left\{ \frac{P_{st}}{\zeta} \frac{\partial V}{\partial x} + \frac{\partial}{\partial x} [D(x)P_{st}] \right\} = 0, \quad (2.22)$$

where the diffusion coefficient $D(x)$ is expanded as a power series in $\hbar^2$, viz.

$$D(x) = (\zeta\beta)^{-1} + \hbar^2 d_2(x) + \hbar^4 d_4(x) + \dots \quad (2.23)$$

Substituting Eq. (2.23) into Eq. (2.22), one finds the spatially dependent $D(x)$ given by Eq. (2.16). Thus the imposition of the Wigner configuration space distribution $P_{st}(x)$ as the equilibrium solution of Eq. (2.22), yielding a diffusion coefficient $D(x)$ depending on the derivatives of the potential, is the exact analogue of the *Ansatz* of a Boltzmann stationary solution in the classical theory.

We remark that in the derivation of $D(x)$ above, we have imposed $P_{st}(x)$ as the stationary solution of the QSE, as determined from the stationary Wigner phase space distribution function $W_{st}(x, p)$ in the approximation of frequency-independent damping. Hence, the same temperature restriction (2.10) applies [30, 31, 72].

2.5 Brinkman's method and the noninertial limit

We have just seen how the imposition of the Wigner equilibrium solution in configuration space $P_{st}(x) = \int_{-\infty}^{\infty} W_{st}(x, p) dp$ as the stationary solution of the Smoluchowski equation, whereby one expands the diffusion coefficient as a power series in $\hbar^2$ (see Eq. (2.23) above), leads to a quantum Smoluchowski equation with the diffusion coefficient depending on the derivatives of the potential. An alternative, more rigorous method is afforded by Brinkman's method.

In 1956 Brinkman [46] demonstrated a method by which a partial-differential recurrence relation representation of the Klein-Kramers equation in configuration space x may be obtained by expanding the momentum part of the solution of the Klein-Kramers equation in an orthonormal basis of Weber (harmonic oscillator) functions $D_n(y)$. The result is known as Brinkman's hierarchy and can be solved using a method based on matrix continued fractions developed in 1983 by Risken [7]. Following Brinkman, Eq. (2.9) may be rewritten as a partial differential-recurrence relation in configuration space x by expanding the momentum part of the distribution function, $W(x, p, t)$ in an orthonormal basis of Weber functions $D_n(y)$, viz.

$$W(x, p, t) = e^{-\beta p^2/4m} \sum_{n=0}^{\infty} D_n \left(p\sqrt{\beta/m} \right) \phi_n(x, t), \quad (2.24)$$

where $D_n(y) = 2^{-n/2} e^{-y^2/4} H_n(y/\sqrt{2})$ and $H_n(z)$ is the Hermite polynomial of order n . Here the Fourier coefficients $\phi_n(x, t)$ ($n \geq 0$) are the configuration space functions. In particular, $\phi_0(x, t) = \int W(x, p, t) dp$ yields the configuration space distribution function. After a tedious calculation using the raising property of the Weber functions, namely

$$\frac{d}{dy} \left(e^{-y^2/4} D_n(y) \right) = -e^{-y^2/4} D_{n+1}(y),$$

and the recurrence relation

$$D_{n+1}(y) = yD_n(y) - nD_{n-1}(y),$$

together with their orthogonality relations, we have the quantum recurrence equations

$$\begin{aligned}
\frac{\partial \phi_n}{\partial t} &+ n\gamma \left[1 + \frac{6\Lambda^2(n+1)}{5\beta} \frac{\partial^4 V}{\partial x^4} \right] \phi_n \\
&= -\sqrt{\frac{\beta}{m}} \phi_{n-1} \frac{\partial V}{\partial x} - \frac{1}{\sqrt{\beta m}} \left(\frac{\partial \phi_{n-1}}{\partial x} + (n+1) \frac{\partial \phi_{n+1}}{\partial x} \right) \\
&+ \Lambda \left(2\gamma \phi_{n-2} \frac{\partial^2 V}{\partial x^2} + \frac{1}{\sqrt{\beta m}} \phi_{n-3} \frac{\partial^3 V}{\partial x^3} \right) \\
&- \frac{3\Lambda^2}{10\sqrt{m\beta^3}} \phi_{n-5} \frac{\partial^5 V}{\partial x^5} - \frac{2\gamma\Lambda^2}{5} \left\{ \left[6 \frac{\partial^3 V}{\partial x^3} \frac{\partial V}{\partial x} + 2 \left(\frac{\partial^2 V}{\partial x^2} \right)^2 \right. \right. \\
&+ \left. \left. \frac{6(n-3)}{\beta} \frac{\partial^4 V}{\partial x^4} \right] \phi_{n-2} + \frac{3}{\beta} \frac{\partial^4 V}{\partial x^4} \phi_{n-4} \right\}. \tag{2.25}
\end{aligned}$$

We note that setting $\Lambda = 0$ in Eq. (2.25) yields Brinkman's original representation [7, 46] of the classical Klein-Kramers equation as a recurrence relation. We now make the time-dependent perturbation expansion

$$\phi_n = \phi_n^{(0)} + \Lambda \phi_n^{(1)} + \Lambda^2 \phi_n^{(2)} + \dots$$

in Eq. (2.25). Just as in the classical case, by seeking an asymptotic solution of Eq. (2.25) for $\phi_0(x, t)$ in the powers of inverse damping γ^{-1} , the Brinkman method leads in the zero-inertia or high damping limit, $\gamma^{-1} = m/\zeta \rightarrow 0$, to the continuity equation (see Appendix 2.A for details)

$$\frac{\partial \phi_0}{\partial t} + \frac{\partial j}{\partial x} = 0, \tag{2.26}$$

for the probability current

$$j(x, t) = j^{(0)}(x, t) + \Lambda j^{(1)}(x, t) + \Lambda^2 j^{(2)}(x, t) + \dots,$$

where

$$\begin{aligned}
j^{(0)} &= \frac{1}{\gamma\beta m} \left(\frac{\partial \phi_0^{(0)}}{\partial x} + \beta \phi_0^{(0)} \frac{\partial V}{\partial x} \right), \\
j^{(1)} &= \frac{1}{\gamma\beta m} \left(\frac{\partial \phi_0^{(1)}}{\partial x} + \beta \phi_0^{(1)} \frac{\partial V}{\partial x} \right) + \frac{2}{\gamma\beta m} \frac{\partial}{\partial x} \left(\phi_0^{(0)} \frac{\partial^2}{\partial x^2} V(x) \right), \\
j^{(2)} &= \frac{1}{\gamma\beta m} \left(\frac{\partial \phi_0^{(2)}}{\partial x} + \beta \phi_0^{(2)} \frac{\partial V}{\partial x} \right) + \frac{2}{\gamma\beta m} \frac{\partial}{\partial x} \left\{ \frac{\partial^2 V}{\partial x^2} \phi_0^{(1)} \right. \\
&\quad \left. - \frac{2}{5} \left[\left(\frac{\partial^2 V}{\partial x^2} \right)^2 + 3 \frac{\partial^3 V}{\partial x^3} \frac{\partial V}{\partial x} - \frac{3}{\beta} \frac{\partial^4 V}{\partial x^4} \right] \phi_0^{(0)} \right\}.
\end{aligned}$$

Equivalently, Eq. (2.26) can be written as a quantum Smoluchowski equation for the configuration space distribution function $\phi_0(x, t) = P(x, t)$, viz.

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{P}{\zeta} \frac{\partial V}{\partial x} + \frac{\partial}{\partial x} [D(x)P] \right\}, \quad (2.27)$$

where $D(x)$ is the diffusion coefficient given by

$$D(x) = \frac{1}{\zeta\beta} \left\{ 1 + 2\Lambda V'' - \frac{4\Lambda^2}{5} [V''^2 + 3V'V''' - 3\beta^{-1}V''''] \right\}. \quad (2.28)$$

In writing Eqs. (2.26) and (2.27), we have noted that the classical functions $\phi_n^{(0)}(x, t)$ (being the coefficients of the harmonic oscillator functions in the momentum) all vanish for $n > 0$ in the *noninertial limit* because the equilibrium distribution of the momenta has set in. We emphasise that Eq. (2.27) comprises exactly the quantum Smoluchowski equation to $o(\Lambda^2)$ as previously obtained in much simpler fashion directly from Eq. (2.27), whereby, adapting Einstein's method, imposing the Wigner configuration space distribution as the stationary solution (rendering the probability current zero), rather than the Maxwell-Boltzmann distribution, one can determine the diffusion coefficient $D(x)$ explicitly. Finally, the quantum effects should become more pronounced at lower temperatures T , smaller mass m , and larger potential barriers, and should be detectable when the dimensionless quantum correction terms in Eq. (2.28) [e.g., $\beta\Lambda V''(x)$, etc.] are comparable with unity (however, the quantum correction parameter must not be too large in order to guarantee convergence of the perturbation expansion of D in Λ).

2.6 The quantum Brownian harmonic oscillator

We now illustrate the validity of the *equilibrium Ansatz* of semiclassical Brownian motion, namely that *the equilibrium distribution of the non-dissipative system is the stationary distribution of the dissipative system* by considering the quantum harmonic oscillator introduced in § 1.7. As we have seen, for the harmonic oscillator potential $V(x) = m\omega_0^2 x^2/2$ the normalised Wigner function is available in the simple exact form (see Eq. (1.35))

$$W_{st}(x, p) = Z^{-1} \exp \left\{ -\frac{1}{2} \left(\frac{x^2}{\langle x^2 \rangle} + \frac{p^2}{\langle p^2 \rangle} \right) \right\}, \quad (2.29)$$

where $\langle x^2 \rangle$, $\langle p^2 \rangle$ and the partition function Z are given by Eqs. (1.36) - (1.38) respectively. By now postulating this closed system distribution as the equilibrium distribution of the open system we may readily evaluate the coordinate, momentum and time-independent parameters of the collision kernel

$$\hat{M}_D W = \frac{\partial}{\partial p} \left[D_p p W + D_{pp} \frac{\partial W}{\partial p} + D_{xp} \frac{\partial W}{\partial x} \right].$$

Using the fact that Eq. (2.29) must satisfy $\hat{M}_D W_{st} = 0$, we find $D_p = \gamma$, $D_{xp} = 0$ and

$$\begin{aligned} D_{pp} &= \frac{m\gamma}{\beta} \left(1 + \frac{\hbar^2 \beta^2 \omega_0^2}{12} - \frac{\hbar^4 \beta^4 \omega_0^4}{720} + \dots \right) \\ &= \gamma \frac{m\hbar\omega_0}{2} \coth \frac{\beta\hbar\omega_0}{2} = \gamma \langle p^2 \rangle, \end{aligned}$$

where $\langle p^2 \rangle$ is as given by Eq. (1.37). Thus the resulting quantum master equation is

$$\frac{\partial W}{\partial t} + \frac{p}{m} \frac{\partial W}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} = \gamma \frac{\partial}{\partial p} \left[p W + \langle p^2 \rangle \frac{\partial W}{\partial p} \right].$$

This coincides exactly with the master equation of Agarwal [5] (see his Eq. (2.11) with $\lambda = 0$ and $(e^{\beta\omega_0-1})^{-1}$ expanded in a Taylor series). As mentioned in § 1.1, Agarwal developed a detailed theory of Brownian motion in the weak coupling limit, yielding an approximate model for the kinetics of a quantum Brownian oscillator for relatively high temperatures, $\beta\hbar\gamma \ll 1$.

2.A Noninertial limit of Brinkman's hierarchy

The quantum Brinkman equations to second order in the quantum parameter Λ are

$$\begin{aligned} \frac{\partial \phi_n}{\partial t} &= -\frac{1}{\sqrt{\beta m}} \left(\frac{\partial \phi_{n-1}}{\partial x} + (n+1) \frac{\partial \phi_{n+1}}{\partial x} \right) - \sqrt{\frac{\beta}{m}} V' \phi_{n-1} - \gamma n \phi_n \\ &\quad - \frac{3\Lambda^2}{10\sqrt{m}\beta^3} V'''' \phi_{n-5} + \Lambda \left[2\gamma V'' \phi_{n-2} + \frac{1}{\sqrt{\beta m}} V''' \phi_{n-3} \right] \\ &\quad - \frac{\gamma 2\Lambda^2}{5} [6V''' V' + 2(V'')^2 + 6(n-3)\beta^{-1} V''''] \phi_{n-2} \\ &\quad - \gamma \frac{6\Lambda^2}{5\beta} V'''' [\phi_{n-4} + n(n+1)\phi_n], \quad n \geq 0. \end{aligned} \tag{2.30}$$

We make the following perturbation expansion of the configuration space functions

$$\phi_n(x, t) = \phi_n^{(0)}(x, t) + \Lambda \phi_n^{(1)}(x, t) + \Lambda^2 \phi_n^{(2)}(x, t) + \dots \tag{2.31}$$

Substituting Eq. (2.31) into Eq. (2.30) we obtain the second order perturbation of the quantum Brinkman equations as

$$\begin{aligned}
\frac{\partial \phi_n^{(2)}}{\partial t} = & -\frac{1}{\sqrt{\beta m}} \left(\frac{\partial \phi_{n-1}^{(2)}}{\partial x} + (n+1) \frac{\partial \phi_{n+1}^{(2)}}{\partial x} \right) - \sqrt{\frac{\beta}{m}} V' \phi_{n-1}^{(2)} - \gamma n \phi_n^{(2)} \\
& - \frac{3\Lambda^2}{10\sqrt{m}\beta^3} V'''' \phi_{n-5}^{(0)} + \Lambda \left[2\gamma V'' \phi_{n-2}^{(1)} + \frac{1}{\sqrt{\beta m}} V''' \phi_{n-3}^{(1)} \right] \\
& - \frac{\gamma 2\Lambda^2}{5} [6V'''V' + 2(V'')^2 + 6(n-3)\beta^{-1}V''''] \phi_{n-2}^{(0)} \\
& - \gamma \frac{6\Lambda^2}{5\beta} V'''' [\phi_{n-4}^{(0)} + n(n+1)\phi_n^{(0)}].
\end{aligned} \tag{2.32}$$

We proceed to solve Eq. (2.32) for $\partial \phi_0^{(2)}/\partial t$ by forming the hierarchy of equations $n = 0, 1, 2, \dots$

$$\begin{aligned}
\frac{\partial \phi_0^{(2)}}{\partial t} &= \gamma J_D \phi_1^{(2)} \\
\frac{\partial \phi_1^{(2)}}{\partial t} &= -\gamma A \phi_1^{(0)} + \gamma J \phi_0^{(2)} - \gamma \phi_1^{(2)} + 2\gamma J_D \phi_2^{(2)} \\
\frac{\partial \phi_2^{(2)}}{\partial t} &= \gamma(B+A)\phi_0^{(0)} - \gamma 3A\phi_2^{(0)} + \gamma 2V''\phi_0^{(1)} + \gamma J \phi_1^{(2)} - \gamma 2\phi_2^{(2)} + 3\gamma J_D \phi_3^{(2)} \\
\frac{\partial \phi_3^{(2)}}{\partial t} &= \gamma B \phi_1^{(0)} - \gamma 6A\phi_3^{(0)} + \frac{V'''}{\sqrt{\beta m}} \phi_0^{(1)} + \gamma 2V''\phi_1^{(1)} + \gamma J \phi_2^{(2)} - \gamma 3\phi_3^{(2)} + 4\gamma J_D \phi_4^{(2)} \\
\frac{\partial \phi_4^{(2)}}{\partial t} &= -\gamma \frac{A}{2} \phi_0^{(0)} + \gamma(B-A)\phi_2^{(0)} - \gamma 10A\phi_4^{(0)} + \frac{V'''}{\sqrt{\beta m}} \phi_1^{(1)} + \gamma 2V''\phi_2^{(1)} + \gamma J \phi_3^{(2)} \\
& - \gamma 4\phi_4^{(2)} + 5\gamma J_D \phi_5^{(2)} \\
& \dots \quad \dots \quad \dots \quad \dots
\end{aligned} \tag{2.33}$$

where the Brinkman current operators J and J_D are

$$J = -\frac{1}{\gamma\sqrt{m}\beta} \left[\frac{\partial}{\partial x} + \beta \frac{\partial V(x)}{\partial x} \right], \quad J_D = -\frac{1}{\gamma\sqrt{m}\beta} \frac{\partial}{\partial x}, \tag{2.34}$$

and for brevity we have introduced

$$A = \frac{12}{5\beta} V'''' , \quad B = -\frac{2}{5} [6V'''V' + 2V''^2]. \tag{2.35}$$

The system of equations (2.33) may be closed by setting $\phi_5^{(2)}(x, t) = 0$ without any loss of terms to the second order of perturbation so that, using the Heisenberg representation of the differential operators viz.

$$\gamma J_D \rightarrow -D \quad \gamma J \rightarrow -\hat{D}, \tag{2.36}$$

the closed hierarchy can be written in the matrix form

$$\dot{\mathbf{Y}}^{(2)}(t) = \mathbf{B}\mathbf{Y}^{(2)}(t) + \mathbf{C}\mathbf{Y}^{(1)}(t) + \mathbf{D}\mathbf{Y}^{(0)}(t), \quad (2.37)$$

where the dot denotes $\partial/\partial t$, the column vectors $\mathbf{Y}^{(i)}(t)$ ($i = 0, 1, 2$) are

$$\mathbf{Y}^{(i)}(t) = \begin{pmatrix} \phi_0^{(i)}(x, t) \\ \phi_1^{(i)}(x, t) \\ \phi_2^{(i)}(x, t) \\ \phi_3^{(i)}(x, t) \\ \phi_4^{(i)}(x, t) \end{pmatrix},$$

and the matrices $\mathbf{B}$, $\mathbf{C}$ and $\mathbf{D}$ are given by

$$\mathbf{B} = \begin{pmatrix} 0 & -\mathbf{D} & 0 & 0 & 0 \\ -\hat{\mathbf{D}} & -\gamma\mathbf{I} & -2\mathbf{D} & 0 & 0 \\ 0 & -\hat{\mathbf{D}} & -2\gamma\mathbf{I} & -3\mathbf{D} & 0 \\ 0 & 0 & -\hat{\mathbf{D}} & -3\gamma\mathbf{I} & -4\mathbf{D} \\ 0 & 0 & 0 & -\hat{\mathbf{D}} & -4\gamma\mathbf{I} \end{pmatrix},$$

$$\mathbf{C} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \gamma 2V'' & 0 & 0 & 0 & 0 \\ (\beta m)^{-1/2}V''' & \gamma 2V'' & 0 & 0 & 0 \\ 0 & (\beta m)^{-1/2}V''' & \gamma 2V'' & 0 & 0 \end{pmatrix},$$

$$\mathbf{D} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & -\gamma A & 0 & 0 & 0 \\ \gamma(B+A) & 0 & -\gamma 3A & 0 & 0 \\ 0 & \gamma B & 0 & -\gamma 6A & 0 \\ -\gamma A/2 & 0 & \gamma(B-A) & 0 & -\gamma 10A \end{pmatrix}.$$

The formal solution of Eq. (2.37) in the Laplace domain is

$$\tilde{\mathbf{Y}}^{(2)}(s) = (s\mathbf{I} - \mathbf{B})^{-1}\mathbf{Y}^{(2)}(0) + (s\mathbf{I} - \mathbf{B})^{-1}\mathbf{C}\tilde{\mathbf{Y}}^{(1)}(s) + (s\mathbf{I} - \mathbf{B})^{-1}\mathbf{D}\tilde{\mathbf{Y}}^{(0)}(s), \quad (2.38)$$

where $\mathbf{Y}^{(2)}(0)$ is the initial value vector. In order to obtain the noninertial limit of Eq. (2.38), we must take the limit of $m \rightarrow 0$ for each element of the three matrices $(s\mathbf{I} - \mathbf{B})^{-1}$, $(s\mathbf{I} - \mathbf{B})^{-1}\mathbf{C}$ and $(s\mathbf{I} - \mathbf{B})^{-1}\mathbf{D}$, noting that $\mathbf{D}\hat{\mathbf{D}} \sim o(m^{-1})$ and $\gamma^{-1} \sim o(m)$. In the noninertial limit these matrices reduce to

$$\begin{aligned}
(s\mathbf{I} - \mathbf{B})^{-1} &= \begin{pmatrix} (s - D\hat{D}/\gamma)^{-1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \\
(s\mathbf{I} - \mathbf{B})^{-1}\mathbf{C} &= \begin{pmatrix} (s - D\hat{D}/\gamma)^{-1}DD(2V'')/\gamma & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ V'' & 0 & 0 & 0 & 0 \\ 0 & 2V''/3 & 0 & 0 & 0 \\ 0 & 0 & V''/2 & 0 & 0 \end{pmatrix}, \\
(s\mathbf{I} - \mathbf{B})^{-1}\mathbf{D} &= \begin{pmatrix} \frac{DD(A+B)/\gamma}{(s-D\hat{D}/\gamma)} & \infty & \frac{DD(-3A)/\gamma}{(s-D\hat{D}/\gamma)} & 0 & 0 \\ 0 & \frac{(-As)}{(s-D\hat{D}/\gamma)} & 0 & 0 & 0 \\ (A+B)/2 & 0 & -3A/2 & 0 & 0 \\ 0 & B/3 & 0 & -2A & 0 \\ -A/8 & 0 & (B-A)/4 & 0 & -5A/2 \end{pmatrix}.
\end{aligned}$$

We notice that only the initial condition of the second order perturbation function, $\phi_0^{(2)}(x, t)$, which is the $o(\Lambda^2)$ part of the Wigner configuration space distribution

$$\phi_0(x, t) = \phi_0^{(0)}(x, t) + \Lambda\phi_0^{(1)}(x, t) + \Lambda^2\phi_0^{(2)}(x, t), \quad (2.39)$$

will contribute on taking the noninertial limit. This is completely consistent with the *Ansatz* of the Smoluchowski equation, namely that the equation holds only for times much greater than the inertial time m/ζ , in which case one expects the coefficients $\phi_n(x, t)$ of all momentum functions

$$D_n(p\sqrt{\beta/m}), \quad n > 0,$$

to have reached their final equilibrium values, no longer remembering their initial values. Only the coefficient $\phi_0^{(2)}(x, t)$, which varies extremely slowly, will not have reached its equilibrium value and so its initial condition will contribute. In other words, the friction is so high that the particles are always in thermal equilibrium in the momentum space and the distribution function is therefore independent of the initial momentum distribution. The initial values $\phi_n(x, 0)$, $n > 0$, of the configuration space distributions determine the evolution of arbitrary momenta distributions $D_n(p\sqrt{\beta/m})$, $n > 0$ (including any such initial distributions) and since these distributions by the very *Ansatz* of the noninertial limit

have attained equilibrium then their coefficients must become the *Wigner configuration space equilibrium distribution*. Consequently, the functions $\phi_n(x, t)$, $n > 0$, and their initial conditions play no role in the Smoluchowski equation.

Alternatively, one may consider that since on forming the Brinkman equations (2.30) the inertia of the particle essentially becomes encoded in the interaction (the algebraic interplay) of the configuration space distribution functions $\phi_n(x, t)$, $n > 0$, neither the distribution functions nor their initial conditions can play a part in the noninertial limit wherein their interplay must be ignored. Thus, in the noninertial limit of Eq. (2.38) [justly ignoring the contributions from the classical functions $\tilde{\phi}_1^{(0)}(x, s)$ and $\tilde{\phi}_2^{(0)}(x, s)$], we have

$$\begin{aligned} s\tilde{\phi}_0^{(2)}(x, s) - \phi_0^{(2)}(x, 0) &= \frac{D\hat{D}}{\gamma}\tilde{\phi}_0^{(2)}(x, s) + \frac{DD(2V'')}{\gamma}\tilde{\phi}_0^{(1)}(x, s) \\ &+ \frac{DD(A+B)}{\gamma}\tilde{\phi}_0^{(0)}(x, s). \end{aligned} \quad (2.40)$$

Taking the inverse Laplace transform and substituting back in D , $\hat{D}$, A and B we obtain the time evolution of $\phi_0^{(2)}(x, t)$, namely

$$\begin{aligned} \frac{\partial \phi_0^{(2)}}{\partial t} &= \frac{\partial}{\partial x} \left\{ \frac{\phi_0^{(2)}}{\zeta} \frac{\partial V}{\partial x} + \frac{\partial}{\partial x} \left(\frac{1}{\zeta\beta} \left[\phi_0^{(2)} + 2\Lambda V''(x)\phi_0^{(1)} \right. \right. \right. \\ &\quad \left. \left. \left. - \frac{4\Lambda^2}{5} (3V'''(x)V'(x) + V''(x)^2 - 3\beta^{-1}V''''(x))\phi_0^{(0)} \right] \right) \right\} \end{aligned} \quad (2.41)$$

Since

$$P(x, t) = \int W(x, p, t) dp \equiv \phi_0(x, t),$$

this is simply the quantum Smoluchowski equation

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{P(x, t)}{\zeta} V'(x) + \frac{\partial}{\partial x} [D(x)P(x, t)] \right\}, \quad (2.42)$$

where the diffusion coefficient to second order in Λ is

$$D(x) = \frac{1}{\zeta\beta} \left\{ 1 + 2\Lambda V''(x) - \frac{4\Lambda^2}{5} [3V'''(x)V'(x) + V''(x)^2 - 3\beta^{-1}V''''(x)] \right\}. \quad (2.43)$$

The Smoluchowski equation governs the time behaviour of classical point Brownian particles in configuration space if the energy loss per cycle of the almost-periodic motion of a particle moving along a saddle point of the potential (that is, on an escape trajectory in phase space) is much greater than the thermal energy. The high damping condition

is tantamount to assuming in the Fokker-Planck equation for the joint distribution of the positions and momenta of the particle that the momentum p has reached the equilibrium Maxwellian distribution, while the position x has not yet had sufficient time to reach the Boltzmann distribution.

Chapter 3

The tilted cosine potential:

Linear response

The quantum Smoluchowski equation for the time evolution of the distribution function in configuration space introduced in § 2.3 is now solved in order to treat quantum corrections to the non-inertial Brownian motion of a particle in a one-dimensional tilted cosine potential in the high temperature and weak bath-particle coupling limit. In a particular application to the dynamics of a point Josephson junction, the theoretical predictions are compared in detail with those of a quantum Smoluchowski equation proposed by Ankerhold *et al.* [97]. Various characteristics (stationary distribution, current-voltage characteristics, mean first passage time, linear a.c. response) are evaluated via continued fractions and finite integral representations in the manner customarily used for the classical Smoluchowski equation.

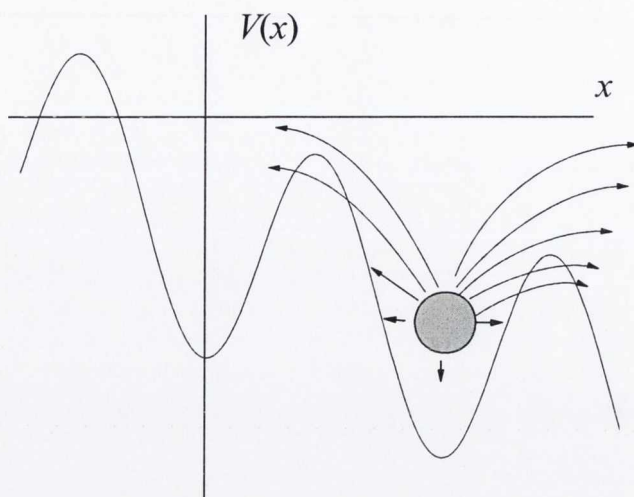


Figure 3.1: Overdamped quantum Brownian motion of a particle in a tilted periodic potential: the particle may escape from a potential well both over (due to thermal agitation) and below (due to tunneling through) the higher and lower potential barriers.

3.1 Introduction

The quantum Smoluchowski equation presented in § 2.3 is solved for the particular case of a tilted cosine (or biased washboard) potential in order to evaluate quantum corrections (at relatively high temperatures) to various characteristics to first and second order of perturbation theory in $\hbar^2$. The model of Brownian motion of a particle in a tilted cosine potential (see Fig. 3.1) arises in a number of important physical applications. We mention Josephson junctions [84–86], ring-laser gyroscopes [87], the dynamics of a charged density wave condensate in an electric field [88], etc. and many other processes involving quantum and classical Brownian motion in periodic structures [89].

As a particular example of an application of the QSE, quantum effects in the dynamics of a point Josephson junction as modelled by a resistively shunted junction (RSJ) are estimated. In the context of the classical Brownian motion, this system has been described in detail in Refs. [84–86] (see also [82], Chapter 5). The dc current-voltage characteristics of a Josephson junction in the classical Smoluchowski regime were derived by Halperin and Ambegaokar [90] and by Ivanchenko and Zil'berman [91]. Various aspects of quantum effects in the characteristics of Josephson junctions have already been analysed, e.g. in Refs. [92–96]. Here, quantum effects shall be included in the stationary distribution, the dc current-voltage characteristic, the normalized differential resistance, and the non-stationary problem of the *linear* impedance of a point Josephson junction (ignoring the

capacitance, which corresponds to the non-inertial or very high damping limit) by solving the QSE using the continued fraction methods already developed for the classical problem [7, 82]. Moreover, it is demonstrated that the effective eigenvalue method [82] yields closed analytic solutions for the junction impedance in the form of two Lorentzians just as in the classical problem [82]. These have a simple physical explanation as a damped resonant circuit with the decay rate and resonant frequency of the oscillations given by the real and imaginary parts of the effective eigenvalue.

The mean first passage time for a particle to leave a well of the potential is also considered. The mean first passage time may be determined, just as the classical case, knowing the quantum diffusion coefficient and stationary distribution only [7]. Finally, the convergence of the perturbation procedure in $\hbar^2$ will be tested by comparing the first and second order of perturbation theory solutions. All the foregoing results will then be compared with those calculated from the QSE recently proposed by Ankerhold *et al.* [97] from the path-integral representation of dissipative quantum mechanics. This equation has already been used in many applications of the quantum Brownian motion in a periodic potential (see, e.g. [95, 96, 98, 101]).

A feature of the present problem is that the first-order perturbation solution of the QSE reduces to a three-term *scalar* recurrence relation, just as the corresponding classical problem [7]. This relation may then be solved using scalar continued fractions. If the calculation is carried to the second order of perturbation theory however, one must always resort to *matrix* continued fractions as a five-term recurrence relation is now involved. Nevertheless, the matrix continued fraction so generated is much simpler than that obtained [74] using the master equation (which is valid for all dissipation regimes) for the phase space distribution $W(x, p, t)$.

3.2 Application to a point Josephson junction: RSJ model

The Josephson junction as described by the resistively shunted junction (RSJ) model comprises two superconductors separated by a thin layer of oxide. The phase difference $x = \phi_l - \phi_r$ between the wave functions of the right and left superconductors is given by the Josephson equation [84, 85]

$$\frac{d}{dt}x(t) = \frac{2ev(t)}{\hbar}, \quad (3.1)$$

where $v(t)$ is the potential difference across the oxide layer and e is the charge of the electron. If the junction is small enough (a point Josephson contact), it may be mod-

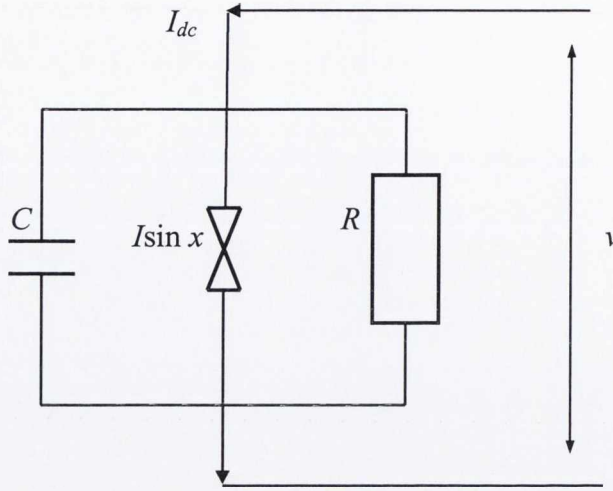


Figure 3.2: The circuit diagram of the resistively shunted junction (RSJ) model of a point Josephson junction.

elled [84, 85] by a resistance R in parallel with a phase-dependent current generator, $I \sin x$, representing the Josephson supercurrent due to the Cooper pairs tunnelling through the junction, which has capacitance C . The junction is connected to an external current generator I_{dc} , representing the bias current applied to the junction (see Fig 3.2).

In the classical RSJ model, the dynamics of the junction (in the zero capacitance limit) in the presence of thermal agitation are described by the classical Smoluchowski equation [84, 85] for the time evolution of the configuration space distribution function, where the mass m and the friction coefficient ζ of the Brownian particle are replaced by the corresponding electrical parameters via

$$m = C(\hbar/2e)^2, \quad \zeta = (\hbar/2e)^2/R. \quad (3.2)$$

Thus, the junction is treated as a purely classical system, where the phase difference x across the junction and the charge Cv on the junction are considered as classical variables which can be determined with arbitrary accuracy [85]. However, the classical accuracy is inherently limited by Heisenberg's uncertainty principle which in this case is $\Delta x \Delta N \geq 1$, where N is the number of Cooper pairs transferred across the junction. Hence, the results of classical theory (in particular, those arising from the classical Smoluchowski equation) require modification when quantum effects become important, e.g. at very low temperatures $T < 0.1$ K [85].

In order to treat quantum effects in a point Josephson junction [84–86] using the quantum Smoluchowski equation (2.15), we consider the tilted cosine potential

$$V(x) = -V_0 \cos(2\pi x/a) - Fx, \quad (3.3)$$

where V_0 is the potential amplitude, a is a characteristic length and F is a constant tilt (slope). On introducing, the normalized coordinate x , time t , tilt y , barrier parameter b , and quantum parameter Λ as

$$\begin{aligned} \frac{2\pi x}{a} \rightarrow x, \quad \frac{t}{\tau} \rightarrow t, \quad \tau = \frac{\zeta \beta a^2}{4\pi^2}, \\ \Lambda \frac{8\pi^2}{\beta a^2} \rightarrow \Lambda, \quad \beta V(x) \rightarrow V(x), \quad y = \frac{aF}{2\pi V_0}, \quad \beta V_0 = b, \end{aligned} \quad (3.4)$$

the QSE (2.15), becomes

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left\{ V' P + \frac{\partial}{\partial x} \left[1 + \Lambda V'' - \frac{\Lambda^2}{5} (V''^2 + 3V'V^{(3)} - 3V^{(4)}) \right] P \right\}, \quad (3.5)$$

where the potential in dimensionless variables is

$$V(x) = -b(\cos x + yx). \quad (3.6)$$

In the context of the point Josephson junction, the parameter b represents the normalized (in the thermal energy kT) Josephson coupling energy, the tilt parameter y is the ratio of the bias current I_{dc} to the supercurrent amplitude I , while the dimensionless coordinate x is the phase difference between the wave functions for two superconductors, as given by the Josephson equation (3.1) [84–86].

The validity of the QSE (3.5) for the problem in question may be justified as follows. Noting that $\gamma = \zeta/m = 1/(RC)$, we can estimate T_0 in the right-hand side of Eq. (2.10) for typical values of R and C for real Josephson junctions, as studied, for example, by Anderson and Goldman [102] and Falco *et al.* [103]. The results are shown in Table 3.1.

Ref. [102]	$R = 1.3\Omega$	$C = 245 \text{ pF}$	$T_0 \sim 0.004\text{K}$
Ref. [103]	$R = 0.2\Omega$	$C = 1200 \text{ pF}$	$T_0 \sim 0.005 \text{ K}$

Table 3.1: Typical values of R and C for real Josephson junctions.

In Refs. [102] and [103], the effects of thermal noise on current-voltage characteristics of Josephson junctions have been measured experimentally and have been compared with the model of Ambegaokar and Halperin [90] and Ivanchenko and Zil'berman [91]. For the two junctions presented in Table 3.1, experimental data were given in the temperature range $T \sim 1.4 - 4.2 \text{ K}$. Thus, the condition of applicability of the QSE $T \gg T_0$ is perfectly

fulfilled (at least for the two examples above). One can also estimate the Josephson plasma frequency $\omega_0 = \sqrt{2eI/(\hbar C)}$ for the above two examples. This characteristic frequency determines the conditions of applicability of Ankerhold's QSE

$$T \gg T_A = \frac{\hbar \omega_0^2}{2\pi k\gamma}.$$

From the experimental data of Refs. [102] and [103], we have, respectively, $\omega_0 \sim 6 \times 10^9 \text{ s}^{-1}$ yielding $T_A \sim 0.01 \text{ K}$ (i.e. $T_A > T_0$), and $\omega_0 \sim 6 \times 10^8 \text{ s}^{-1}$ yielding $T_A \sim 0.00015 \text{ K}$ (i.e. $T_A < T_0$). Hence, the temperature T_A is also very low and can be both smaller and larger than T_0 .

In many physical applications, a periodic solution $P(x, t)$ of Eq. (3.5) is required. This may be expanded in a Fourier series in x , viz. [7, 82]

$$P(x, t) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} c_n(t) e^{inx}. \quad (3.7)$$

By substituting Eq. (3.7) into Eq.(3.5), we find that the Fourier coefficients (statistical moments)

$$c_n(t) = \langle e^{-inx} \rangle(t) = \int_0^{2\pi} e^{-inx} P(x, t) dx$$

satisfy the following differential-recurrence relation to second order in the perturbation parameter Λ

$$\begin{aligned} \frac{d}{dt} c_n(t) + (n^2 + inby) c_n(t) &= \frac{bn}{2} [(1 - n\Lambda) c_{n-1}(t) - (1 + n\Lambda) c_{n+1}(t)] \\ + \frac{bn^2 \Lambda^2}{10} [2bc_{n-2}(t) + 3(1 - iby) c_{n-1}(t) - 2bc_n(t) &+ 3(1 + iby) c_{n+1}(t) + 2bc_{n+2}(t)]. \end{aligned} \quad (3.8)$$

This recurrence relation will yield the time-dependent periodic solution in the second order of perturbation theory. It is obvious that the first-order perturbation solution constitutes a three-term recurrence relation similar to that encountered in the classical case [7, 82].

Now, the QSE deduced by Ankerhold *et al.* [97] is *very similar* but not *identical* to Eq. (2.15). In the high temperature limit, that equation reads (in our notation)

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{P}{\zeta} \frac{\partial}{\partial x} V_{ef} + \frac{\partial}{\partial x} [DP] \right\}, \quad (3.9)$$

where $V_{ef} = V(x) + \Lambda V''(x)/\beta$ is the effective potential. We see that Eq. (3.9) differs from Eq. (2.15) by the additional term in V_{ef} . However, this difference is important, because the stationary solution of Eq. (3.9) is

$$P_A(x) \sim e^{-\beta V(x)} \{1 + \Lambda [\beta V'(x)^2 - 3V''(x)] + \dots\}. \quad (3.10)$$

Hence, the Wigner equilibrium distribution in configuration space $P_W(x)$ given by Eq. (2.21) does not coincide with the stationary distribution $P_A(x)$ and so *does not satisfy* Eq. (3.9).

Now the periodic solution $P^A(x, t)$ of Eq. (3.9) can also be expanded in a Fourier series in x . Thus substituting $P^A(x, t) = \sum_{n=-\infty}^{\infty} c_n^A(t) e^{inx}/2\pi$ into Eq. (3.9), the corresponding Fourier coefficients $c_n^A(t)$ again satisfy a three term differential-recurrence relation to first order in Λ , viz.

$$\begin{aligned} \frac{d}{dt} c_n^A(t) = & - (n^2 + inby) c_n^A(t) \\ & + \frac{bn}{2} \{ [1 - (n + 1/2) \Lambda] c_{n-1}^A(t) - [1 + (n - 1/2) \Lambda] c_{n+1}^A(t) \}. \end{aligned} \quad (3.11)$$

In the classical limit ($\Lambda = 0$), both Eqs. (3.8) and (3.11) become the known differential-recurrence relation for the classical statistical moments [7, 82]. Methods of solution of Eqs. (3.8) and (3.11) are described in detail in Refs. [7, 82]. We shall first consider the *stationary* solution of Eq. (3.8) using these. To simplify the analysis and the comparison with predictions of the QSE of Ankerhold *et al.* [97], Eq. (3.9), we may neglect the second-order correction term in Eq. (3.8) [so that just as the classical case, the differential-recurrence equation becomes a three-term recurrence relation] and present the solution to terms linear in the quantum parameter Λ , i.e. $o(\Lambda)$.

3.3 Stationary periodic solution of the QSE

The periodic stationary solution $P_{st}(x)$ of Eq. (3.5) can be obtained following the method used in [7] for the classical Smoluchowski equation from the equation for the probability current J (which is constant in this case)

$$P_{st} \left(\frac{\partial V}{\partial x} + \Lambda \frac{\partial^3 V}{\partial x^3} \right) + \left(1 + \Lambda \frac{\partial^2 V}{\partial x^2} \right) \frac{\partial P_{st}}{\partial x} = -J. \quad (3.12)$$

Solving Eq. (3.12) for $P_{st}(x)$ and using the properties of the periodic solution $P_{st}(x + 2\pi n) = P_{st}(x)$ for all n , we have

$$\begin{aligned} P_{st}(x) = & N \left\{ P_W(x) \left[I - (1 - e^{-2\pi by}) \int_0^x e^{V(z)} dz \right] \right. \\ & \left. - \frac{\Lambda}{2} e^{-V(x)} \left[I_1 - (1 - e^{-2\pi by}) \int_0^x e^{V(z)} (V')^2 dz \right] \right\}, \end{aligned} \quad (3.13)$$

where $I = \int_0^{2\pi} e^{V(x)} dx$, $I_1 = \int_0^{2\pi} [V'(x)]^2 e^{V(x)} dx$, and N is the normalizing constant determined by $\int_0^{2\pi} P_{st}(x) dx = 1$. For zero tilt, i.e. $y = 0$, the stationary solution Eq. (3.13) reduces to the Wigner distribution in configuration space (2.21), viz. $P_{st}(x) = NP_W(x)$. The stationary solution $P_{st}^A(x)$ of Eq. (3.9) can be found in like manner. In the classical limit, Eq. (3.13) has been used in Refs. [90] and [91] in order to calculate the dc current-voltage characteristics.

However, as shown by Risken [7] and Coffey *et al.* [82], the most efficient method of calculation of both stationary and non-stationary solutions is via continued fractions as they circumvent the problem of evaluating integrals of transcendental functions similar to those encountered in the stationary solution, Eq. (3.13). Moreover, continued fractions lend themselves very naturally to computational algorithms. We may implement this method by recalling that, in the stationary state, the periodic distribution function $P_{st}(x)$ can be expanded in a Fourier series in x [7], viz.

$$P_{st}(x) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} C_n e^{inx}, \quad (3.14)$$

where $C_n = \langle e^{-inx} \rangle_0 = \int_0^{2\pi} e^{-inx} P_{st}(x) dx$ and the angular braces (with zero subscript) denote the stationary ensemble average. Either using this expansion directly in Eq. (3.5) or simply omitting the time derivative and the second-order terms in Eq. (3.8), we obtain the recurrence relation for the Fourier coefficients C_n to terms linear in Λ , viz.

$$Q_n C_n + Q_n^+ C_{n+1} + Q_n^- C_{n-1} = 0, \quad (3.15)$$

where

$$Q_n = -(n/b + iy), \quad Q_n^\pm = \mp(1 \pm n\Lambda)/2. \quad (3.16)$$

Equation (3.15) can be rearranged as the infinite continued fraction $S_n = C_n/C_{n-1}$ so that

$$S_n = \frac{Q_n^-}{-Q_n - Q_n^+ S_{n+1}} = \frac{Q_n^-}{-Q_n - \frac{Q_n^+ Q_{n+1}^-}{-Q_{n+1} - \frac{Q_{n+1}^+ Q_{n+2}^-}{\dots}}}. \quad (3.17)$$

Thus, just as the classical case [82], all the C_n can simply be calculated via continued fractions as

$$C_n = S_n C_{n-1} = S_n S_{n-1} \dots S_1, \quad (3.18)$$

(noting that $C_0 = 1$). In particular, we have

$$C_1 = S_1. \quad (3.19)$$

Having determined C_n , we can calculate the stationary distribution Eq. (3.14).

In the classical limit ($\Lambda = 0$), Eqs. (3.17) and (3.19) yield the known results [82]

$$S_n^{cl} = \frac{1/2}{nb^{-1} + iy + \frac{1/4}{(n+1)b^{-1} + iy + \frac{1/4}{(n+2)b^{-1} + iy + \dots}}} = \frac{I_{n+iyb}(b)}{I_{n-1+iyb}(b)}, \quad (3.20)$$

and

$$C_1^{cl} = I_{1+iyb}(b)/I_{iyb}(b), \quad (3.21)$$

respectively, where $I_\nu(z)$ is the modified Bessel function of the first kind of order ν [104]. The stationary solution of Ankerhold's Eq. (3.9) may be determined in like manner. We recall that all such solutions are valid only to terms linear in Λ . The solution of Eq. (3.8) to $o(\Lambda^2)$ is given in Appendix 3.A using matrix continued fractions.

3.4 Mean first passage time and escape rates

The QSE can be used to estimate quantum effects in the various characteristic times of the system (such as the inverse escape rate, mean first passage time, etc.) in the noninertial limit. These times are important parameters of the Josephson junction or the ring laser gyroscope as they effectively yield a measure of the phase slip. For simplicity, we consider zero tilt only, i.e. $y = 0$. A semiclassical correction to the classical Kramers escape rate Γ_{cl} of a Brownian particle over a potential barrier ΔV in the non-inertial limit and above the crossover temperature T_C (at which the parabolic or inverted harmonic oscillator approximation for the potential is valid near the top of the barrier) can be written [31]

$$\Gamma = \Xi \Gamma_{cl}. \quad (3.22)$$

Equation (3.22) constitutes the classical very high damping (VHD) Kramers escape rate

$$\Gamma_{cl} = \frac{m\omega_c\omega_a}{2\pi\zeta} e^{-\beta\Delta V},$$

multiplied by Wigner's quantum correction factor derived using transition state theory [30, 72]

$$\Xi = \frac{\omega_c}{\omega_a} \frac{\sinh(\hbar\beta\omega_a/2)}{\sin(\hbar\beta\omega_c/2)} = 1 + \frac{\beta^2\hbar^2}{24} (\omega_c^2 + \omega_a^2) + \dots,$$

where $\omega_c = \sqrt{|V''(x_c)|/m}$ and $\omega_a = \sqrt{V''(x_a)/m}$ are the barrier and the well frequencies [points c and a are, respectively, the maximum and minimum of the potential $V(x)$]. The form of Eq. (3.22) reinforces our previous contention [31] that we are essentially treating our system at $T > T_C$ as a *quantum particle* embedded in a *classical bath*, where the diffusion coefficient is modified to take into account quantum dissipative effects due to the bath-particle interactions. The quantum correction terms in Eq. (3.22) are (as they must be) in complete agreement with Wigner's calculation of the escape rate [60] and in effect reduce the barrier height. The physical origin of the corrections is tunnelling at relatively high temperatures near the top of the barrier. In the context of the quantum intermediate to high damping (IHD) Kramers rate [31], we remark that the appropriate quantum correction factor was first derived by Wolynes [105] and later by Pollak [106]. The quantum (IHD) correction factor yielded by these calculations for Ohmic friction is [105]

$$\Xi_W = \prod_{n=1}^{\infty} \frac{\omega_a^2 + (2\pi n/\hbar\beta)^2 + 2\pi n\gamma/\hbar\beta}{-\omega_c^2 + (2\pi n/\hbar\beta)^2 + 2\pi n\gamma/\hbar\beta}. \quad (3.23)$$

A comprehensive analysis of Eq. (3.23) has been made by Grabert *et al.* [107], Hänggi *et al.* [108] and also by Weiss [72], where it is shown how Wigner's quantum correction Ξ is recovered in the high temperature limit. In this particular instance the *damping independent* Ξ is a fair approximation to Ξ_W in the VHD limit. This result suggests that replacement of the equilibrium distribution function by that of the closed system may ultimately yield reasonable semiclassical approximations to the actual time-dependent quantum distribution. We shall meet the Wolynes factor Ξ_W and the approximation Ξ again in Chapter 7, where comparison of the longest relaxation time predicted by the semiclassical master equation of Coffey *et al.* with the prediction of various other quantum master equations is made.

The longest relaxation time τ_L can now be estimated as $\tau_L \sim \Gamma^{-1}$. However, noting the explicit forms of the diffusion coefficient $D(x)$ and stationary distributions $P_W(x)$ and $P_A(x)$, one can also estimate the longest relaxation time τ_L using the mean first passage time τ_{MFPT} . For a cosine potential, the mean first passage times for both the QSE of Coffey *et al.*, Eq. (2.15), and Ankerhold *et al.*, Eq. (3.9), may be given by quadratures just as for the classical Smoluchowski equation. Following the methods described in [7], we have

$$\tau_{\text{MFPT}} = \int_0^{2\pi} \frac{dx}{P_W(x)D(x)} \int_0^x P_W(y)dy, \quad (3.24)$$

and

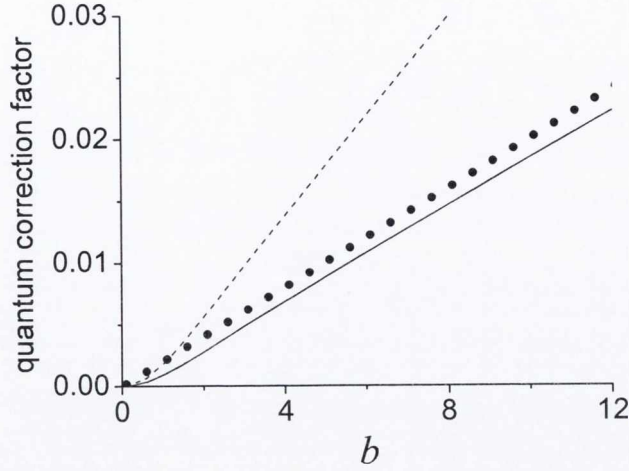


Figure 3.3: The quantum correction factors $\Xi - 1 = \Gamma/\Gamma_{cl} - 1 = 2b\Lambda$ (filled circles), $\tau_{MFPT}^{cl}/\tau_{MFPT} - 1$ (solid line) and $\tau_{MFPT}^{cl}/\tau_{MFPT}^A - 1$ (dashed line) vs. b (Josephson coupling energy) with $\Lambda = 0.001$.

$$\tau_{MFPT}^A = \int_0^{2\pi} \frac{dx}{P_A(x)D(x)} \int_0^x P_A(y)dy, \quad (3.25)$$

respectively. In the classical limit, $\Lambda \rightarrow 0$, both equations reduce to the classical τ_{MFPT}^{cl} .

In Fig. 3.3, we have plotted the quantum correction factors

$$\Xi - 1 = \frac{\Gamma}{\Gamma_{cl}} - 1 = 2b\Lambda, \quad \frac{\tau_{MFPT}^{cl}}{\tau_{MFPT}} - 1, \quad \frac{\tau_{MFPT}^{cl}}{\tau_{MFPT}^A} - 1.$$

Clearly, the correction factor $\tau_{MFPT}^{cl}/\tau_{MFPT}^A - 1$ using Eq. (3.25) derived from the QSE (3.9) of Ankerhold *et al.* [97] deviates considerably from the Wigner correction $\Xi - 1$ while the QSE of Coffey *et al.* predicts the *same* quantitative behaviour of $\tau_{MFPT}^{cl}/\tau_{MFPT} - 1$ as the Wigner correction. The discrepancy in the two results is entirely due to the different behaviour of the stationary distributions $P_{st}(x)$ and $P_{st}^A(x)$. Therefore, it appears that Eq. (3.25) exaggerates the quantum effects.

3.5 DC current-voltage characteristics of a point Josephson junction

Now, the tilted cosine potential model may also be used to calculate the dc current-voltage characteristics of a point Josephson junction, which of course depend only on the equilibrium distribution. In order to determine these, we first note that, ignoring the capacitance, the current balance equation for the junction becomes in dimensionless variables [82]

$$\langle v \rangle_0 = y - \langle \sin x \rangle_0, \quad (3.26)$$

with $\langle v \rangle_0 = \langle \dot{x} \rangle_0$ denoting the dimensionless average voltage in the stationary state. We can find $\langle \sin x \rangle_0$ merely by extracting the imaginary part of C_1 given by the continued fraction Eq. (3.19) since

$$C_1 = \langle e^{-ix} \rangle_0 = \langle \cos x \rangle_0 - i \langle \sin x \rangle_0.$$

Thus, we have

$$\langle v \rangle_0 = y + \text{Im} [C_1]. \quad (3.27)$$

We can also calculate from Eq. (3.27) the normalised differential resistance of the junction, namely

$$\frac{d}{dy} \langle v \rangle_0 = 1 + \frac{d}{dy} \text{Im} [C_1]. \quad (3.28)$$

As shown in Appendix 3.B, the coefficient C_1 from Eq. (3.19) can also be expressed in terms of the modified Bessel functions of the first kind, $I_\nu(z)$, as

$$\begin{aligned} C_1 &= C_1^{cl} + \Lambda C_1^{(1)} + \dots = \frac{I_{1+iyb}(b)}{I_{iyb}(b)} \\ &+ \frac{\Lambda}{I_{iyb}^2(b)} \sum_{n=1}^{\infty} \{(-1)^n n I_{n+iyb}(b) [I_{n+1+iyb}(b) + I_{n-1+iyb}(b)]\} + \dots \end{aligned} \quad (3.29)$$

In the classical limit, Eqs. (3.27) and (3.28) yield the known results [82] for the characteristics

$$\langle v \rangle_0 = y + \text{Im} [I_{1+iyb}(b)/I_{iyb}(b)], \quad (3.30)$$

and

$$\frac{d}{dy} \langle v \rangle_0 = 1 - \text{Re} \left[\frac{2}{I_{iyb}^2(b)} \int_0^b I_{iyb}(z) I_{1+iyb}(z) dz \right]. \quad (3.31)$$

The current-voltage characteristic, Eq. (3.27), and normalised differential resistance, Eq. (3.28), for both forms of the QSE, Eqs. (2.15) and (3.9), calculated using C_1 to $o(\Lambda)$, rendered by the continued fraction solution, are shown in Fig. 3.4 along with the classical results from Eqs. (3.30) and (3.31). The quantum effects due to high temperature non-dissipative tunnelling near the top of the barrier are readily detectable for large supercurrents and relatively small bias. They comprise an enhanced current for a given

voltage, Fig. 3.4(a), and an enhanced slope of the differential resistance, Fig. 3.4(b). We note the *unphysical behaviour* of the characteristics calculated from the QSE proposed by Ankerhold *et al.* [97] for large barrier values b (where the superconducting behaviour is pronounced), whereby *negative resistance* is predicted for zero voltage, Fig. 3.4(a). This behaviour is particularly pronounced in Fig. 3.4(b), where the continued fraction generated by Eq. (3.9) predicts *negative differential-resistance*. In all cases the deviation from the classical behaviour is most marked for large b , i.e. large Josephson coupling energy. In Fig. 3.5, the convergence of the perturbation procedure is investigated by comparing the first- and second-order perturbation solutions of the QSE, Eq. (2.15) obtained by solving Eq. (3.8) to $o(\Lambda^2)$. Clearly, the first-order perturbation solution closely approximates the second-order one for small Λ (here for $\Lambda = 0.1$). Moreover, the greater Λ and b are, the higher the order of perturbation theory required.

Having determined the stationary solution, we now consider the non-stationary problem of the linear impedance of the junction for the QSE, Eq. (3.5). The impedance can be found using the continued fraction method or in *approximate* closed form as two Lorentzians from the effective eigenvalue after-effect solution just as in the classical case [82].

3.6 Linear response of the Josephson junction to an applied alternating current

In order to evaluate the linear ac response of the Josephson junction, we suppose that the tilt now becomes modulated so that $y \rightarrow y + y_m e^{-i\omega t}$, where $by_m \ll 1$ so that the tilt is weakly perturbed (corresponding to a small signal ac superimposed on the dc bias current). We can then make the following perturbation expansion

$$c_n = c_n^0 + A_n(\omega) y_m e^{-i\omega t} + \dots, \quad (3.32)$$

with $A_0(\omega) = 0$ and $c_n^0 = \prod_{k=1}^n S_k$ is the unperturbed solution. In particular, simply by evaluating the Fourier amplitude $A_1(\omega)$, one may evaluate the linear impedance $Z(\omega) = R_\omega - iX_\omega$ of the junction (here R_ω and X_ω are the dynamic resistance and the reactance, respectively) by recalling that the averaged current-balance equation in the presence of the ac is

$$\langle v \rangle_0 + \langle v \rangle_1 = y + y_m e^{-i\omega t} - \langle \sin x \rangle_0 - \langle \sin x \rangle_1,$$

where the subscript "0" on the angular braces denotes the average in the absence of the ac and the subscript "1" the portion of the average which is linear in y_m . Thus we have

$$\langle v \rangle_1 = y_m e^{-i\omega t} - \langle \sin x \rangle_1 = Z(\omega) I_m e^{-i\omega t} / (RI),$$

where $Z(\omega)$ is the linear impedance of the junction given by

$$Z(\omega) = R \{1 - i [A_1(\omega) - A_{-1}(\omega)] / 2\}. \quad (3.33)$$

By substituting Eq. (3.32) into Eq. (3.8), replacing y by $y + y_m e^{-i\omega t}$, and keeping only terms linear in $y_m e^{-i\omega t}$ and Λ , we obtain the inhomogeneous three-term recurrence relation for the Fourier amplitudes $A_n(\omega)$, viz.

$$Q_n^- A_{n-1}(\omega) + Q_n^+ A_{n+1}(\omega) + [Q_n + i\omega / (bn)] A_n(\omega) = i c_n^0. \quad (3.34)$$

The exact solution of the three-term recurrence relation (3.34) is [82]

$$A_1(\omega) = -i \sum_{n=1}^{\infty} c_n^0 \prod_{k=1}^n Q_{k-1}^+ \Delta_k(\omega), \quad (3.35)$$

where the continued fraction $\Delta_k(\omega)$ is defined by the recurrence equation

$$\Delta_k(\omega) = [-i\omega / (bn) - Q_n - Q_k^+ Q_{k+1}^- \Delta_{k+1}(\omega)]^{-1}.$$

Noting that $S_k = Q_k^- \Delta_k(0)$ so that $c_n^0 = \prod_{k=1}^n Q_k^- \Delta_k(0)$, we can rewrite Eq. (3.35) as

$$A_1(\omega) = 2i \sum_{n=1}^{\infty} \prod_{k=1}^n Q_{k-1}^+ Q_k^- \Delta_k(0) \Delta_k(\omega). \quad (3.36)$$

We remark that $A_{-1}(\omega)$ can be calculated as $A_{-1}(\omega) = A_1^*(-\omega)$ [82]. Equation (3.36) combined with Eq. (3.33) constitutes the first-order perturbation solution for the linear ac response in terms of sums of products of continued fractions, allowing one to evaluate the linear impedance of the Josephson junction. When $\omega = 0$, Eqs. (3.33) and (3.36) yield the differential resistance of the junction $Z(0)/R = d\langle v \rangle_0 / dy$, Eq. (3.28), as they should.

Although Eqs. (3.33), and (3.36) are simple as far as numerical computation is concerned, their analytic form is rather cumbersome rendering a clear physical interpretation of the behaviour difficult, so that simplified equations are preferable. These may be obtained by using the effective eigenvalue method just as in the classical case [28]. The method yields a simple analytic expression for the impedance as we shall now illustrate. By substituting the perturbation expansion $c_n(t) = c_n^0 + c_n^1(t) + \dots$, where the superscript

denotes the power of the applied field, into Eq. (3.8) and replacing y by $y + y_m e^{-i\omega t}$, we obtain for $n = \pm 1$

$$\frac{d}{dt}c_{\pm 1}^1(t) + (1 \pm iby)c_{\pm 1}^1(t) = -\frac{b}{2}(1 + \Lambda)c_{\pm 2}^1(t) \mp iby_m c_{\pm 1}^0 e^{-i\omega t}. \quad (3.37)$$

Equation (3.37) is a differential-recurrence relation for the linear response, which is *not closed*. Nevertheless, by using the effective eigenvalue method (see Ref. [82] for details), we can rewrite Eq. (3.37) as two approximate *closed* ordinary differential equations

$$\frac{d}{dt}c_{\pm 1}^1(t) + \lambda_{\text{ef}}^{\pm} c_{\pm 1}^1(t) = \mp iby_m c_{\pm 1}^0 e^{-i\omega t}, \quad (3.38)$$

where $\lambda_{\text{ef}}^{\pm} = 1/\tau_{\text{ef}}^{(\pm 1)} = \lambda' \pm i\lambda''$ are a pair of effective eigenvalues and the effective relaxation times $\tau_{\text{ef}}^{(\pm 1)}$ are given in terms of continued fractions in Appendix 3.C. The steady state solution of Eq. (3.38) is given by the single-pole approximation

$$c_{\pm 1}^1 = \mp \frac{ibS_{\pm 1}}{\lambda_{\text{ef}}^{\pm} - i\omega} y_m e^{-i\omega t}, \quad (3.39)$$

where $S_{-1} = S_1^*$ are the equilibrium continued fraction solutions defined by Eq. (3.17). According to Eqs. (3.33) and (3.39), $1 - (c_{-1}^1 - c_1^1)/2i = Z(\omega)y_m e^{-i\omega t}/R$, so that we obtain the impedance $Z(\omega)$ in terms of the effective eigenvalues as

$$\frac{Z(\omega)}{R} = 1 - \frac{b}{2} \left(\frac{S_1}{\lambda_{\text{ef}}^+ - i\omega} + \frac{S_1^*}{\lambda_{\text{ef}}^- - i\omega} \right). \quad (3.40)$$

This expansion merely comprises two Lorentzians, representing damped oscillatory behaviour since $\lambda_{\text{ef}}^{\pm}$ is complex, and so is much simpler than the continued fraction solution rendered by Eq. (3.36). When $\omega = 0$, Eq. (3.40) again yields the correct value of the differential resistance of the junction $Z(0)/R = d\langle v \rangle_0 / dy$, Eq. (3.28). In the classical limit, one can also express the impedance of the junction $Z(\omega)$ in terms of the modified Bessel functions $I_\nu(z)$ using Eq. (3.20), yielding [82]

$$\frac{Z(\omega)}{R} = 1 - \frac{b}{2} \left[\frac{I_{1+iyb}(b)}{I_{iyb}(b)(\lambda_{\text{ef}}^+ - i\omega)} + \frac{I_{1-iyb}(b)}{I_{-iyb}(b)(\lambda_{\text{ef}}^{+*} - i\omega)} \right], \quad (3.41)$$

where λ_{ef}^+ is determined by Eq. (3.61) of Appendix 3.C.

The results for the impedance $Z(\omega)$ calculated from the approximate Eqs. (3.40) and (3.41) with the continued fraction solution [Eqs. (3.33), and (3.36)] are shown in Figs. 3.6 and 3.7. It is apparent by inspection that, the simple effective eigenvalue solution corresponds almost perfectly to the continued fraction solution for a wide range of the parameters y and b in both the classical and quantum cases. Moreover, it allows one to represent

the impedance of the junction $Z(\omega)$ by the simple analytic formula of Eq. (3.40), which merely constitutes a damped resonance with natural angular frequency λ'' and damping constant λ' , taking into account the effects of macroscopic tunnelling near the top of the barrier. We also remark that the deviations from the classical solution Eq. (3.41) predicted by the QSE are significant. The deviations are exemplified in Fig. 3.6, where for large b , corresponding to a large Josephson coupling energy, the resonant peak is considerably enhanced (i.e. we have a higher Q -factor) in comparison to the classical one. The reduction in the damping is particularly marked for large barriers and moderate tilts. This is corroborated by Figs. 3.8 and 3.9, where the real part of the effective eigenvalue is reduced due to the *dissipative tunnelling near the top of the barrier*. This phenomenon represents a decrease in the damping factor of the Josephson oscillations due to dissipative tunnelling so enhancing the resonant peak. However, the imaginary part of the effective eigenvalue or the resonant frequency remains substantially unaltered, again supporting the above conclusion. The nature of the ac response suggests that measurements of this response based on the behaviour of the Q factor may constitute a useful estimate of the role played by dissipative macroscopic quantum tunnelling in a Josephson junction. The situation should be mirrored in measurements [109] of ferromagnetic resonance in the dynamics of the magnetisation of fine single-domain ferromagnetic particles insofar as such experiments should also yield information concerning macroscopic tunnelling in these systems.

3.7 Concluding remarks

It has been demonstrated how the quantum Smoluchowski equation of Coffey *et al.* may be used to calculate quantum corrections to the various characteristics of the Josephson tunnelling junction in the zero capacitance and high temperature limits. One of the most useful conclusions is that for small values of the quantum parameter all the characteristics may be calculated using a three-term scalar recurrence relation essentially similar to that encountered in the classical solution. Thus in the first order of perturbation theory one may obtain analytic formulae very similar to those of the classical case. The quantum deviations from the classical result so produced are, however, detectable (see Fig. 3.6). The convergence of the perturbation method has been demonstrated by comparing the results for the dc characteristics in first and second order of perturbation theory. Thus it appears that the first-order approximation, which is relatively easy to compute, is valid for small values of the quantum parameter. We have also compared our results with those yielded by another form of the QSE, in which the drift as well as the diffusion coefficient

is altered, proposed by Ankerhold *et al.* [97] and subsequently used by other authors [96, 99, 101]. This equation, however, appears to predict unphysical results such as a *negative* resistance for zero voltage and *negative* differential resistance. Moreover, the equilibrium solution of this equation does not reduce to the Wigner configuration space equilibrium distribution. This appears to be a consequence of neglecting the p^2 term in the Wigner phase space distribution as already discussed in Ref. [30]. One must remark however, that in subsequent publications [79, 172] and in recent books [72, 110] the form of the QSE proposed by Coffey *et al.* has been accepted by Ankerhold [cf. his Eq. (6.121), p. 161, which is identical to Eq. (2.15)]. In other words, quantum effects should appear in the diffusion coefficient alone.

Finally, the treatment of the tilted cosine potential outlined here may be extended to the general inertial or nonzero capacitance case. In the classical limit, this has already been accomplished in Ref. [111], where the governing Klein-Kramers equation in phase space, giving rise to Brinkman's hierarchy of partial-differential recurrence relations (see § 2.5) in configuration space (which are now obtained rather than the Smoluchowski equation), has been solved using matrix continued fractions, yielding the escape rate and dynamic structure factor. Moreover, the results agree with Melnikov's [112] asymptotic expression for the escape rate for all values of the damping. These continued fraction calculations have been extended [74] to the quantum case using the semiclassical master equation (2.9) of Coffey *et al.* for zero tilt. The escape rate so calculated again agrees with Melnikov's asymptotic expression for the quantum escape rate [112, 113]. Thus it is clearly evident that with certain minor modifications, all these calculations could be applied to the evaluation of quantum effects in the characteristics of the Josephson junction including the capacitance. This of course corresponds to a solution valid for all damping ranges since the capacitance of the junction plays the role of inertia in the mechanical particle.

3.A Stationary matrix continued fraction solution of Eq. (3.8)

In the stationary state, we have from Eq. (3.8)

$$Q'_n C_n + Q_n'^- C_{n-1} + Q_n'^+ C_{n+1} + Q_n'' (C_{n-2} + C_{n+2}) = 0, \quad (3.42)$$

where $Q'_n = -(nb^{-1} + iy + nb\Lambda^2/5)$, $Q_n'^{\pm} = \mp [1 \pm n\Lambda \mp 3n\Lambda^2(1 \pm iby)/5] / 2$, and $Q_n'' = bn\Lambda^2/5$. In order to solve Eq. (3.42), we introduce the column vectors

$$C_{\pm n} = \begin{pmatrix} C_{\pm 2n} \\ C_{\pm(2n-1)} \end{pmatrix}, \quad C_n = C_{-n}^*,$$

and the single-element initial vector $C_0 = (1)$. Noting that $C_{-1} = C_1^*$, we rewrite Eq. (3.42) as the set of matrix *three-term* recurrence equations

$$Q_1^- C_0 + Q_1 C_1 + Q_1^+ C_2 = -F C_1^*,$$

$$Q_n^- C_{n-1} + Q_n C_n + Q_n^+ C_{n+1} = 0,$$

for $n = 1$ and $n > 1$, respectively, where the matrices Q_n and $Q_n^\pm$ are given by

$$Q_n = \begin{pmatrix} Q'_{2n} & Q'^-_{2n} \\ Q'^+_{2n-1} & Q'_{2n-1} \end{pmatrix}, \quad Q_n^+ = \begin{pmatrix} Q''_{2n} & Q'^+_{2n} \\ 0 & Q''_{2n-1} \end{pmatrix}, \quad Q_n^- = \begin{pmatrix} Q''_{2n} & 0 \\ Q'^-_{2n-1} & Q''_{2n-1} \end{pmatrix}$$

, with Q_1^- and F defined as

$$Q_1^- = \begin{pmatrix} Q''_2 \\ Q'^-_1 \end{pmatrix}, \quad F = \begin{pmatrix} 0 & 0 \\ 0 & Q''_1 \end{pmatrix}.$$

Thus the vectors C_n can be calculated via matrix continued fractions as [82]

$$C_1 = \Delta_1 (Q_1^- C_0 + F C_1^*), \quad (3.43)$$

$$C_n = \Delta_n Q_n^- \dots \Delta_2 Q_2^- C_1, \quad (3.44)$$

where Δ_n are the matrix continued fractions defined by the recurrence equation

$$\Delta_n = (-Q_n - Q_n^+ \Delta_{n+1} Q_{n+1}^-)^{-1}.$$

We represent the complex vectors and matrices in Eq. (3.43) as $C_1 = C'_1 + iC''_1$, $\Delta_1 Q_1^- = S'_1 + iS''_1$, and $\Delta_1 F = f + ig$. Equating the real and imaginary parts of Eq. (3.43), we obtain simultaneous equations for the unknowns C'_1 and C''_1 ,

$$(I - f)C'_1 - gC''_1 = S'_1 C_0, \quad (3.45)$$

$$(I + f)C''_1 - gC'_1 = S''_1 C_0, \quad (3.46)$$

where I is the unit matrix. On solving Eqs. (3.45) and (3.46) for C'_1 and C''_1 , we find

$$\mathbf{C}'_1 = [\mathbf{I} - \mathbf{f} - \mathbf{g}(\mathbf{I} + \mathbf{f})^{-1}\mathbf{g}]^{-1}[\mathbf{S}'_1 + \mathbf{g}(\mathbf{I} + \mathbf{f})^{-1}\mathbf{S}''_1]\mathbf{C}_0, \quad (3.47)$$

$$\mathbf{C}''_1 = [\mathbf{I} + \mathbf{f} - \mathbf{g}(\mathbf{I} - \mathbf{f})^{-1}\mathbf{g}]^{-1}[\mathbf{S}''_1 + \mathbf{g}(\mathbf{I} - \mathbf{f})^{-1}\mathbf{S}'_1]\mathbf{C}_0. \quad (3.48)$$

The dc characteristics determined from Eqs. (3.27), (3.28), (3.47), and (3.48) are plotted in Figs. 3.5(a) and 3.5(b). The matrix continued fraction algorithm presented can be applied to the calculation of the second-order correction in the linear impedance of the junction. Furthermore, it can be adapted to any desired order of Λ .

3.B Proof of Eq. (3.29)

We seek a perturbation solution of Eq. (3.15) as $C_n = C_n^{cl} + \Lambda C_n^1$. The recurrence equations for C_n^{cl} and C_n^1 become

$$Q_n C_n^{cl} + Q_n^+ C_{n+1}^{cl} + Q_n^- C_{n-1}^{cl} = 0, \quad (3.49)$$

$$Q_n C_n^1 + Q_n^+ C_{n+1}^1 + Q_n^- C_{n-1}^1 = n (C_{n+1}^{cl} + C_{n-1}^{cl}) / 2, \quad (3.50)$$

where Q_n and $Q_n^\pm$ are defined by Eq. (3.16). The solution of the homogeneous recurrence equation (3.49) is given by [82]

$$C_n^{cl} = S_n^{cl} S_{n-1}^{cl} \dots S_1^{cl} = I_{n+iyb}(b) / I_{iyb}(b),$$

where $S_n^{cl} = C_n^{cl} / C_{n-1}^{cl} = I_{n+iyb}(b) / I_{n-1+iyb}(b)$. This is easily proved by comparing the continued fraction S_n^{cl} , viz.

$$S_n^{cl} = \frac{1/2}{n/b + iy + S_{n+1}^{cl}/2}, \quad (3.51)$$

with the corresponding continued fraction for the modified Bessel functions $I_\nu(z)$, viz. [82]

$$\frac{I_\nu(z)}{I_{\nu-1}(z)} = \frac{1/2}{\nu/z + I_{\nu+1}(z) / [2I_\nu(z)]}, \quad (3.52)$$

which follows from the underlying recurrence relation for $I_\nu(z)$, viz. $I_{\nu-1}(z) - I_{\nu+1}(z) = (2\nu/z)I_\nu(z)$ [104]. By inspection, the continued fraction S_n^{cl} given by Eq. (3.51) is identical to Eq. (3.52) if $\nu = n + iyb$ and $z = b$. The solution of the inhomogeneous recurrence equation (3.50) for C_1^1 can be obtained by the standard methods described in [82] and is given by

$$\begin{aligned}
C_1^1 &= \sum_{n=1}^{\infty} (-1)^n n (C_{n+1}^{cl} + C_{n-1}^{cl}) \prod_{k=1}^n S_k^{cl} \\
&= \frac{1}{I_{iyb}^2(b)} \sum_{n=1}^{\infty} (-1)^n n I_{n+iyb}(b) [I_{n+1+iyb}(b) + I_{n-1+iyb}(b)].
\end{aligned}$$

Thus we obtain Eq. (3.29).

3.C The effective relaxation time and after-effect solution

Suppose that at a time $t = -\infty$ the tilt y is incremented by a small value Δ , where $b\Delta \ll 1$. This increment vanishes at $t = 0$. The relaxation functions $f_n(t) = c_n(t) - c_n(\infty)$ or after-effect solutions then obey the differential-recurrence relation

$$\frac{d}{dt} f_n(t) + (n^2 + inby) f_n(t) = \frac{bn}{2} [(1 - n\Lambda) f_{n-1}(t) - (1 + n\Lambda) f_{n+1}(t)]. \quad (3.53)$$

Equation (3.53) is valid only for $t > 0$. Now we could solve Eq. (3.53) exactly for the linear response, which in general comprises an infinite number of closely spaced exponential relaxation modes, using continued fractions, viz. $f_n(t) = \sum_k a_k^n e^{-t/\tau_k^{(n)}}$. However, the effective relaxation time method [82], whereby the multimodal response is represented by a single mode $f_n(t) \approx f_n(0) e^{-t/\tau_{\text{ef}}^{(n)}}$, which is complex, meaning that the effective relaxation functions display damped oscillatory behaviour, yields a close approximation to the exact solution at all times. In order to apply this method, it is supposed that, taking $n = 1$ for example,

$$f_1(t) = f_1(0) e^{-t/\tau_{\text{ef}}^{(1)}}.$$

Thus the normalised effective relaxation time τ_{ef}^1 is given by [82]

$$\tau_{\text{ef}}^1 = - f_1(t) / \dot{f}_1(t) \Big|_{t=0}. \quad (3.54)$$

An explicit evolution equation for $f_1(t)$ can be obtained from Eq. (3.53); we have

$$\frac{d}{dt} f_1(t) + (1 + iby) f_1(t) = -\frac{b}{2} (1 + \Lambda) f_2(t), \quad (3.55)$$

where we have noted that $f_0(t) = 0$. Equations (3.54) and (3.55) thus imply that the *effective* relaxation time is

$$\tau_{\text{ef}}^1 = \left[1 + iby + b(1 + \Lambda) \frac{f_2(0)}{2f_1(0)} \right]^{-1}. \quad (3.56)$$

Here $f_n(0) = c_n(0) - c_n(\infty)$ at $n = 1, 2$ can be evaluated in terms of continued fractions since the initial and final values $c_n(0)$ satisfy the recurrence relation

$$(Q_n - ib\Delta) c_n(0) + Q_n^+ c_{n+1}(0) + Q_n^- c_{n-1}(0) = 0, \quad (3.57)$$

while the final values $c_n(\infty)$ also satisfy Eq. (3.57) with $\Delta = 0$. Furthermore, as far as the linear response of the junction is concerned we are only interested in terms linear in Δ . Thus we may express the initial values $c_n(0)$ as a power series in the perturbation Δ , viz.

$$c_n(0) = c_n(\infty) + \Delta \partial_y c_n(0) + o(\Delta). \quad (3.58)$$

The derivatives $\partial_y c_n(0)$ must now be evaluated, which is done as follows. On substituting Eq. (3.58) into Eq. (3.57) and noting that $c_n(\infty)$ satisfies $Q_n c_n(\infty) + Q_n^+ c_{n+1}(\infty) + Q_n^- c_{n-1}(\infty) = 0$, we have the recurrence relations for $\partial_y c_n(0)$ as

$$Q_n \partial_y c_n(0) + Q_n^- \partial_y c_{n-1}(0) + Q_n^+ \partial_y c_{n+1}(0) = i c_n(\infty), \quad (3.59)$$

where $c_n(\infty)$ can be expressed [noting Eq. (3.18)] in terms of products of continued fractions as

$$c_n(\infty) = S_n S_{n-1} \dots S_1. \quad (3.60)$$

The solution of the inhomogeneous recurrence Eq. (3.59) for $\partial_y c_1(0)$ can be obtained by standard methods [82] and is given by [noting Eq. (3.60)]

$$\partial_y c_1(0) = 2i \sum_{n=1}^{\infty} \prod_{k=1}^n (Q_{k-1}^+ / Q_k^-) S_k^2.$$

Since $\partial_y c_2(0)$ can be obtained from Eq. (3.59) for $n = 1$ as

$$\partial_y c_2(0) = [i c_1(\infty) - Q_1 \partial_y c_1(0)] / Q_1^+,$$

the effective relaxation time from Eq. (3.56) is then

$$\tau_{\text{ef}}^{(1)} = \left[1 + iby + \frac{b}{2}(1 + \Lambda) \frac{\partial_y c_2(0)}{\partial_y c_1(0)} \right]^{-1} = i \frac{\partial_y c_1(0)}{b c_1(\infty)} = -\frac{2}{b S_1} \sum_{n=1}^{\infty} \prod_{k=1}^n (Q_{k-1}^+ / Q_k^-) S_k^2.$$

The effective relaxation time $\tau_{\text{ef}}^{(-1)}$ for $f_{-1}(t)$ is related to τ_{ef}^1 by $\tau_{\text{ef}}^{(-1)} = \tau_{\text{ef}}^{1*}$.

The behaviour of the real and imaginary parts of the inverse of the effective relaxation time $\lambda_{\text{ef}}^+ = 1/\tau_{\text{ef}}^1 = \lambda' + i\lambda''$ as a function of the barrier height b and bias parameter y is

illustrated in Figs. 3.8 and 3.9. In the classical limit, λ_{ef}^+ can be given in terms of modified Bessel functions of the first kind as

$$\lambda_{\text{ef}}^+|_{\Lambda=0} = \frac{b I_{iyb}(b) I_{1+iyb}(b)}{2 \int_0^b I_{iyb}(z) I_{1+iyb}(z) dz}. \quad (3.61)$$

The deviations from the classical equation (3.61) are appreciable as illustrated by Figs. 3.8 and 3.9.

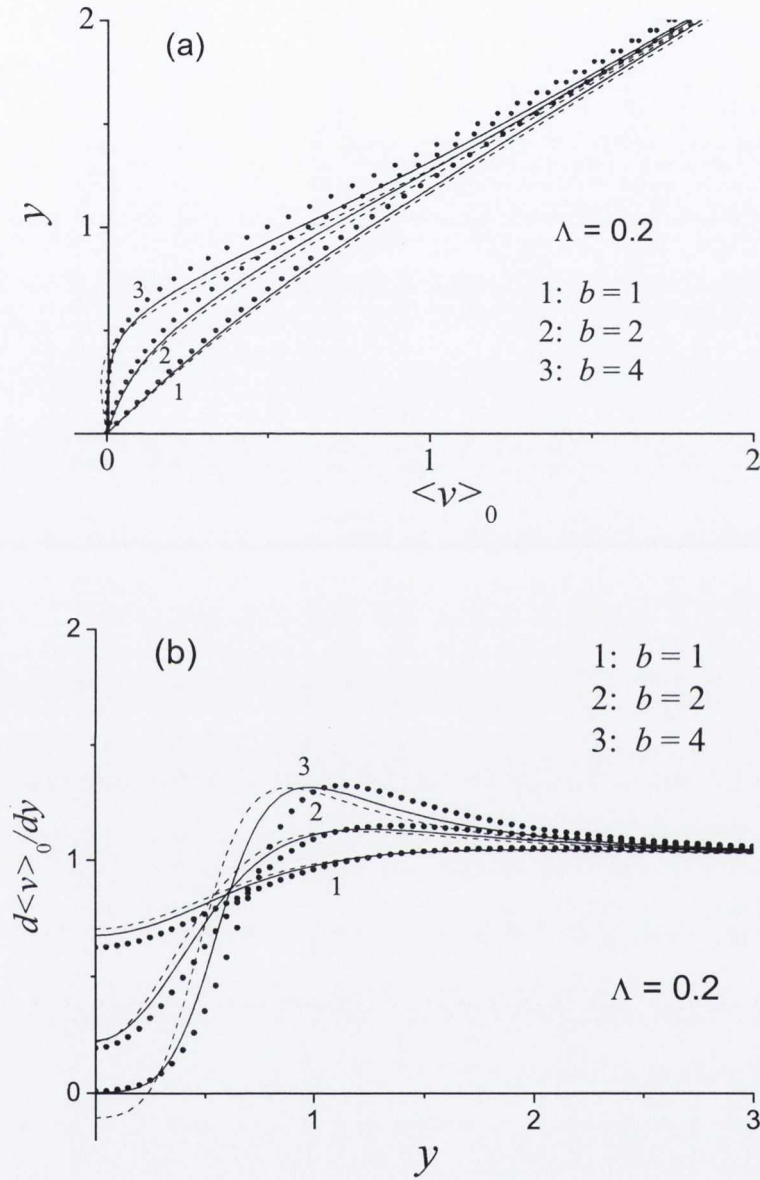


Figure 3.4: (a) Quantum effects on the current-voltage [Eq. (3.27)] and (b) differential resistance-current [Eq. (3.28)] characteristics of a Josephson junction in the presence of noise for $\Lambda = 0.2$ and various values of the Josephson coupling energy $b = 1, 2$, and 4 . Solid and dashed lines are the predictions of Eq. (2.15) and of the Ankerhold equation (3.9), respectively. Dots: classical limit $\Lambda = 0$.

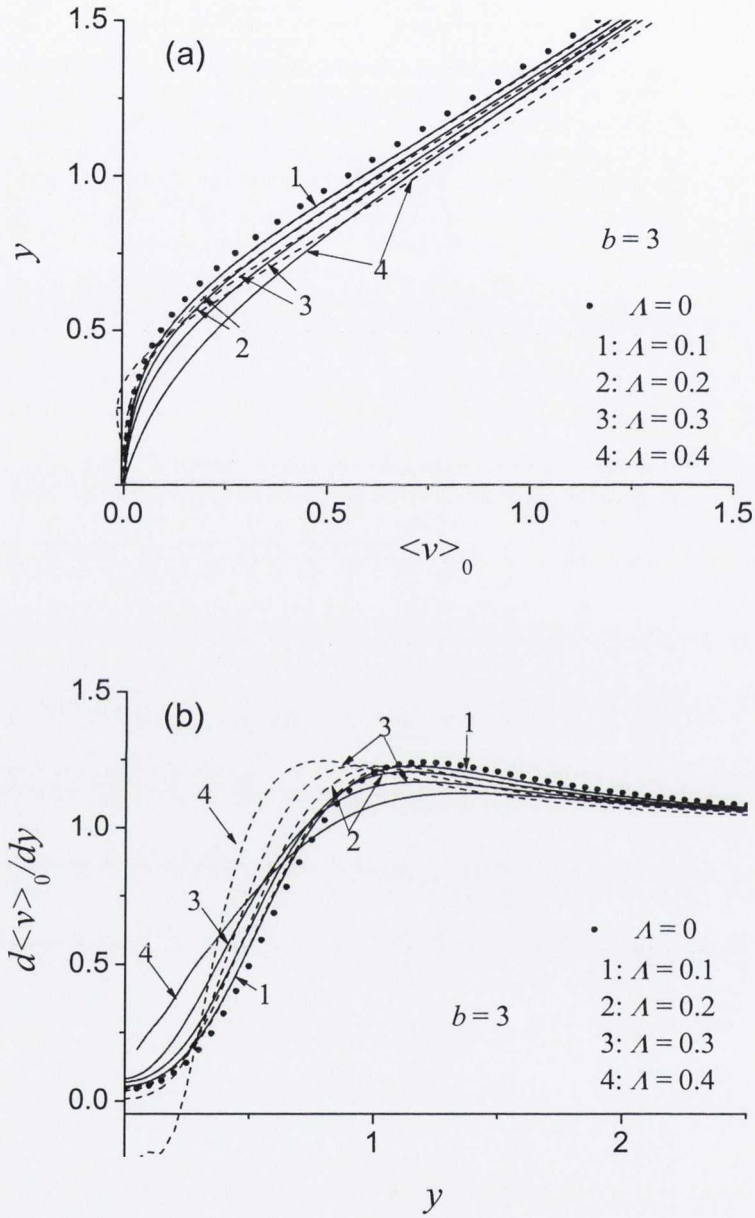


Figure 3.5: (a) Quantum effects on the current-voltage [Eq. (3.27)] and (b) differential resistance-current [Eq. (3.28)] characteristics of a Josephson junction in the presence of noise for $b = 3$ and various values of the quantum parameter $\Lambda = 0$ (dots; classical limit), 0.1 (curves 1), and 0.2 (curves 2), 0.3 (curves 3), and 0.4 (curves 4). Dashed and solid lines: first- and second-order corrections, respectively.

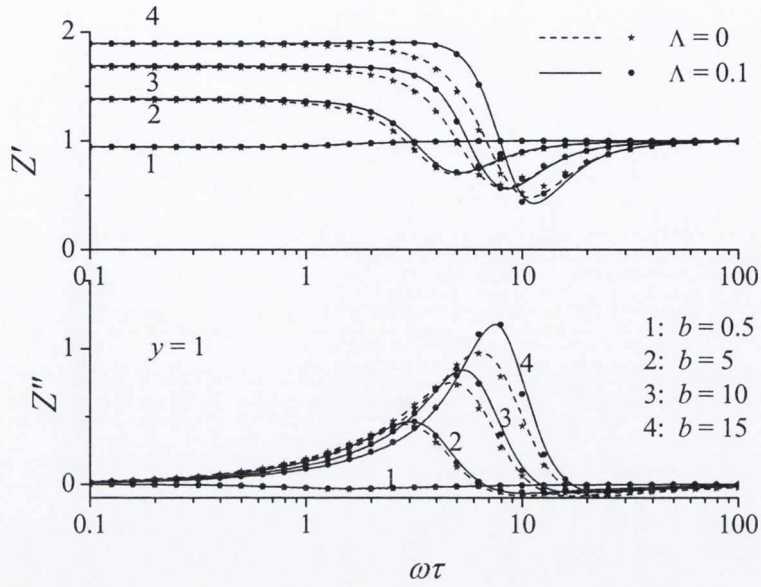


Figure 3.6: Quantum effects on the real and imaginary parts of the normalised impedance $Z = Z' - iZ''$ vs. normalised angular frequency $\omega\tau$ for various values of the Josephson coupling energy b . Comparison of the quantum (solid lines) and classical (dashed lines) solutions from Eq. (3.33), with the approximate solutions Eqs. (3.40) and (3.41) [stars and filled circles], respectively.

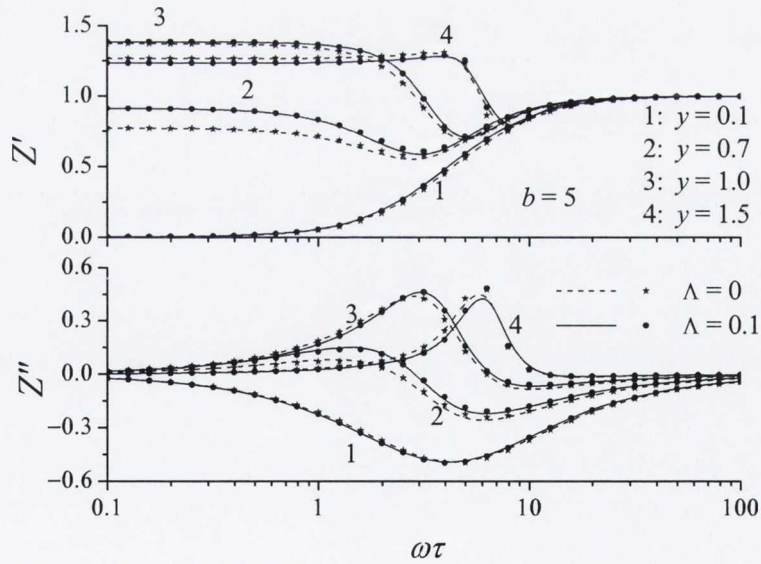


Figure 3.7: Quantum effects on the real and imaginary parts of the normalised impedance vs. $\omega\tau$ for various values of the tilt parameter $y = 0.1, 0.7, 1.0, 1.5$, and $b = 5$. Key as in Fig. 3.6

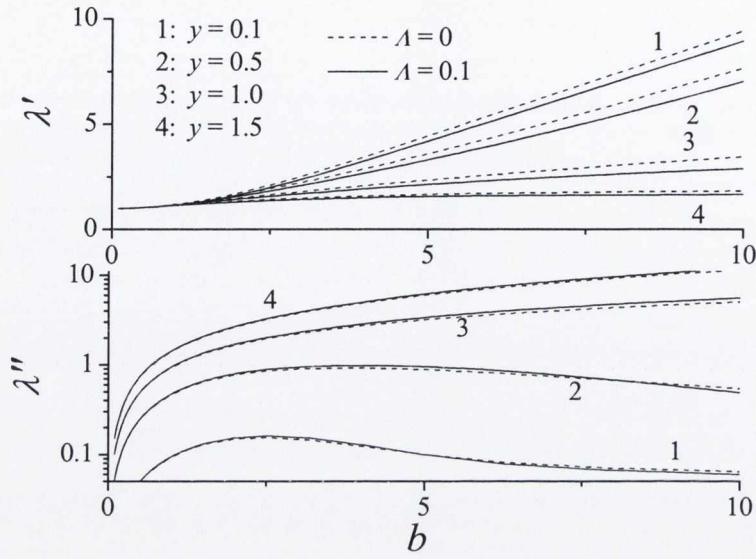


Figure 3.8: Quantum effects on the real and imaginary parts of the effective eigenvalue $\lambda_{\text{ef}}^+ = \lambda' + i\lambda''$ vs. b for various values of $y = 0.1, 0.5, 1.0$, and 1.5 . Solid and dashed lines are the predictions of Eq. (3.24) for $\Lambda = 0.1$ and $\Lambda = 0$ (classical limit), respectively.

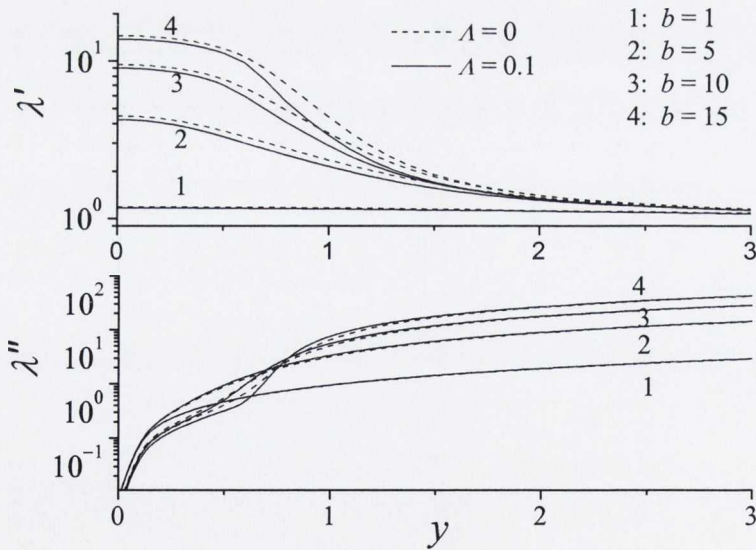


Figure 3.9: Quantum effects on the real and imaginary parts of the effective eigenvalue vs. y for various values of $b = 1, 5, 10$, and 15 . Key as in Fig. 3.8.

Chapter 4

The tilted cosine potential:

Nonlinear response

Quantum effects in the nonlinear response of the model point Josephson junction introduced in Chapter 3 (namely a resistively shunted junction (RSJ) model in the presence of noise) to a microwave ac driving current of *arbitrary* amplitude are estimated by considering the quantum Smoluchowski equation for the reduced Wigner function in configuration space (thus ignoring the capacitance of the junction). The solution of the resulting recurrence relations for the Fourier amplitudes of the statistical moments, describing the nonlinear dynamics of the junction (nonlinear microwave impedance, frequency dependence of the dc current-voltage characteristic, etc.), is obtained using the matrix continued fractions previously developed for the stationary ac field solution of the corresponding classical problem.

4.1 Introduction

Following directly on from Chapter 3, where quantum effects on the *linear* dynamics of a point Josephson junction in the zero capacitance limit [84, 85] were estimated using the resistively shunted junction (RSJ) model, the *nonlinear* dynamics are now considered.

Despite its limitations [84, 85], the RSJ model yields, for the *linear response* of the junction to an ac driving current, a relatively simple treatment of both the dc current-voltage characteristic and the impedance, both in the classical [84, 85, 118] and quantum [119] cases. In the quantum case, the dc current-voltage characteristic and the differential resistance may be expressed [119] as modified Bessel functions of the first kind just as in the classical limit [118]. Moreover, the linear impedance characteristic resembles that of a simple resonant (acceptor) circuit where the real part exhibits a pronounced minimum at the resonant frequency and the imaginary part a pronounced maximum. In particular, the quantum effects are discernible in the linear response as an enhanced current for a given voltage in the dc current-voltage characteristic and as an enhanced slope in the differential resistance which, besides the impedance, are the other quantities of physical interest [119].

As far as the dc characteristics in the linear regime are concerned, the quantum effects arise [119] due to *high temperature non-dissipative tunnelling near the top of a barrier* and are readily detectable for a relatively large supercurrent and small bias. This behaviour is due to the effective reduction of the barrier height, associated with a well of the inclined washboard potential, due to tunnelling near the top of a barrier. This barrier lowering mechanism was originally identified by Wigner in his quantum transition state theory [52, 90], based on the closed Wigner-Moyal equation (see § 1.5), which of course ignores the dissipation to the bath. On the other hand, in the resonant peak in the impedance curve, the quantum effects manifest themselves essentially [119] as an enhancement of the Q -factor, which is an example of *dissipative tunnelling* reducing the damping of the Josephson oscillations near the top of a barrier.

However, the restriction of the treatment of the Josephson junction to linear response means that many important features of both the dc and the ac microwave behaviour cannot be reproduced. For example, in the dc response these include the ubiquitous Shapiro steps [91] in the obviously time-independent (but frequency-dependent) dc current-voltage characteristics. The steps are due to dynamical phase slips caused by change of the phase locking of the Josephson oscillator at multiple harmonics of the frequency of the applied ac current as that current is increased. This behaviour constitutes a form of modulation

due to *nonlinear* effects. Other non-reproducible effects include the manifold oscillations (see, e.g. Refs. [60, 82, 120] and references cited therein) appearing in the reactive part of the nonlinear impedance (again due to dynamical phase slips) and the threshold points and saturation behaviour of the resistive part, whereby the dynamic resistance approaches the shunt resistance of the junction. Hitherto, the nonlinear ac response (mainly, the microwave resistance and reactance) to a strong probing ac current has usually been calculated via perturbation theory (e.g. Ref. [82]). However, this approach is valid for small ac current amplitudes only, or in the noiseless limit, where the governing nonlinear equation of motion can be solved numerically [60, 120].

As far as experimental observations are concerned, nonlinear effects in the microwave resistance have been presented and explained (using the classical RSJ model) in Refs. [60] and [121]. Experimental data [122] on the nonlinear microwave surface impedance Z_s of high temperature superconducting thin films have also been interpreted [123, 125] using the classical RSJ model and qualitative agreement with experimental measurements of Z_s has been reported, showing that these systems also behave like a Josephson junction. Moreover, the RSJ model can also describe the main features of the nonlinear surface impedance, namely the steps in the ac current dependence of the resistance [82, 91], the threshold points and saturation [124, 125]. Amongst other experiments, which can be analysed using the classical RSJ model, are microwave absorption measurements in weak-link Josephson junctions [126] in high- T_c superconductors, where the microwave surface resistance R_s is studied. Furthermore, as shown in Ref. [126], the numerical solution of the nonlinear dynamical equation governing the *noiseless* RSJ model agrees closely with experiment. Finally, the nonlinear ac response of a point Josephson junction in the presence of noise has been evaluated in Refs. [127] and [128] using the matrix continued fraction technique.

Mindful of the several distinctive features of the nonlinear stationary response, summarised above, the purpose of this chapter is to extend the calculations of the classical nonlinear stationary response [131, 132], to the *quantum* nonlinear stationary response in the zero capacitance limit. This will be accomplished by solving the QSE (2.15) for the nonlinear stationary ac response in a tilted cosine potential for an ac driving current of *arbitrary* amplitude, using the matrix continued fraction method as developed in Refs. [131, 132] for the corresponding classical problem. In particular, we shall calculate the nonlinear impedance and the frequency-dependent dc current-voltage characteristics, noting that certain aspects of quantum effects in the characteristics of Josephson junctions have already been analysed, e.g. in Refs. [92, 129–132]. We remark that a matrix con-

tinued fraction is invariably involved in the solution of the nonlinear response rather than the scalar continued fraction of the linear response (see § 3.A). This is so because the distribution function for the phase variable must now be expanded in a double Fourier series in both space and time, because of the coupling between the time varying harmonic components of the driving force induced by the nonlinearity. This behaviour is of course not evident in the linear response approximation where the ac response is simply the stimulus shifted in amplitude and phase (so that no harmonics of the stimulus occur) along with a dc response independent of the ac response.

4.2 QSE for the RSJ model

We now apply the QSE (2.15) to evaluate quantum corrections to the nonlinear non-inertial response to a strong ac force $f \cos \omega t$ of a Brownian particle moving in a tilted cosine (or inclined washboard) potential with amplitude V_0 , characteristic length a and constant tilt (slope) F , viz.

$$V(x) = -V_0 \cos(2\pi x/a) - xF - xf \cos \omega t. \quad (4.1)$$

In addition to the normalised variables given by (3.4) we introduce the dimensionless ac current amplitude

$$\xi = \frac{af}{2\pi V_0},$$

so that the potential (4.1) for the Brownian particle subject to an applied ac current in the dimensionless variables is

$$V(x) = -b[\cos x + x(y + \xi \cos \omega t)]. \quad (4.2)$$

In application to the RSJ model of a point Josephson junction, the applied current (shown as I_{dc} in Fig. 3.2) now consists of a dc current I_{dc} and an ac current $I_m \cos \omega t$ of arbitrary amplitude I_m . Hence $b = \hbar I \beta / (2e)$ is the normalised Josephson coupling energy (the parameter b also characterises the noise strength), $y = I_{dc}/I$ and $\xi = I_m/I$ are the ratios of the dc and ac current amplitudes to the supercurrent amplitude (tilt and nonlinear parameters). Thus in the present context, treating the nonlinear dynamics of a point Josephson junction in the zero capacitance limit is formally equivalent to describing a Brownian particle moving along the x -axis in a tilted cosine potential in the non-inertial limit. Thus, using the dimensionless variables (3.4), the QSE for the reduced Wigner function in configuration space $P(x, t)$ is

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left\{ V' P + \frac{\partial}{\partial x} \left[1 + \Lambda V'' - \frac{\Lambda^2}{5} (V''^2 + 3V'V^{(3)} - 3V^{(4)}) \right] P \right\}, \quad (4.3)$$

where the dimensionless potential is given by Eq. (4.2).

4.3 Nonlinear response: Matrix continued fraction solution

In order to calculate the nonlinear impedance of the Josephson junction from the QSE, we note that the spatially periodic function $P(x, t)$ can be expanded in a Fourier series in x [7, 118], viz.

$$P(x, t) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} c_n(t) e^{inx}. \quad (4.4)$$

By substituting Eq. (4.4) into the QSE (4.3), we find that the Fourier coefficients (statistical moments) $c_n(t) = \langle e^{-inx} \rangle(t)$ satisfy the five-term differential recurrence relation to second order in the quantum correction parameter Λ

$$\begin{aligned} \frac{d}{dt} c_n(t) &+ \left[n^2 + \frac{(bn\Lambda)^2}{5} + inb(y + \xi \cos \omega t) \right] c_n(t) \\ &= \frac{bn}{2} [(1 - n\Lambda)c_{n-1}(t) - (1 + n\Lambda)c_{n+1}(t)] \\ &+ \frac{bn^2\Lambda^2}{10} \left\{ 2bc_{n-2}(t) + 3[1 - ib(y + \xi \cos \omega t)] c_{n-1}(t) \right. \\ &\left. + 3[1 + ib(y + \xi \cos \omega t)] c_{n+1}(t) + 2bc_{n+2}(t) \right\}. \end{aligned} \quad (4.5)$$

Setting the ac amplitude $\xi = 0$, the recurrence relation (4.5) of course reduces to Eq. (3.8). Equation (4.5) may also be obtained directly from the appropriate quantum Langevin equation by averaging that equation over its realisations in configuration space, as is illustrated in Appendix 4.A.

Considering the nonlinear *stationary* ac response only, where the ac has been applied for a very long time, one may seek a solution independent of the initial conditions. Thus the time-dependent coefficients $c_n(t)$ may be expanded as [84, 85]

$$c_n(t) = \sum_{k=-\infty}^{\infty} c_n^k(\omega) e^{ik\omega t}, \quad (4.6)$$

accounting for the infinite number of harmonics of the stimulus produced by the nonlinear characteristics of the junction. The Fourier coefficients have the following properties

$c_n^k(\omega) = c_{-n}^{k*}(-\omega) = c_{-n}^{-k*}(\omega)$ arising ultimately from the fact that $P(x, t)$ must be real (asterisk denotes complex conjugate). By substituting Eq. (4.6) into Eq. (4.5), we have the dual-index algebraic recurrence relation for the Fourier amplitudes $c_n^k(\omega)$, viz.

$$\begin{aligned} & i z_n^k(\omega) c_n^k(\omega) + q_n^+ c_{n+1}^k(\omega) + q_n^- c_{n-1}^k(\omega) \\ & + \bar{q}_n [c_{n-2}^k(\omega) + c_{n+2}^k(\omega)] + i \xi \{c_n^{k-1}(\omega) + c_n^{k+1}(\omega) \\ & - (3/4) \bar{q}_n [c_{n-1}^{k-1}(\omega) + c_{n-1}^{k+1}(\omega) - c_{n+1}^{k-1}(\omega) - c_{n+1}^{k+1}(\omega)] \} = 0, \end{aligned} \quad (4.7)$$

where n and k are integers varying from $-\infty$ to ∞ , $c_0^0(\omega) = 1$, $c_0^k(\omega) = 0$ ($k > 0$), and

$$z_n^k(\omega) = 2 \left(\frac{k\omega}{nb} - \frac{in}{b} + y - \frac{ibn\Lambda^2}{5} \right),$$

$$q_n^\pm = \pm [1 \pm n\Lambda \mp 3n\Lambda^2(1 \pm iby)/5],$$

$$\bar{q}_n = -2bn\Lambda^2/5.$$

Thus, invoking the familiar general matrix continued fraction method for solving multi-index recurrence relations generated by Fokker-Planck equations [7, 118], one may obtain the solution of the differential recurrence equation (4.7) (details of this solution are given in Appendix 4.B).

An intrinsic feature of the nonlinear response is the modulation of the dc current-voltage characteristic giving rise, for example, to the famous Shapiro steps originating in the phase locking. Here, the *time-independent* but *frequency-dependent* dimensionless average dc voltage $\langle v \rangle$ in the presence of an alternating force $\xi \cos \omega t$ is given by

$$\langle v \rangle = y + \text{Im}\{c_1^0(\omega)\}, \quad (4.8)$$

while the *nonlinear* impedance is given by [recalling that $c_{-1}^k(\omega) = c_1^{k*}(-\omega)$]

$$Z(\omega) = R_\omega - iX_\omega = R \{1 - i\xi^{-1} [c_1^1(\omega) - c_1^{1*}(-\omega)]\}, \quad (4.9)$$

where R_ω and X_ω are the dynamic resistance and the reactance, respectively. One immediately recognises the similarity between Eqs. (4.8) and (4.9), and their *linear* counterparts Eqs. (4.8) and (3.33) considered in Chapter 3.

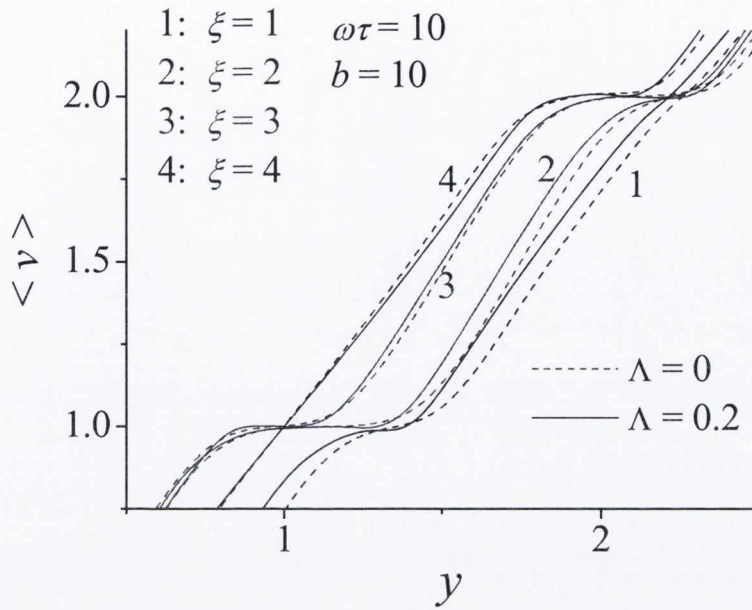


Figure 4.1: Averaged dc voltage $\langle v \rangle$ vs normalised dc bias current amplitude $y = I_{dc}/I$ for various values of the normalised ac amplitude $\xi = I_m/I$, fixed frequency $\omega\tau = 10$, and coupling energy $b = 10$ showing the stimulus induced Shapiro steps for classical (dashed lines) and quantum (solid lines $\Lambda = 0.2$) cases.

4.4 Results and discussion

In Fig. 4.1 we show the averaged dc voltage $\langle v \rangle$ versus the normalised dc bias current y for fixed dimensionless frequency $\omega\tau$ and coupling energy b , showing the stimulus-induced Shapiro steps, occurring at integer multiples of the fundamental frequency due to dynamical phase slips, and the difference between the quantum and classical results. In Fig. 4.2 we show the average frequency-dependent dc voltage $\langle v \rangle$ for various values of the applied ac current ξ . The effect of nonlinearity is to modulate the dc response, i.e. to induce large frequency-dependent troughs and peaks in the previously constant curve of the dc voltage vs. normalised frequency $\omega\tau$ characteristic of the linear response. In other words *the time-dependent response now affects the dc response*. In general, the effect of the quantum corrections for the ac amplitude between 0.1 and 1.0 is to *enhance* the troughs and peaks in the response. However, as the amplitude of the driving current increases above unity the quantum effects decrease so that the quantum curves are very close to the corresponding classical curves, except at high frequencies, where the quantum peaks decrease more slowly. Thus it appears in this instance that *relatively large* nonlinear effects will *mask* the quantum effects. The enhancement of the nonlinear effects at intermediate

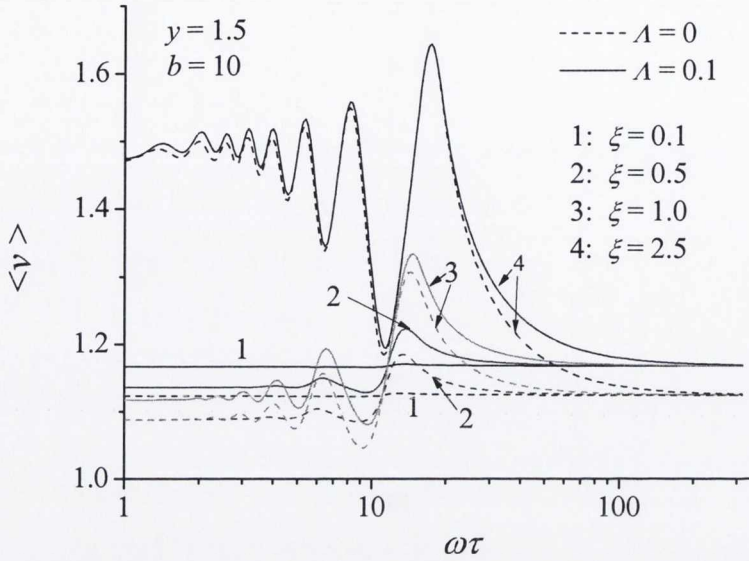


Figure 4.2: Averaged dc voltage $\langle v \rangle$ vs dimensionless frequency ω for various values of the applied ac stimulus ξ for classical (dashed lines) and quantum (solid lines) cases. Strong nonlinearity, corresponding to large ξ , causes pronounced oscillatory behaviour of the dc voltage with numerous frequency-dependent troughs and peaks as opposed to the smooth behaviour associated with the linear response. The quantum effects, which are most pronounced at intermediate ξ (curves 1, 2, and 3), comprising an increase in amplitude of the extrema and a shift of these to higher frequencies, diminish as ξ increases (curve 4).

amplitudes of the applied current is also evident in Fig. 4.3, where for all coupling energies the quantum effects (solid lines) enhance the relative heights of the classical peaks and troughs (dashed lines) and also cause a shift of these extrema towards higher frequencies. This behaviour appears to be entirely consistent with the enhancement of the Q -factor caused by dissipative quantum tunnelling near the top of the barrier (reducing the damping of the Josephson oscillations) in the linear response impedance characteristic [119] and is an example of how dissipative tunnelling can now affect the dc characteristics.

The convergence of the perturbation procedure in Λ is demonstrated in Fig. 4.4 by comparing the first and second order of perturbation theory solutions. Here we show the averaged dc voltage vs. frequency for various values of Λ to first (dashed lines) and second (solid lines) order in Λ , showing that the quantum effects invariably enhance the troughs and peaks (the dotted line corresponds to the classical solution, i.e. the recurrence Eq. (4.5) ignoring all quantum terms). Clearly, the first-order perturbation solution closely

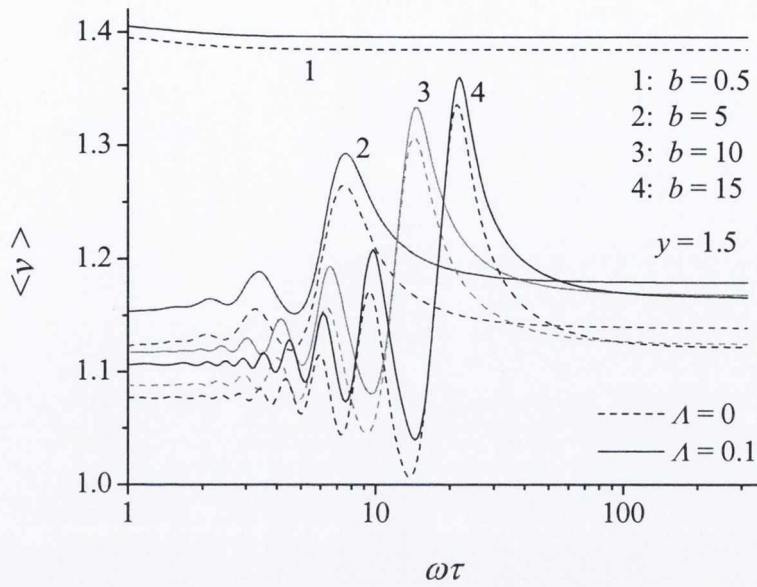


Figure 4.3: $\langle v \rangle$ vs frequency for various values of the normalised Josephson coupling energy b (or noise strength) and ac strength $\xi = 1$; classical (dashed lines) and quantum (solid lines) results. The quantum effects enhance the nonlinear behaviour for all values of b

approximates the second-order one for small values of $\Lambda < 0.2/b$. Moreover, inclusion of the second order term is essential for the calculations at higher values of Λ , as is obvious in curve 3. Another interesting point concerning Fig. 4.4 is that the main peak in the frequency curve is so enhanced in comparison to the classical case as to be experimentally detectable. Furthermore, its height is rather sensitive to Λ , as is again obvious from curve 3 of Fig. 4.4. We remark that the diffusion coefficient $D(x)$ in Eq. (4.3) is written explicitly to $\mathcal{O}(\Lambda^2)$ and that the greater the values of Λ and b , the higher the order of perturbation theory required. Higher order correction terms to the diffusion coefficient $D(x)$ may be calculated as described in Ref. [119]. Thus, the QSE Eq. (2.15) can be given, in principle, to any desired degree r of Λ^r .

In Fig. 4.5 we show the normalised dynamic resistance R_ω/R and reactance X_ω/R versus the driving amplitude ξ for various dc bias current amplitudes y ($b = 10$, $\omega = 5$). The results display strong nonlinearity for small bias and Ohmic-resistance-like behaviour for high bias. Again, little difference is apparent between the classical and quantum corrected curves for high driving amplitudes ξ , demonstrating that quantum effects are most pronounced in the linear region (small ξ) being negligible for large ξ , showing once again how nonlinear effects mask the quantum effects for large ξ . This is corroborated in Fig. 4.6,

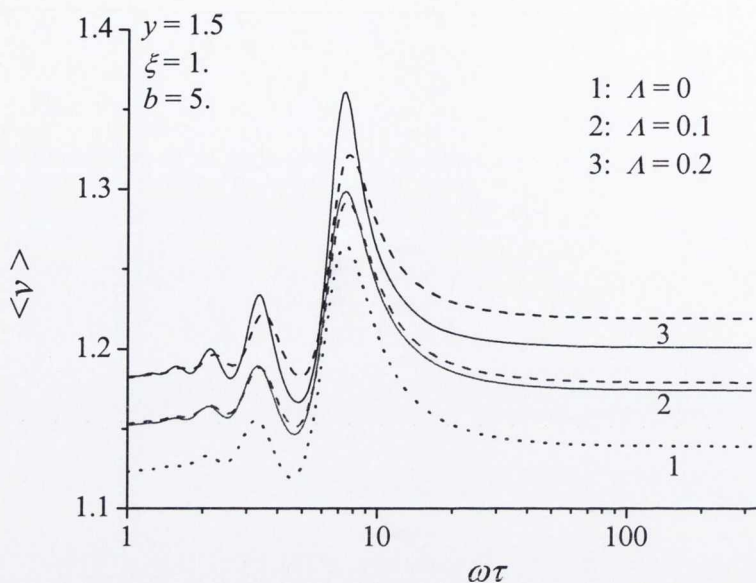


Figure 4.4: $\langle v \rangle$ vs $\omega\tau$ for various values of the quantum correction parameter Λ to first- (dashed lines) and second- (solid lines) order quantum corrections in Λ showing throughout that the quantum effects emphasise the troughs and peaks. Dotted line: classical limit, $\Lambda = 0$. Inclusion of the second order term is essential for higher values of $\Lambda = 0.2$ (curve 3).

where again the quantum effects are most obvious in the linear response region $\xi = 0.01$. On increasing ξ , that is, proceeding from the linear region to the nonlinear region, one also perceives masking by the nonlinearity, which is evident in Fig. 4.7.

To conclude, it has been demonstrated how the QSE may be used to calculate quantum corrections to the nonlinear impedance and current-voltage characteristics of the Josephson tunnelling junction in the zero capacitance limit, by evaluating the ac nonlinear response in the presence of noise for wide ranges of the noise strength b , the dc bias current y and the nonlinearity ξ . In order to obtain these results, we have solved the QSE using matrix continued fractions, allowing us to determine various characteristics of the non inertial Brownian motion in a tilted cosine potential in the presence of a large ac driving force. Finally, the treatment outlined here may be extended to the general inertial (or nonzero capacitance) case. The zero capacitance or high damping (non-inertial) limit used in the present paper automatically restricts the band of frequencies in which the model is applicable to frequencies much less than the Josephson plasma frequency [84, 85]. If one wishes to treat accurately the GHz and THz regions, the complete phase space distribution $W(x, p, t)$ must be used, giving rise [7, 31, 74, 118] on expansion of the momentum part

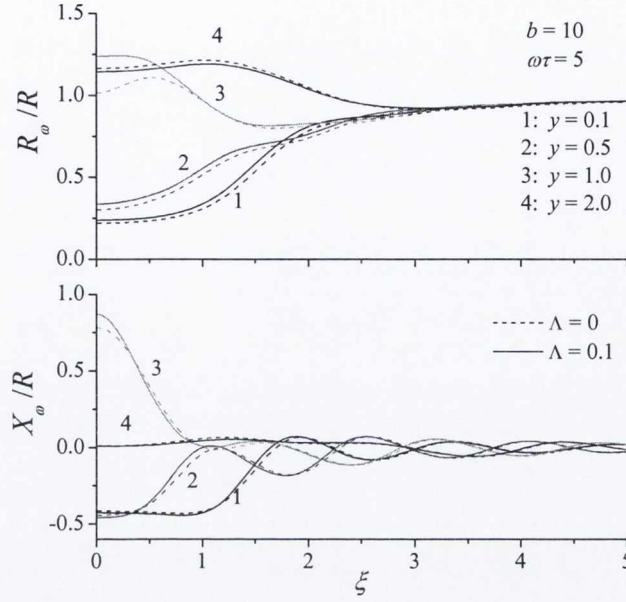


Figure 4.5: Normalised dynamic resistance R_ω/R and reactance X_ω/R vs applied ac stimulus amplitude ξ for various dc bias current amplitudes y and $b = 10$, $\omega\tau = 5$, showing strong nonlinearity for small bias and ohmic-resistance-like behaviour for high bias.

of the distribution in orthogonal Hermite polynomials, to a *hierarchy* of partial differential recurrence relations in configuration space. The actual configuration space distribution $P(x, t)$ must then be extracted from the hierarchy, usually by continued fractions, with the much simpler QSE naturally emerging [30, 31, 74] from the hierarchy in the high damping limit as originally demonstrated by Brinkman for the classical case [102].

4.A Derivation of Eq. (4.5) directly from the quantum Langevin equation

By way of illustration of the Langevin equation method of generating the hierarchy of differential-recurrence relations for the statistical moments we shall demonstrate how averaging of the semiclassical non-inertial Langevin equation over its realisations yields the same hierarchy of equations as the QSE. The Langevin equation corresponding to Eq. (2.15) in the Stratonovich interpretation [133] for the random variable $x(t)$ reads

$$\dot{x}(t) = -\frac{1}{\zeta} \partial_x \left\{ V[x(t)] + \frac{\zeta}{2} D[x(t)] \right\} + \sqrt{\frac{\beta}{\zeta}} D[x(t)] L(t), \quad (4.10)$$

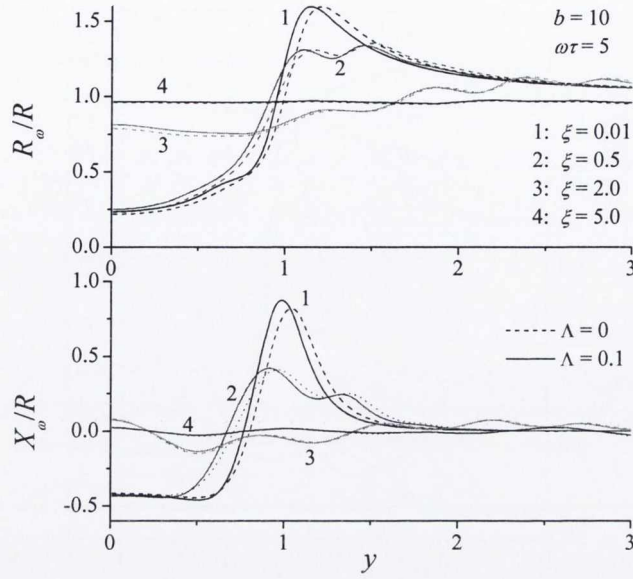


Figure 4.6: Normalised dynamic resistance R_ω/R and reactance X_ω/R vs the dc bias amplitude y for various ac amplitudes ξ and $b = 10$, $\omega\tau = 5$, showing relatively strong quantum effects for small stimuli (curve 1) indicating that the quantum behaviour depends more strongly on the dc bias for small ac amplitudes than relatively large ones (curves 3 and 4).

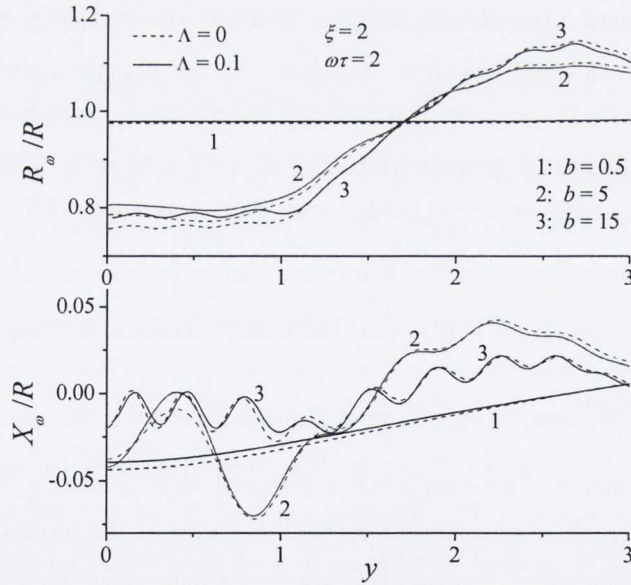


Figure 4.7: Normalised dynamic resistance R_ω/R and reactance X_ω/R vs the dc bias amplitude y for various Josephson coupling energies b and $\xi = 2$, $\omega = 2$, showing that the quantum effects are relatively small compared to the nonlinear ones. Dashed and solid lines are the classical and quantum results, respectively.

where the dot denotes the time derivative and $L(t)$ is a random force with Gaussian white noise properties, viz.

$$\overline{L(t)} = 0, \quad \overline{L(t)L(t')} = \frac{2kT}{R}\delta(t - t').$$

However, one must remember that the quantum Langevin equation is written down from *a priori* knowledge of the QSE, which is *dissimilar* to the situation encountered in the classical case. There the Langevin equation is written down independently of either the Fokker-Planck or Smoluchowski equation and the results of the two methods only coincide as a consequence of the Gaussian white noise properties of $L(t)$, particularly Isserlis's theorem (Wick's theorem) [118] is satisfied. This theorem allows multiple time correlations of Gaussian random variables to be expressed as two time correlations. Now $x(t)$ is governed by the Langevin equation (4.10), which contains a multiplicative noise term and is of the standard classical form [7]

$$\dot{x}(t) = h[x(t)] + g[x(t)]L(t). \quad (4.11)$$

The corresponding Langevin equation for the evolution of an *arbitrary* function $f[x(t)]$ whose expectation value we wish to calculate is then

$$\dot{f}[x(t)] = h[x(t)]\frac{d}{dx}f[x(t)] + g[x(t)]\frac{d}{dx}f[x(t)]L(t). \quad (4.12)$$

Here we have noted that in the transformation of variables in a Stratonovich stochastic differential equation, one can apply the usual rules of calculus [7, 118]. Next, we recall the theorem [7, 118] that the averaged evolution equation for a function $f[x(t)]$ is given by

$$\frac{d}{dt}\langle f(x) \rangle = \left\langle h(x)\frac{d}{dx}f(x) \right\rangle + \frac{2kT}{R}\left\langle g(x)\frac{d}{dx}\left[g(x)\frac{d}{dx}f(x)\right] \right\rangle. \quad (4.13)$$

Hence, with

$$f[x(t)] = e^{-inx(t)}, \quad (4.14)$$

Eq. (4.13) with the potential Eq. (4.2) yields the recurrence equation (4.5) for $c_n(t) = \langle e^{-inx(t)} \rangle$.

4.B Matrix continued fraction solution of Eq. (4.7)

The dual-index scalar five-term recurrence relation, Eq. (4.7), can be rewritten in terms of solvable matrix three-term recurrence relations as

$$\mathbf{Q}_1^- \mathbf{C}_0 + \mathbf{Q}_1 \mathbf{C}_1 + \mathbf{Q}_1^+ \mathbf{C}_2 = -\mathbf{F} \mathbf{C}_1^*, \quad (4.15)$$

and

$$\mathbf{Q}_n^- \mathbf{C}_{n-1} + \mathbf{Q}_n \mathbf{C}_n + \mathbf{Q}_n^+ \mathbf{C}_{n+1} = 0. \quad (4.16)$$

Here the column vectors $\mathbf{C}_{\pm n}$ are

$$\mathbf{C}_0 = (\mathbf{c}_0), \quad \mathbf{C}_{\pm n} = \begin{pmatrix} \mathbf{c}_{\pm 2n} \\ \mathbf{c}_{\pm(2n-1)} \end{pmatrix}, \quad n = \pm 1, \pm 2, \dots,$$

$$\mathbf{c}_0 = \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}, \quad \mathbf{c}_n = \begin{pmatrix} \vdots \\ c_n^{-1}(\omega) \\ c_n^0(\omega) \\ c_n^1(\omega) \\ \vdots \end{pmatrix},$$

the supermatrices $\mathbf{Q}_n$, $\mathbf{Q}_n^\pm$ and $\mathbf{F}$ are given by

$$\mathbf{Q}_n = \begin{pmatrix} \mathbf{q}_{2n} & \mathbf{q}_{2n}^- \\ \mathbf{q}_{2n-1}^+ & \mathbf{q}_{2n-1} \end{pmatrix}, \quad \mathbf{Q}_n^+ = \begin{pmatrix} \bar{\mathbf{q}}_{2n} \mathbf{i} & \mathbf{q}_{2n}^+ \\ 0 & \bar{\mathbf{q}}_{2n-1} \mathbf{i} \end{pmatrix}, \quad \mathbf{Q}_n^- = \begin{pmatrix} \bar{\mathbf{q}}_{2n} \mathbf{i} & 0 \\ \mathbf{q}_{2n-1}^- & \bar{\mathbf{q}}_{2n-1} \mathbf{i} \end{pmatrix}$$

with

$$\mathbf{Q}_1^- = \begin{pmatrix} \bar{\mathbf{q}}_2 \mathbf{i} \\ \mathbf{q}_1^- \end{pmatrix} \quad \text{and} \quad \mathbf{F} = \begin{pmatrix} 0 & 0 \\ 0 & \bar{\mathbf{q}}_1 \mathbf{f} \end{pmatrix},$$

where $\mathbf{i}$ denotes the unit matrix, and $\mathbf{f}$ is given by

$$\mathbf{f} = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \dots & 0 & 0 & 1 & \dots \\ \dots & 0 & 1 & 0 & \dots \\ \dots & 1 & 0 & 0 & \dots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{q}_n = i \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & z_n^{-1}(\omega) & \xi & 0 & \cdots \\ \cdots & \xi & z_n^0(\omega) & \xi & \cdots \\ \cdots & 0 & \xi & z_n^1(\omega) & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{q}_n^\pm = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & q_n^\pm & \pm 3i\xi\bar{q}_n/4 & 0 & \cdots \\ \cdots & \pm 3i\xi\bar{q}_n/4 & q_n^\pm & \pm 3i\xi\bar{q}_n/4 & \cdots \\ \cdots & 0 & \pm 3i\xi\bar{q}_n/4 & q_n^\pm & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

Thus, the column vectors $\mathbf{C}_n$ can be calculated from Eqs. (4.15) and (4.16) via matrix continued fractions as the matrix products [118]

$$\mathbf{C}_n = \mathbf{S}_n \mathbf{S}_{n-1} \cdots \mathbf{S}_2 \mathbf{C}_1, \quad (4.17)$$

$$\mathbf{C}_1 = \mathbf{S}_1 \mathbf{C}_0 + \Delta_1 \mathbf{F} \mathbf{C}_1^*, \quad (4.18)$$

where $\mathbf{S}_n$ and Δ_1 are matrix continued fractions defined by the recurrence equation

$$\mathbf{S}_n = (-\mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{S}_{n+1})^{-1} \mathbf{Q}_n^-,$$

$$\Delta_n = (-\mathbf{Q}_n - \mathbf{Q}_n^+ \Delta_{n+1} \mathbf{Q}_{n+1}^-)^{-1}.$$

Next we introduce complex vectors and matrices via

$$\mathbf{C}_1 = \mathbf{C}'_1 + i\mathbf{C}''_1, \quad \mathbf{S}_1 = \mathbf{S}'_1 + i\mathbf{S}''_1, \quad \Delta_1 \mathbf{F} = \mathbf{F}' + i\mathbf{F}'',$$

so that we have from Eq. (4.18)

$$(\mathbf{I} - \mathbf{F}')\mathbf{C}'_1 - \mathbf{F}''\mathbf{C}''_1 = \mathbf{S}'_1 \mathbf{C}_0, \quad (4.19)$$

$$(\mathbf{I} + \mathbf{F}')\mathbf{C}''_1 - \mathbf{F}''\mathbf{C}'_1 = \mathbf{S}''_1 \mathbf{C}_0, \quad (4.20)$$

where $\mathbf{I}$ denotes the unit matrix. Ultimately, we have for the real and imaginary parts in the simultaneous matrix Eqs. (4.19) and (4.20)

$$\mathbf{C}'_1 = [\mathbf{I} - \mathbf{F}' - \mathbf{F}''(\mathbf{I} + \mathbf{F}')^{-1}\mathbf{F}'']^{-1}[\mathbf{S}'_1 + \mathbf{F}''(\mathbf{I} + \mathbf{F}')^{-1}\mathbf{S}''_1]\mathbf{C}_0,$$

$$\mathbf{C}''_1 = [\mathbf{I} + \mathbf{F}' - \mathbf{F}''(\mathbf{I} - \mathbf{F}')^{-1}\mathbf{F}'']^{-1}[\mathbf{S}''_1 + \mathbf{F}''(\mathbf{I} - \mathbf{F}')^{-1}\mathbf{S}'_1]\mathbf{C}_0.$$

Chapter 5

The double well potential

Quantum effects in the non-inertial Brownian motion of a particle in a double well potential are treated via the quantum Smoluchowski equation (2.15), allowing one to evaluate the position correlation function, its characteristic relaxation times, and dynamic susceptibility using matrix continued fractions and finite integral representations in the manner of the classical Smoluchowski equation treatment. Reliable approximate analytic solutions based on the exponential separation of the time scales of the fast intrawell and slow over-barrier relaxation processes are given. Moreover, the effective and the longest relaxation times of the position correlation function yield accurate predictions of both the low and high frequency relaxation behaviour. The low frequency part of the dynamic susceptibility associated with the Kramers escape rate behaves as a single Lorentzian with characteristic frequency given by the quantum-mechanical reaction rate solution of the Kramers problem. As a particular example, quantum effects in the stochastic resonance are estimated.

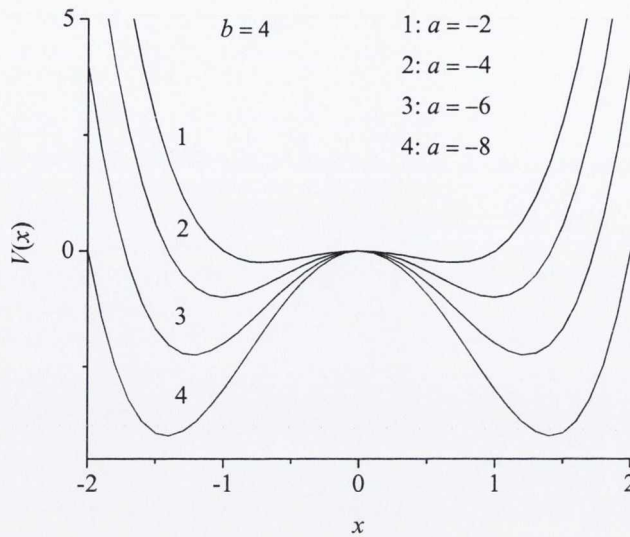


Figure 5.1: The double well potential, Eq. (5.1) for $b = 4$ and various values of a .

5.1 Introduction

The Brownian motion in the double well potential

$$V(x) = \frac{1}{2}ax^2 + \frac{1}{4}bx^4, \quad -\infty < x < \infty, \quad (5.1)$$

where a and b are constants, is ubiquitous in the modelling of diverse physical problems involving bistability and noise activated transitions between the minima of a bistable potential. Examples are simple isometrization processes, chemical reaction rate theory, bistable nonlinear oscillators, second order phase transitions, nuclear fission and fusion (see, e.g. Refs. [136–139] and references cited therein). The dynamics of a classical Brownian particle in the double well potential in the very high damping limit, where the inertia of the particle may be neglected, have been extensively studied using the Smoluchowski equation for the evolution of the distribution function in configuration space (see, e.g. Refs. [140–144]) because that equation essentially circumvents the mathematical difficulties associated with the exact phase space treatment using the Klein-Kramers equation. Comparatively, the quantum Smoluchowski equation has been used in many applications of the quantum Brownian motion in a potential [110, 145, 146]. Certain aspects of quantum effects in the Brownian motion in a double well potential have already been analysed, e.g. in Refs. [75] and [147]–[151].

The QSE (2.15) is now used to evaluate quantum corrections in the Brownian motion of the particle moving in the double well potential given by Eq. (5.1). In particular, quantum

effects in the equilibrium position correlation function $C(t) = \beta^{-1} \left\langle \int_0^\beta \hat{x}(-i\lambda\hbar) \hat{x}(t) d\lambda \right\rangle_0$, its spectrum and characteristic relaxation times, dynamic susceptibility, and stochastic resonance are estimated by solving the quantum Smoluchowski equation using the matrix continued fraction methods already developed for the classical problem [139]. The symbol $\langle \rangle_0$ denotes equilibrium ensemble averages. The calculations will illustrate how one may evaluate observables in the familiar classical manner. In particular, the single mode approximation for the correlation function spectrum yields closed analytic solutions for the dynamic susceptibility at low frequencies. Finally, the correlation time and the mean first passage time for a Brownian particle to leave a well of the potential are considered. These times may be determined, just as the classical case, knowing the quantum diffusion coefficient and stationary distribution only [82].

5.2 Representation of the quantum Smoluchowski equation as a recurrence relation

Introducing the dimensionless variables

$$y = x / \langle x^2 \rangle_{\text{cl}}^{1/2}, \quad \tau = \zeta \beta \langle x^2 \rangle_{\text{cl}}, \quad 2\Lambda / \beta \langle x^2 \rangle_{\text{cl}} \rightarrow \Lambda, \\ A = \beta a \langle x^2 \rangle_{\text{cl}} / 2, \quad B = \beta b \langle x^2 \rangle_{\text{cl}}^2 / 4, \quad (5.2)$$

where $\langle x^2 \rangle_{\text{cl}}$ is the classical value of the mean square displacement, the QSE (2.15), to first order in Λ , becomes

$$\tau \frac{\partial P}{\partial t} = \frac{\partial}{\partial y} \left[P \frac{\partial V}{\partial y} + \frac{\partial}{\partial y} \left(1 + \Lambda \frac{\partial^2 V}{\partial y^2} \right) P \right], \quad (5.3)$$

where the dimensionless potential is

$$V(y) = \beta V(x) = Ay^2 + By^4.$$

For $A < 0$ and $B > 0$, i.e. for the case of distinct double wells (see Fig. 5.1), the potential $V(y)$ has two minima separated by a maximum at $y = 0$ with a potential barrier of $\Delta V = Q = A^2/4B$. The normalization condition $\langle y^2 \rangle_{\text{cl}} = 1$ implies that the constants A and B are not independent but are related via [143, 144]

$$B(Q) = \frac{1}{8} \left[\frac{D_{-3/2}(-\sqrt{2Q})}{D_{-1/2}(-\sqrt{2Q})} \right]^2, \quad (5.4)$$

where $D_v(z)$ is Whitaker's parabolic cylinder function of order v [7]. For $Q \gg 1$, $B \sim Q$, while for small Q ,

$$B = \frac{\Gamma^2(3/4)}{\Gamma^2(1/4)} + \frac{\Gamma(3/4) [\Gamma^2(1/4) + \Gamma(-1/4)\Gamma(3/4)]}{\Gamma^3(1/4)} \sqrt{Q} + \dots,$$

where $\Gamma(z)$ is the gamma function [7].

The stationary solution of Eq. (5.3) is simply the stationary Wigner distribution function in configuration space [cf. Eq. (2.21)], which in the dimensionless variables (5.2) reads (restricted to second-order terms in Λ) [31]

$$\begin{aligned} P_{st}(y) = Z^{-1} e^{-\beta V(y)} \left\{ 1 + \frac{\Lambda}{2} \left[(V'(y))^2 - 2V''(y) \right] \right. \\ \left. + \frac{\Lambda^2}{40} \left[5(V'(y))^4 + 36(V''(y))^2 + 48V'''(y)V'(y) \right. \right. \\ \left. \left. - 44V''(y)(V'(y))^2 - 24V^{(4)}(y) \right] \right\}, \end{aligned} \quad (5.5)$$

where $Z = \int_{-\infty}^{\infty} P_{st}(y) dy$ is the quantum partition function. The partition function Z can also be expressed in terms of Whitaker's functions as

$$Z = Z_{cl} (1 + \Lambda z_1 + \dots), \quad (5.6)$$

where $Z_{cl} = \int_{-\infty}^{\infty} e^{-V(y)} dy$ is the classical partition function given by

$$Z_{cl} = \int_{-\infty}^{\infty} e^{-V(y)} dy = \sqrt{\pi} (2B)^{-1/4} e^{Q/2} D_{-1/2}(-\sqrt{2Q}), \quad (5.7)$$

and

$$\begin{aligned} z_1 &= \frac{1}{2Z_{cl}} \int_{-\infty}^{\infty} [V'^2(y) - 2V''(y)] e^{-V(y)} dy \\ &= -\sqrt{2B} \frac{D_{1/2}(-\sqrt{2Q}) + D_{-3/2}(-\sqrt{2Q})}{D_{-1/2}(-\sqrt{2Q})} \end{aligned} \quad (5.8)$$

constitutes the first order quantum correction to it.

Now, in order to calculate the quantum position correlation function

$$C(t) = \beta^{-1} \left\langle \int_0^\beta \hat{y}(-i\lambda\hbar) \hat{y}(t) d\lambda \right\rangle_0, \quad (5.9)$$

from linear response theory [43], the decay transient of the system of quantum Brownian particles, following instantaneous switch-off of an external constant field of small magnitude ε , is required. The small magnitude condition implies that having suddenly removed the field at time $t = 0$, one is solely interested in the relaxation of the system from an equilibrium state I with the potential $V(y) - \varepsilon y$ and the distribution function $P_{st}^\varepsilon(t \leq 0)$ to a

new equilibrium state II with the unperturbed potential $V(y)$ and the distribution function $P_{st}(t \rightarrow \infty)$ given by Eq. (5.5). Using linear response theory, whereby *one evaluates the decay transient directly*, circumvents the difficulties associated with the symmetrisation of correlation functions in quantum mechanics (cf. Ref. [43], §4.4.1). The initial stationary distribution function P_{st}^ε is given in linear response by

$$P_{st}^\varepsilon(y) \cong P_{st}(y) + \varepsilon \left\{ y P_{st}(y) - \frac{e^{-V(y)}}{Z} [\Lambda V'(y) + \frac{\Lambda^2}{10} [12V'''(y) - 22V''(y)V'(y) + 5V'(y)]] + \dots \right\}. \quad (5.10)$$

Note that the transient response so formulated is truly *linear* because the change in amplitude ε of the external field is infinitesimally small, $\varepsilon \rightarrow 0$.

Now, unlike the tilted cosine potential considered in Chapters 3 and 4, the double well potential is not periodic in 2π . Hence, the distribution function cannot be represented as a Fourier series but must be represented as set of orthonormal functions appropriate to the boundary conditions of the double well potential. Just as in the classical case, the solution of Eq. (5.3) for $t \geq 0$ may be expanded as a series of Hermite polynomials H_q in the position variable, viz.

$$P(y, t) = P_{st}(y) + \varepsilon \kappa e^{-[\kappa^2 y^2 + V(y)]/2} \sum_{q=0}^{\infty} \frac{c_q(t) H_q(\kappa y)}{\sqrt{\pi 2^q q!}}, \quad (5.11)$$

where κ is a scaling factor chosen so as to ensure optimum convergence of the continued fractions for the Fourier coefficients involved as suggested by Voigtlaender and Risken [136] (all results for the observables are independent of the chosen value of κ). The initial condition for $P(y, t)$ at $t = 0$ is obviously $P(y, 0) = P_{st}^\varepsilon(y)$. We remark in passing that the solution in the classical case may be expressed as a hierarchy of three-term differential recurrence relations in y^n as described in Ref. [137], Ch. 6. However, these recurrence relations *diverge* for the potential of greatest interest, namely, $A < 0$, and so are useless for calculating the after-effect solution, unlike those resulting from an orthogonal expansion of the form of Eq. (5.11).

By substituting Eq. (5.11) into Eq. (5.3) and noting the recurrence relations [7]

$$dH_n(z)/dz = 2nH_{n-1}(z),$$

and

$$H_{n+1}(z) = 2zH_n(z) - 2nH_{n-1}(z),$$

we have after lengthy calculations, a nine-term recurrence relation for the time-dependent Fourier coefficients $c_q(t)$ restricted to terms linear in the quantum parameter Λ

$$\begin{aligned} \tau \frac{d}{dt} c_q(t) = & h_q c_{q+8}(t) + g_q^+ c_{q+6}(t) + f_q^+ c_{q+4}(t) \\ & + e_q^+ c_{q+2}(t) + d_q c_q(t) + e_{q-2}^- c_{q-2}(t) \\ & + f_{q-4}^- c_{q-4}(t) + g_{q-6}^- c_{q-6}(t) + h_{q-8} c_{q-8}(t), \end{aligned} \quad (5.12)$$

where

$$\begin{aligned} d_n &= d_n^0 + \Lambda d_n^1 \\ &= -\frac{\sqrt{B}}{2\alpha^6} [4\sqrt{Q}\alpha^6 + (\alpha^4 + 4Q - 6)(2n+1)\alpha^4 \\ &\quad - 12\sqrt{Q}\alpha^2(2n^2 + 2n + 1) + 5(2n+1)(2n^2 + 2n + 3)] \\ &\quad + \frac{\Lambda B}{\alpha^8} [2\sqrt{Q}(\alpha^4 - 4Q + 12)(2n+1)\alpha^6 - 3(2n^2 + 2n - 1)\alpha^8 + 12(2n^2 + 2n + 1)(5Q - 3)\alpha^4 \\ &\quad - 70(2n^2 + 2n + 3)(2n+1)\sqrt{Q}\alpha^2 + 105(2n^4 + 4n^3 + 10n^2 + 8n + 3)], \\ e_n^\pm &= e_n^{0\pm} + \Lambda e_n^{1\pm} \\ &= \frac{\sqrt{B}}{2\alpha^6} \sqrt{(n+1)(n+2)} \{ (\alpha^4 - 4Q + 6)\alpha^4 + 8\sqrt{Q}\alpha^2(2n+3) - 15(n^2 + 3n + 3) \} \\ &\quad + \frac{4\Lambda\sqrt{B}}{\alpha^2} [-\sqrt{Q}\alpha^{10} \mp 2(2Q - 3)\alpha^8 - 4(\mp(6 + 4n) + Q - 3)\sqrt{Q}\alpha^6 \\ &\quad + (\mp 15(n^2 + 3n + 3) + 4(2n+3)(5Q - 3))\alpha^4 - 105(n^2 + 3n + 3)\sqrt{Q}\alpha^2 + 42(2n+3)(n^2 + 3n + 5)] \}, \\ f_n^\pm &= f_n^{0\pm} + \Lambda f_n^{1\pm} \\ &= -\frac{\sqrt{B}}{2\alpha^6} \sqrt{(n+1)(n+2)(n+3)(n+4)} \{ [-4\sqrt{Q}\alpha^2 + 3(2n+5)] \\ &\quad - \frac{2\Lambda\sqrt{B}}{\alpha^2} [3\alpha^8 \pm 16\sqrt{Q}\alpha^6 + 4(5Q - 3)\alpha^4 - 6(2n+5)\alpha^2(7\sqrt{Q} \pm 2\alpha^2) + 42(2n^2 + 10n + 15)] \}, \\ g_n^\pm &= g_n^{0\pm} + \Lambda g_n^{1\pm} \\ &= -\frac{\sqrt{B}}{2\alpha^6} \sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)(n+6)} \{ 1 - \frac{4\Lambda\sqrt{B}}{\alpha^2} [\mp 3\alpha^4 - 7\sqrt{Q}\alpha^2 + 12n + 42] \} \\ h_n &= \Lambda h_n^1 = \frac{3\Lambda B}{\alpha^8} \sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)(n+6)(n+7)(n+8)}, \end{aligned}$$

and $\alpha = \kappa/B^{1/4}$. Now, Eq. (5.12), in the usual manner of perturbation theory, represents to zero order in Λ the classical recurrence relation and also that relation forced by the quantum terms to first order in Λ . By invoking the familiar general matrix continued fraction method for solving classical recurrence relations generated by the Fokker-Planck equation [46, 82], we have the solution of the differential recurrence Eq. (5.12) (details of this solution are given in Appendix 5.A). Having evaluated the Fourier coefficients $c_q(t)$, we have the probability density $P(y, t)$ and observables such as the position correlation function, its characteristic relaxation times, dynamic susceptibility, etc.

5.3 Calculation of observables

In transient relaxation of a system of nonlinear oscillators starting from an equilibrium state I with the distribution function $P_{st}^\varepsilon(y)$ ($t \leq 0$) given by Eq. (5.10) to a new equilibrium state II with the distribution function $P_{st}(y)$ ($t \rightarrow \infty$) given by Eq. (5.5), the averaged displacement $\langle \hat{y} \rangle(t)$ relaxes from the equilibrium value $\langle \hat{y} \rangle_\varepsilon$ to the value $\langle \hat{y} \rangle_0 = 0$, the transient being described by an appropriate relaxation function. Noting that the Weyl symbol of the coordinate operator $\hat{y}$ is y [76], we have via the Weyl correspondence the averaged displacement $\langle \hat{y} \rangle(t)$ following removal of the small external constant field as

$$\langle \hat{y} \rangle(t) = \int_{-\infty}^{\infty} y P(y, t) dy. \quad (5.13)$$

By using the orthogonality properties of the Hermite polynomials, we have from Eqs. (5.11) and (5.13) the average $\langle \hat{y} \rangle(t)$ as a linear combination of the time-dependent Fourier coefficients $c_{2q-1}(t)$

$$\langle \hat{y} \rangle(t) = \varepsilon \frac{\alpha Z_{cl} B^{1/4}}{\sqrt{\pi}} \sum_{q=1}^{\infty} c_{2q-1}(0) c_{2q-1}(t). \quad (5.14)$$

According to linear response theory [43], $\langle \hat{y} \rangle(t)$ is related to the linear response after-effect function, that is the position correlation function $C(t)$ from Eq. (5.9), via

$$\langle \hat{y} \rangle(t) = \varepsilon C(t). \quad (5.15)$$

Thus we have the position correlation function in series form directly from the after-effect solution as

$$C(t) = \frac{\alpha Z B^{1/4}}{\sqrt{\pi}} \sum_{q=1}^{\infty} c_{2q-1}(0) c_{2q-1}(t). \quad (5.16)$$

The corresponding spectrum $\tilde{C}(\omega) = \int_0^\infty C(t) e^{-i\omega t} dt$ is

$$\tilde{C}(\omega) = \frac{\alpha Z B^{1/4}}{\sqrt{\pi}} \sum_{q=1}^{\infty} c_{2q-1}(0) \tilde{c}_{2q-1}(\omega), \quad (5.17)$$

and so we have the dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ as [43]

$$\begin{aligned} \chi(\omega) &= - \int_0^\infty \frac{d}{dt} C(t) e^{-i\omega t} dt \\ &= C(0) - i\omega \tilde{C}(\omega). \end{aligned} \quad (5.18)$$

Moreover, the correlation time τ_{int} [the area under the relaxation function $C(t)$] is given by

$$\tau_{\text{int}} = \tilde{C}(0)/C(0). \quad (5.19)$$

Now, one may formally introduce another time constant characterising the time behaviour of $C(t)$. This is the effective relaxation time τ_{ef} defined by

$$\tau_{\text{ef}} = -C(0)/\dot{C}(0), \quad (5.20)$$

yielding precise information on the initial decay of $C(t)$ in the time domain. The relaxation times τ_{int} and τ_{ef} may equivalently be defined in terms of the eigenvalues λ_k of the Fokker-Planck operator L_{FP} because $C(t)$ can be written formally as the discrete set of relaxation modes

$$C(t)/C(0) = \sum_k a_k e^{-\lambda_k t}, \quad (5.21)$$

where $\sum_k a_k = 1$, so that from Eqs. (5.19)-(5.21) $\tau_{\text{int}} = \sum_k a_k / \lambda_k$ and $\tau_{\text{ef}} = (\sum_k \lambda_k a_k)^{-1}$. Thus the relaxation times τ_{int} and τ_{ef} contain contributions from *all* the λ_k . Here, only the smallest non-vanishing eigenvalue λ_1 , which is $\sim e^{-Q} \ll 1$ in the low temperature limit [see Eq. (5.27)], is associated with the slowest relaxation mode; the remaining λ_k ($k \neq 1$) characterise high-frequency “intra-well” modes [82]. The eigenvalue λ_1 is usually associated with the long-time behaviour of $C(t)$ [139] and for sufficiently high potential barriers essentially corresponds to the Kramers escape rate [46, 82]. Here the potential has two equivalent wells, so that the dependencies of τ_{int} and $1/\lambda_1$ on the model parameters are similar.

5.4 Evaluation of the characteristic times

The correlation time τ_{int} , rendered in series form by Eqs. (5.17) and (5.19), can also be obtained in closed integral form because (just as the classical case [46, 82] in all systems with dynamics described by a single variable Fokker-Planck-like equation, of which Eq. (5.3) is a particular example), the correlation time τ_{int} of the position correlation function for the double well potential may be expressed in exact analytical form in terms of the diffusion coefficient and stationary distribution as

$$\tau_{\text{int}} = \frac{\tau}{C(0)} \int_{-\infty}^{\infty} \frac{dy}{D(y)P_{\text{st}}(y)} \int_{-\infty}^y x P_{\text{st}}(x) dx \int_{-\infty}^y \frac{\partial}{\partial \varepsilon} P_{\text{st}}^{\varepsilon}(z) dz, \quad (5.22)$$

where

$$C(0) = \langle y^2 \rangle_0 - \Lambda + \dots, \quad (5.23)$$

$$\int_{-\infty}^y \frac{\partial}{\partial \varepsilon} P_{st}^\varepsilon(z) dz = \int_{-\infty}^y z P_{st}(z) dz + \Lambda \frac{e^{-V(y)}}{Z_{cl}} + \dots,$$

and $\langle y^2 \rangle_0 = \int_{-\infty}^{\infty} y^2 P_{st}(y) dy$. Here we have noted that

$$C(0) = \partial_\varepsilon \langle \hat{y} \rangle_\varepsilon = \int_{-\infty}^{\infty} y \left(y P_{st} - \Lambda \frac{e^{-V}}{Z_{cl}} \frac{\partial V}{\partial y} + \dots \right) dy.$$

Numerical calculation shows that the integral representation of the solution, Eq. (5.22), and the matrix continued fraction solution from Eqs. (5.17) and (5.19) yield the same results.

Now, the effective relaxation time τ_{ef} from Eq. (5.20) is

$$\tau_{\text{ef}} = -\frac{\langle \hat{y} \rangle_\varepsilon}{\partial_t \langle \hat{y} \rangle_\varepsilon} = \tau C(0), \quad (5.24)$$

where we have noted Eq. (5.23) and that

$$\partial_t \langle y \rangle_\varepsilon = -\langle \partial_y V \rangle_\varepsilon = \int_{-\infty}^{\infty} \frac{\partial V}{\partial y} \left[y P_{st} - \frac{\Lambda}{Z_{cl}} e^{-V} \frac{\partial V}{\partial y} \right] dy = 1.$$

In the classical limit, $\Lambda \rightarrow 0$, Eqs. (5.22) and (5.24) reduce to the corresponding classical results [139]

$$\tau_{\text{int}} = \frac{\tau}{Z_{cl}} \int_{-\infty}^{\infty} e^{V(y)} \left[\int_{-\infty}^y z e^{-V(z)} dz \right]^2 dy,$$

$$\tau_{\text{ef}} = \tau. \quad (5.25)$$

In the low temperature limit, $Q \gg 1$, λ_1 (and thus the correlation time τ_{int}) can be estimated in a simple manner as $\lambda_1 \sim \Gamma$, where Γ is the semi-classical Kramers escape rate in the very high damping (VHD) limit. As shown in Ref. [31], in the VHD limit and above the crossover temperature $T > T_C$ between tunnelling and thermal activation the quantum Kramers escape rate Γ_q can be written

$$\Gamma_q = \Xi \Gamma_{\text{cl}}, \quad (5.26)$$

where $\Gamma_{\text{cl}} = (m\omega_c\omega_a/2\pi\zeta)e^{-\beta\Delta V}$ is the classical VHD Kramers escape rate, ΔV is a potential barrier, and Ξ is Wigner's quantum transition state theory correction factor, namely [154]

$$\Xi = \frac{\omega_c}{\omega_a} \frac{\sinh(\hbar\beta\omega_a/2)}{\sin(\hbar\beta\omega_c/2)},$$

where $\omega_c = \sqrt{|V''(x_c)|/m}$ and $\omega_a = \sqrt{V''(x_a)/m}$ are the barrier and the well angular frequencies (points c and a are the maximum and minimum of the potential $V(x)$, respectively). In dimensionless variables, Ξ becomes

$$\Xi = \sqrt{2} \frac{\sinh \sqrt{12\Lambda\sqrt{QB}}}{\sin \sqrt{24\Lambda\sqrt{QB}}} \approx 1 + 6\Lambda\sqrt{QB} + \dots$$

Furthermore, the classical VHD escape rate Γ_{cl} for the double well potential has been estimated, e.g. in Ref. [139] and is given by (in our notation)

$$1/\Gamma_{cl} \sim \frac{\tau\pi e^Q}{4\sqrt{2}Q} \left(1 + \frac{5}{8Q} + \dots\right). \quad (5.27)$$

The above asymptotic equations may be used to estimate λ_1 in the low temperature limit only. In general, λ_1 can be estimated via the mean first passage time (MFPT) [155, 156] as $\lambda_1^{-1} = \tau_{MFPT}$, where τ_{MFPT} is the MFPT for transitions from the point domain y_{min} at the bottom of a well to $y_{max} = 0$, where the potential $V(y)$ attains its maximum. Thus we have τ_{MFPT} in the closed form [156]

$$\tau_{MFPT} = \tau \int_{-\infty}^0 \frac{1}{D(y)P_{st}(y)} \int_{-\infty}^y P_{st}(x) dx dy. \quad (5.28)$$

In the high barrier approximation, $Q \gg 1$, estimation of the integrals in Eq. (5.28) using steepest descents yields the well-known Larsson-Kostin asymptotic formula Eq. (5.27) for the escape rate.

Results of the comparison of the correlation time τ_{int} given by Eq. (5.22) with asymptotic estimates Eq. (5.26) are shown in Fig. 5.2. Equation (5.26) provides an accurate approximation to the correlation time for high barriers ($Q > 3$) which of course fails at low barrier heights. As Q increases, the correlation time τ_{int} and λ_1^{-1} decrease; a phenomenon which can be ascribed to effective lowering of the potential barrier due to quantum tunnelling near the top of the barrier at high temperatures, which *always increases* the quantum escape rate. These quantum effects manifest themselves even for very small values of Λ .

5.5 Linear dynamic susceptibility

According to Eqs. (5.21) and (5.18), the dynamic susceptibility is an infinite sum of Lorentzians, viz.

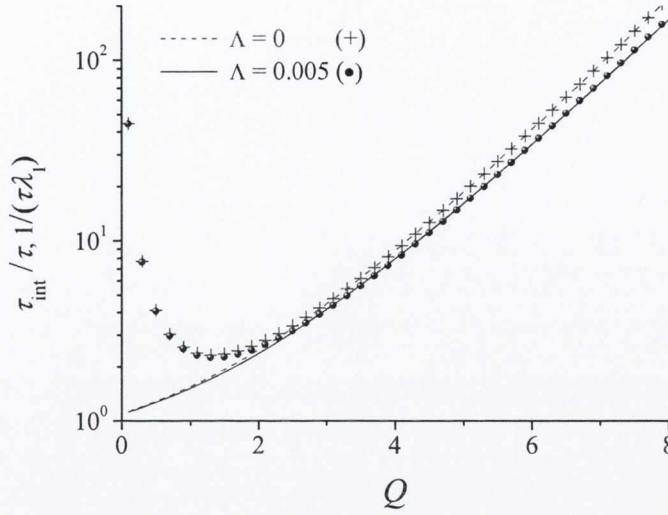


Figure 5.2: Correlation time τ_{int}/τ , Eq. (5.22), vs the barrier parameter Q for $\Lambda = 0$ (classical limit, dashed line) and $\Lambda = 0.005/Q$ (solid line), as compared with $1/(\lambda_1\tau)$ from the asymptotic escape rate Eq. (5.26) (pluses and filled circles).

$$\frac{\chi(\omega)}{\chi} = \sum_p \frac{c_p}{1 + i\omega/\lambda_p}, \quad (5.29)$$

where $\chi = C(0)$ is the static susceptibility. In the low- ($\omega \rightarrow 0$) and high- ($\omega \rightarrow \infty$) frequency limits, the behaviour of the susceptibility may easily be evaluated. We have from Eq. (5.29), respectively, for $\omega \rightarrow 0$ and for $\omega \rightarrow \infty$

$$\chi(\omega) \approx \chi(1 - i\omega\tau_{\text{int}} + \dots), \quad (5.30)$$

$$\chi(\omega) \sim \chi(i\omega\tau_{\text{ef}})^{-1} + \dots. \quad (5.31)$$

However, as we shall see below, only two bands appear in the spectrum of $\chi''(\omega)$ in the low temperature limit $Q \gg 1$ (such behaviour is typical of both classical and quantum systems [82]). The low-frequency band is due to the slowest (overbarrier) relaxation modes. The characteristic frequency and the half-width of this band are determined by λ_1 . The high-frequency band of $\chi''(\omega)$ is due to “intrawell” modes corresponding to the eigenvalues λ_k ($k \geq 2$). These “intrawell” modes are indistinguishable in the frequency spectrum of $\chi''(\omega)$ appearing merely as a single high-frequency Lorentzian band.

Just as the classical case [139], knowledge of λ_1 is sufficient to accurately predict the low frequency part of $\chi(\omega)$ as well as the long time behaviour of the equilibrium correlation function $C(t)$ for all values of the barrier parameter Q . Thus, if one is interested

solely in the low frequency region ($\omega\tau \leq 1$), where the effect of the intrawell modes may be ignored, the dynamic susceptibility $\chi(\omega)$ may be approximated as

$$\frac{\chi(\omega)}{\chi} \approx \frac{1 - \delta}{1 + i\omega/\lambda_1} + \delta, \quad (5.32)$$

where δ is a parameter characterising the contribution of “intrawell” modes, which can be evaluated as [82] $\delta \sim \tau_W/\tau_{\text{ef}}$, where the “effective” relaxation time τ_{ef} is given by Eq. (5.24) and τ_W is the “intrawell” relaxation time. For qualitative evaluation of Eq. (5.32) in the low temperature limit, $Q \gg 1$, one may use the simple estimate $\delta \sim [8QC(0)]^{-1}$.

In order to verify the single Lorentzian approximation, we plot in Fig. 5.3 the real and imaginary parts of $\chi(\omega)$, calculated from the exact continued fraction solution and the approximate Eq. (5.32). It is apparent from Fig. 5.3 that no practical difference exists between the exact solution and the single mode approximation (the maximum relative deviation between the corresponding curves does not exceed a few percent) at low frequencies. It is also apparent from Fig. 5.3 that due to the *quantum tunnelling*, which increases the escape rate, the frequency of the maximum of the low frequency peak in $\chi''(\omega)$ *increases*. Furthermore, the quantum effects decrease at frequencies $\omega \gg \lambda_1$, where barrier crossing is no longer the dominant relaxation process.

5.6 Linear stochastic resonance

A particularly interesting aspect of the Brownian motion in a double well potential is the *stochastic resonance* [137] occurring for very high dissipation (VHD) of the thermal energy of a Brownian particle to its heat bath, whereby a weak periodic forcing synchronised with the thermally activated hopping between the wells greatly enhances the rate of switching between them. Stochastic resonance is now a well-known but still remarkable effect allowing one to control the behaviour of periodic signals passing through noisy systems. As a manifestation of cross-coupling between stochastic and regular motions, the stochastic resonance effect is universal in physics (e.g. optics, mechanics of solids, superconductivity, surface science), communications engineering (optimal detection and tracing of signals) as well as in various branches of chemistry and biology. Comprehensive reviews of diverse aspects of stochastic resonance are available in Ref. [137]. Quantum effects in the stochastic resonance have been discussed by Grifoni *et al.* [147]

Having evaluated the dynamic susceptibility $\chi(\omega)$, one may estimate quantum effects in the signal-to-noise ratio (SNR) in stochastic resonance just as in classical case. Indeed for a weak ac driving force $f(t) = f_0 \cos \omega t$, the SNR $\Upsilon(\omega)$ may be defined using linear

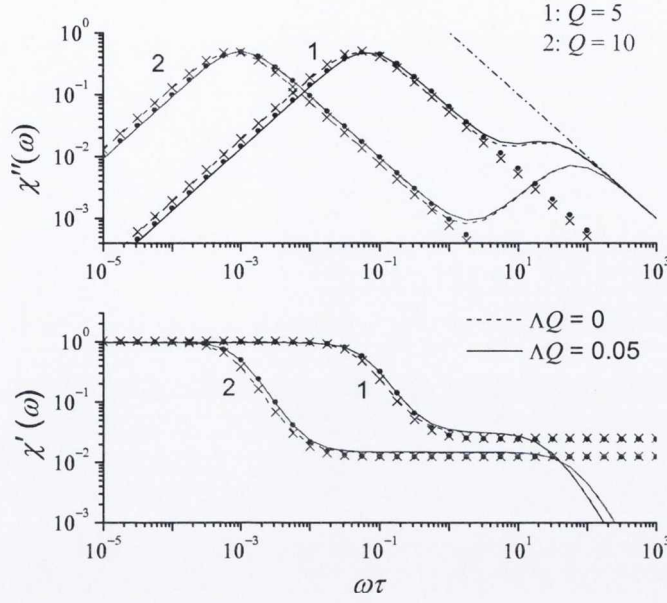


Figure 5.3: Real and imaginary parts of $\chi(\omega)$ vs the normalized frequency $\tau\omega$ for $\Lambda = 0$ (classical limit, dashed lines and crosses) and $\Lambda = 0.05/Q$ (solid lines and filled circles), and barrier height $Q = 5$ and $Q = 10$. Solid and dashed lines are the continued fraction solution [Eq. (5.14) and Appendix 5.A]. Crosses and filled circles are the single Lorentzian approximation, Eq. (5.32) while straight dashed-dotted lines are the high frequency asymptote Eq. (5.31).

response theory as [147]

$$\Upsilon(\omega) = \frac{\pi}{2} \beta f_0^2 \omega \frac{|\chi(\omega)|^2}{\chi''(\omega)}. \quad (5.33)$$

We can rewrite Eq. (5.33) as

$$\Upsilon(\omega) = \frac{\beta \chi f_0^2}{\tau Q^2} R_\omega, \quad (5.34)$$

where

$$R_\omega = \frac{\pi \omega \tau Q^2}{2} \frac{|\chi(\omega)|^2}{\chi \chi''(\omega)} \quad (5.35)$$

is the dimensionless SNR. Noting Eq. (5.30), we see that in the adiabatic limit ($\omega \rightarrow 0$) the SNR is given by

$$R_0 = \frac{\pi \tau}{2 \tau_{\text{int}}} Q^2, \quad (5.36)$$

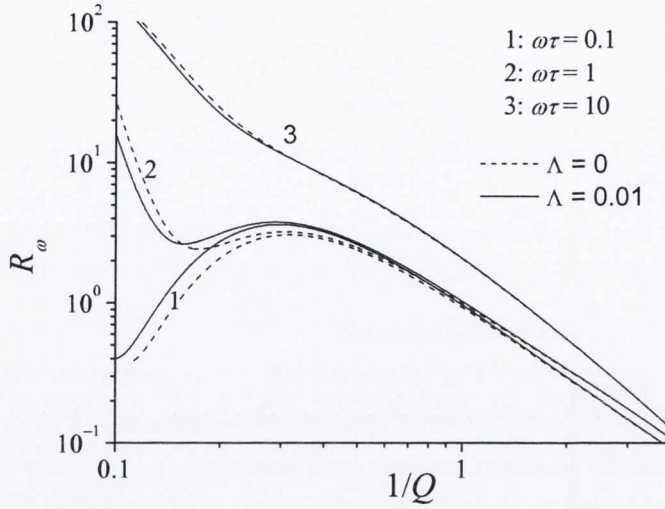


Figure 5.4: SNR vs the inverse barrier height $1/Q$ for various values of $\omega\tau = 0.01$ (1), 1 (2), and 10 (3). Solid lines: Eq. (5.35) for $\Lambda = 0.005$. Dashed lines: the classical limit ($\Lambda = 0$).

where τ_{int} is given by Eq. (5.22). As shown above, the time τ_{int} is very close to $1/\lambda_1$ for all values of $Q \gg 1$ so that either quantity may be used for qualitative estimations.

The function R_ω versus the dimensionless temperature parameter Q^{-1} is shown in Fig. 5.4. For $\omega = 0$, the main maximum of R_0 is attained at $Q \sim 3$ and the quantum effects are most pronounced in the low temperature limit causing amplification of the SNR. In the limit $Q \rightarrow \infty$, $R_0 \rightarrow 0$. Meanwhile, we recall that λ_1 is exponentially small in Q for $Q \gg 1$, and decreases rapidly as the system is cooled, while all other eigenvalues of the quantum Smoluchowski operator λ_k have a non-exponential dependence on Q . Hence, at any finite ω (i.e., outside the adiabatic limit), the ratio ω/λ_1 tends to infinity with decreasing temperature, $T \rightarrow 0$, even at very low frequencies since the overbarrier transition is completely frozen out. However, the Brownian particle, although confined to a particular potential well, is *not completely immobilised* and can still take part in intrawell motion. Thus for $\omega \neq 0$, $R_\omega \rightarrow \text{const}$ as $Q \rightarrow \infty$. Furthermore, for $\omega \neq 0$, the quantum effects can lead to both amplification and attenuation of the SNR. The function R_ω versus the dimensionless frequency $\omega\tau$ is presented in Fig. 5.5, showing that the quantum effects may lead to both amplification and attenuation of the SNR. Here the SNR is a monotonically increasing function from the low frequency limit R_0 to its plateau value, viz.

$$R_{\omega \rightarrow \infty} \sim \pi Q^2 / [2C(0)]. \quad (5.37)$$

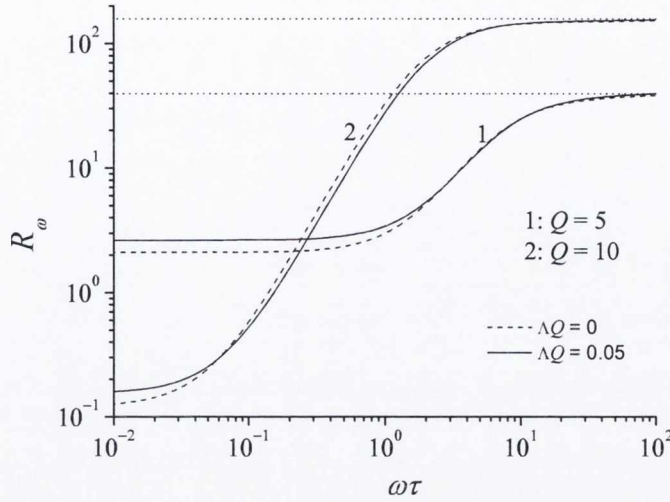


Figure 5.5: SNR vs $\omega\tau$ for $Q = 5$ (1) and 10 (2). Solid lines: Eq. (5.35) for $Q\Lambda = 0.05$. Dashed lines: the classical limit ($\Lambda = 0$). Dotted lines: Eq. (5.37).

5.7 Concluding remarks

We have shown how quantum effects in the Brownian motion of a particle in a double well potential may be studied using a semiclassical Smoluchowski equation, based on the extension of Wigner's phase space formulation of quantum mechanics to an open system. The results agree with quantum reaction rate theory constituting a benchmark solution. The most significant manifestation of the quantum effects above the crossover temperature between tunnelling and thermal activation appears in connection with the low-frequency relaxation via transitions across the potential barrier. In this frequency range, the relaxation process is accurately described by a single Lorentzian with the relaxation time given by the inverse quantum rate, so providing a very simple picture of the quantum relaxation. We must remark, however, that our results can be used only at low frequencies ($\omega\tau \leq 1$) as inertial effects are completely ignored. These effects can be taken account of by considering the phase space master equation (2.9) [75]. Our solutions are valid only for small values of the quantum parameter ($\Lambda \ll 1$), since in our perturbation procedure we have neglected all terms of the order of Λ^2 and higher. In order to improve the accuracy of calculations for larger values of Λ , additional terms of the order of Λ^2 , etc. should be included in the Smoluchowski equation (2.15) as described in Ref. [146].

The main advantage in applying Wigner's phase-space approach to the quantum Brownian motion in a potential is that his formulation proceeds via the quantum Smoluchowski equation (2.15), which is a partial differential equation and so operators are not involved.

Furthermore, the phase-space representation suggests how powerful computation techniques developed for the classical Smoluchowski equation may be extended to the quantum domain rendering a transparent treatment of quantum effects in Brownian motion. Using these techniques quantum effects on diffusive transport properties can in principle be estimated for arbitrary potentials (see, e.g. Ref. [146]).

In addition to the Wigner formulation, we should remark that the quantum Brownian motion in a potential may also be treated using a variety of other methods such as numerical simulations [150, 157], the reduced density matrix [1, 158], path integrals [11, 110], etc. In general, these methods allow one to achieve a deep understanding of the dynamics of dissipative quantum systems. However, in spite of the progress achieved by these methods, they do possess certain practical disadvantages. For example, a simple time evolution equation for the reduced density matrix does not exist [72]. In spite of the formal power of numerical simulation methods, which yield numerically exact solutions of many problems, the understanding and interpretation of the qualitative behaviour of the relevant physical quantities, is sometimes not at all obvious. Path integral approaches for the most part have been confined to harmonic oscillator models since in general it is difficult or indeed impossible to evaluate path integrals for any other potentials [11]. Wigner's phase-space approach, on the other hand, is mostly useful in the high temperature limit $T \gg T_0$ defined by Eq. (2.10). The estimations show [146] that T_0 can be very low in comparison with the temperatures of interest, which can also very low. For example, for point Josephson junctions, where the classical model of Brownian motion in a tilted periodic potential is usually applied to, $T \sim 1.5 - 4$ K and $T_0 \sim 0.1$. For parameter ranges, where the condition (2.10) is invalid (e.g., throughout the very-low-temperature region, $T < T_0$, where non-Markovian effects are substantial) other approaches should be used. One would therefore essentially expect that only combined use of the complementary approaches can yield a comprehensive understanding of the quantum dynamics of the Brownian particle in a potential.

5.A Matrix continued fraction solution of Eq. (5.12)

The nine-term recurrence relation, Eq. (5.12), can be rearranged as a set of matrix three-term recurrence relations, which represent the classical recurrence relation forced by the first order quantum terms, viz.

$$\begin{aligned} \tau \frac{d}{dt} \mathbf{C}_n(t) &= \mathbf{Q}_n^{0-} \mathbf{C}_{n-1}(t) + \mathbf{Q}_n^0 \mathbf{C}_n(t) + \mathbf{Q}_n^{0+} \mathbf{C}_{n+1}(t) \\ &+ \Lambda [\mathbf{Q}_n^{1-} \mathbf{C}_{n-1}(t) + \mathbf{Q}_n^1 \mathbf{C}_n(t) + \mathbf{Q}_n^{1+} \mathbf{C}_{n+1}(t)], \end{aligned} \quad (5.38)$$

where the column vector $\mathbf{C}_n(t)$ ($n \geq 1$) is defined as

$$\mathbf{C}_n(t) = \begin{pmatrix} c_{8n-7}(t) \\ c_{8n-5}(t) \\ c_{8n-3}(t) \\ c_{8n-1}(t) \end{pmatrix},$$

with $\mathbf{C}_0(t) = 0$ and the matrices $\mathbf{Q}_n^i$ and $\mathbf{Q}_n^{i\pm}$ ($i = 0, 1$) given by

$$\begin{aligned} \mathbf{Q}_n^i &= \begin{pmatrix} d_{8n-7}^i & e_{8n-7}^{i+} & f_{8n-7}^{i+} & g_{8n-7}^{i+} \\ e_{8n-7}^{i-} & d_{8n-5}^i & e_{8n-5}^{i+} & f_{8n-5}^{i+} \\ f_{8n-7}^{i-} & e_{8n-5}^{i-} & d_{8n-3}^i & e_{8n-3}^{i+} \\ g_{8n-7}^{i-} & f_{8n-5}^{i-} & e_{8n-3}^{i-} & d_{8n-1}^i \end{pmatrix}, \\ \mathbf{Q}_n^{i+} &= \begin{pmatrix} h_{8n-7}^i & 0 & 0 & 0 \\ g_{8n-5}^{i+} & h_{8n-5}^i & 0 & 0 \\ f_{8n-3}^{i+} & g_{8n-3}^{i+} & h_{8n-3}^i & 0 \\ e_{8n-1}^{i+} & f_{8n-1}^{i+} & g_{8n-1}^{i+} & h_{8n-1}^i \end{pmatrix}, \\ \mathbf{Q}_n^{i-} &= \begin{pmatrix} h_{8n-15}^i & g_{8n-13}^{i-} & f_{8n-11}^{i-} & e_{8n-9}^{i-} \\ 0 & h_{8n-13}^i & g_{8n-11}^{i-} & f_{8n-9}^{i-} \\ 0 & 0 & h_{8n-11}^i & g_{8n-9}^{i-} \\ 0 & 0 & 0 & h_{8n-9}^i \end{pmatrix}. \end{aligned}$$

Next we use perturbation theory to find the solution of Eq. (5.38) as

$$\mathbf{C}_n(t) = \mathbf{C}_n^0(t) + \Lambda \mathbf{C}_n^1(t), \quad (5.39)$$

treating Λ as a small parameter. Substituting Eq. (5.39) into Eq. (5.38) we have in the zero order of perturbation theory the three-term recurrence relation constituting the classical solution

$$\tau \frac{d}{dt} \mathbf{C}_n^0(t) = \mathbf{Q}_n^{0-} \mathbf{C}_{n-1}^0(t) + \mathbf{Q}_n^0 \mathbf{C}_n^0(t) + \mathbf{Q}_n^{0+} \mathbf{C}_{n+1}^0(t), \quad (5.40)$$

and in the first order of perturbation theory the forced three-term recurrence relation

$$\tau \frac{d}{dt} \mathbf{C}_n^1(t) = \mathbf{Q}_n^{0-} \mathbf{C}_{n-1}^1(t) + \mathbf{Q}_n^0 \mathbf{C}_n^1(t) + \mathbf{Q}_n^{0+} \mathbf{C}_{n+1}^1(t) + \mathbf{R}_n(t), \quad (5.41)$$

where the forcing function $\mathbf{R}_n(t)$ is

$$\mathbf{R}_n(t) = \mathbf{Q}_n^{1-} \mathbf{C}_{n-1}^0(t) + \mathbf{Q}_n^1 \mathbf{C}_n^0(t) + \mathbf{Q}_n^{1+} \mathbf{C}_{n+1}^0(t), \quad (5.42)$$

constituting the first order quantum correction to the classical solution. The initial condition vector $\mathbf{C}_n(0) = \mathbf{C}_n^0(0) + \Lambda \mathbf{C}_n^1(0)$ consists of the initial values $c_n(0)$ with an odd value of the index $n = 2p + 1$ so that we have

$$c_{2p+1}(0) = c_{2p+1}^0(0) + \Lambda c_{2p+1}^1(0),$$

where

$$c_{2p+1}^1(0) = \frac{1}{Z_{cl} \sqrt{2^{2p+1}} (2p+1)!} \int_{-\infty}^{\infty} \xi F_1(\xi) H_{2p+1}(\alpha \xi) e^{-(\alpha^2 \xi^2 - 2\sqrt{Q} \xi^2 + \xi^4)/2} d\xi,$$

$$\begin{aligned} F_0(\xi) &= 1/\sqrt{B}, \\ F_1(\xi) &= 4(2\xi^2(\xi^2 - \sqrt{Q})^2 + \sqrt{Q} - 3\xi^2) \\ &\quad + 4\sqrt{B}(\sqrt{Q} - \xi^2) - Z_1 / (Z_{cl} \sqrt{B}), \end{aligned}$$

and

$$\begin{aligned} \frac{Z_1}{Z_{cl} \sqrt{B}} &= \frac{1}{Z_{cl} \sqrt{B}} \int_{-\infty}^{\infty} [V'(x)^2 - 2V''(x)] e^{-V(x)} dx \\ &= -\sqrt{8} \frac{D_{1/2}(-\sqrt{2Q}) + D_{-3/2}(-\sqrt{2Q})}{D_{-1/2}(-\sqrt{2Q})}. \end{aligned}$$

Now, using the one-sided Fourier transform, Eq. (5.40) can be rearranged as the set of matrix *three-term* recurrence relations

$$i\tau\omega \tilde{\mathbf{C}}_n^0 - \tau \mathbf{C}_n^0(0) = \mathbf{Q}_n^0 \tilde{\mathbf{C}}_n^0 + \mathbf{Q}_n^{0+} \tilde{\mathbf{C}}_{n+1}^0 + \mathbf{Q}_n^{0-} \tilde{\mathbf{C}}_{n-1}^0, \quad (5.43)$$

where $\tilde{\mathbf{C}}_n^0 = \int_0^\infty \mathbf{C}_n^0(t) e^{-i\omega t} dt$. By invoking the general method [82] for solving the tridiagonal matrix recurrence relation, Eq. (5.43), we have the zero order perturbation (i.e. classical) solution for $\tilde{\mathbf{C}}_1(\omega)$ in terms of matrix continued fractions, viz.

$$\tilde{\mathbf{C}}_1^0 = \tau \Delta_1^0 \left\{ \mathbf{C}_1^0(0) + \sum_{n=2}^{\infty} \left[\prod_{k=2}^n \mathbf{Q}_{k-1}^{0+} \Delta_k^0 \right] \mathbf{C}_n^0(0) \right\}, \quad (5.44)$$

where Δ_n^i ($i = 0, 1$) are matrix continued fractions defined by the recurrence relation

$$\Delta_n^i = [i\tau\omega\mathbf{I} - \mathbf{Q}_n^i - \mathbf{Q}_n^{i+}\Delta_{n+1}^i\mathbf{Q}_{n+1}^{i-}]^{-1},$$

and $\mathbf{I}$ is the identity matrix. All other $\tilde{\mathbf{C}}_n^0$ can be calculated from Eqs. (5.43) and (5.44) noting that $\tilde{\mathbf{C}}_0^0 = 0$. In like manner, we have the solution for the first order spectrum

$$i\tau\omega\tilde{\mathbf{C}}_n^1 = \mathbf{Q}_n^1\tilde{\mathbf{C}}_n^1 + \mathbf{Q}_n^{1+}\tilde{\mathbf{C}}_{n+1}^1 + \mathbf{Q}_n^{1-}\tilde{\mathbf{C}}_{n-1}^1 + \tau\mathbf{C}_n^1(0) + \tilde{\mathbf{R}}_n, \quad (5.45)$$

and

$$\tilde{\mathbf{C}}_1^1 = \Delta_1^1 \left\{ \tau\mathbf{C}_1^0(0) + \tilde{\mathbf{R}}_1 + \sum_{n=2}^{\infty} \left[\prod_{k=2}^n \mathbf{Q}_{k-1}^{1+}\Delta_k^1 \right] \left(\tau\mathbf{C}_n^0(0) + \tilde{\mathbf{R}}_n \right) \right\}. \quad (5.46)$$

All other $\tilde{\mathbf{C}}_n^1$ can be calculated from Eqs. (5.45) and (5.46) noting that $\tilde{\mathbf{C}}_0^1 = 0$. The spectrum of the position correlation function $C(t)$ is then given by

$$\begin{aligned} \tilde{C}(\omega) &= \frac{\alpha Z_{cl} B^{1/4}}{\sqrt{\pi}} \sum_{n=1}^{\infty} \mathbf{C}_n^T(0) \cdot \tilde{\mathbf{C}}_n \\ &= \frac{\alpha Z_{cl} B^{1/4}}{\sqrt{\pi}} \sum_{q=1}^{\infty} c_{2q-1}(0) \tilde{c}_{2q-1}(\omega), \end{aligned}$$

where $\tilde{c}_{2q-1}(\omega) = \int_0^{\infty} c_{2q-1}(t) e^{-i\omega t} dt$ and the superscript T denotes the transpose. The integral and effective relaxation times can be calculated via matrix continued fractions as

$$\begin{aligned} \tau_{\text{int}} &= \frac{\alpha Z_{cl} B^{1/4}}{\sqrt{\pi}} \sum_{n=1}^{\infty} \mathbf{C}_n^T(0) \cdot \tilde{\mathbf{C}}_n \Big|_{\omega \rightarrow 0}, \\ \tau_{\text{ef}} &= - \left[\frac{\alpha Z_{cl} B^{1/4}}{\sqrt{\pi}} \sum_{n=1}^{\infty} \mathbf{C}_n^T(0) \cdot \dot{\mathbf{C}}_n(0) \right]^{-1}. \end{aligned}$$

Chapter 6

The ratchet potential

Quantum effects in the noninertial Brownian motion of a particle in a one-dimensional ratchet potential are treated in the high temperature and weak bath-particle coupling limit by solving a quantum Smoluchowski equation (2.15) for the time evolution of the Wigner function in configuration space. In particular, an analytical expression for the stationary average drift velocity for constant driving forces is presented including quantum corrections to any order in Planck's constant. The corresponding frequency response is determined using continued fractions in both the linear approximation, holding for small ac driving amplitude, and in the nonlinear regime for arbitrary driving amplitude, exhibiting pronounced ac induced frequency dependence of the dc component of the average drift velocity. Moreover, Shapiro steps are apparent in the dc characteristics for strong ac driving just as in the dc current-voltage characteristics of a point Josephson junction.

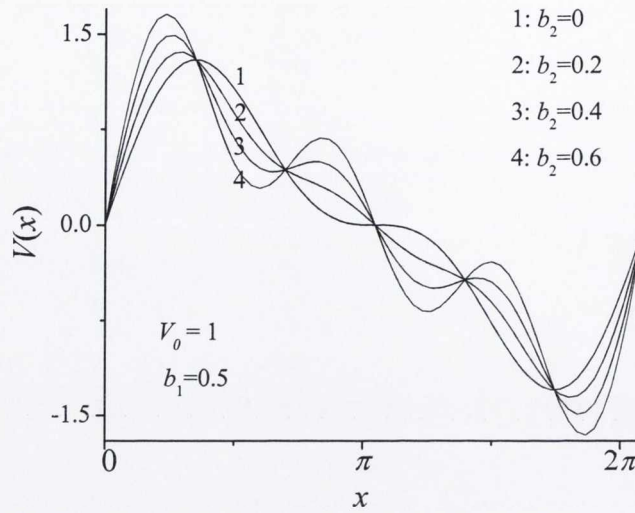


Figure 6.1: The ratchet potential, Eq. (6.6) for $V_0 = 1$, $b_1 = 0.5$ and various values of b_2 .

6.1 Introduction

The rectified current of Brownian particles arising from the combination of an asymmetric, spatially periodic ratchet potential with an unbiased, undulating stimulus coupled to a thermal bath has long been of interest, both as an example of a nonequilibrium system and as a microscopic transport device since it effectively represents a mechanical diode [159, 160]. The abiding interest in forced thermal ratchets is reflected in the diversity of papers [159]–[163] dealing with their transport properties. In general, such ratchets are characterised by periodic potentials with broken spatial symmetry, affording the possibility of extracting a net particle flow from unbiased (i.e. vanishing on time averaging) driving. The ratchet effect has been reported experimentally in a variety of physical and biological systems, which are so small that the thermal noise cannot be ignored, because the energy barriers to thermal activation are just a few kT , unlike in the macroscopic world, where the barriers are effectively infinite [159]. Ratchet effects have also been widely used to explain the action of motor proteins and to suggest novel nanomachines, e.g. Brownian motors, operating far from thermal equilibrium by extracting energy fluctuations to work against external loads [164].

Until comparatively recently, the ratchet system has been studied predominately in the classical limit, where the dynamics in the non-inertial limit are governed by the Smoluchowski equation (1.6). In the case of periodic potentials, expansion of the solution of the Smoluchowski equation in a spatial Fourier series leads to an ordinary differential recurrence relation, recurring only in the order q of the series. For the RSJ-model of the

Josephson junction considered in Chapters 3 and 4, closely related to the ratchet, this recurrence relation reduces to a three-term one (see Eq. (3.8) with $\Lambda = 0$). Hence, it may be solved in the frequency domain using scalar continued fractions, yielding the impedance of the junction [82]. In particular, the time-independent solution yields the dc current-voltage characteristics [82]. For the ratchet potential, however, the scalar recurrence relation does not in general reduce to a three-term one, rather it reduces only to a matrix three-term recurrence relation. Hence, in order to solve it matrix continued fractions must be used, albeit these are considerably simpler than those associated with the exact inertial solution as typically only finite matrices are involved rather than the infinite matrices associated with the order n of the Hermite polynomials of the inertial solution.

Interest has now focused on extending the ratchet to the quantum regime, particularly in the context of molecular-sized physical engines, where it appears that transport properties such as the average drift velocity are considerably modified in relation to their classical counterparts [89]. Quantum ratchets are usually investigated in the context of established devices such as the Josephson junction and a few novel devices such as rocked electron ratchets [165]- [168]. One such analysis of the Josephson junction is given by Zwerger [169], where following an earlier paper on the quantum Brownian motion in a periodic potential [170], he used the influence-functional formalism developed by Feynman and Vernon [9] combined with the system-plus-bath Hamiltonian of Caldeira and Leggett [10] to investigate quantum effects in the dc current-voltage characteristic of a small Josephson junction. The Caldeira-Leggett Hamiltonian was originally used to study the macroscopic quantum tunnelling of the phase difference across a Josephson element in an RF-SQUID ring [10].

It is the purpose of this chapter to demonstrate how the semiclassical approach to quantum Brownian motion of Coffey *et al.* may be used to study high temperature quantum corrections to the average drift velocity of the Brownian ratchet in the non-inertial limit using the quantum Smoluchowski equation (2.15), as accomplished for the Josephson junction [120, 173] (see Chapters 3 and 4). The dc average drift velocity is presented both in closed integral form and as an easily computed continued fraction. Proceeding to the frequency-dependent stationary case, quantum effects in the frequency dependence of the ac average drift velocity are investigated, before both the linear response, valid for small driving amplitudes, and the nonlinear response valid for arbitrary driving amplitude are considered. Furthermore, the nonlinear response exhibits pronounced frequency dependence of the dc average drift velocity as well as Shapiro-like steps in the curve of that quantity versus dc bias, just as the dc current-voltage characteristic of the point Josephson

junction for strong driving current (see § 4.4). In determining the various solutions, the alterations which must be made to the continued fraction as one proceeds from the stationary state to the linear response and finally to the nonlinear response are clearly presented. An attractive feature is the similarity of the fraction for each of the three solutions so that only slight alterations are required in each case.

6.2 Quantum Smoluchowski equation for the ratchet potential

Now, as demonstrated in § 2.3, either integration of Eq. (2.9) over p and proceeding to the noninertial limit just as Klein and Kramers [31, 44] or considering the noninertial limit of the quantum Brinkman hierarchy [31, 46] generated by expanding the momentum dependence of $W(x, p, t)$ in Hermite polynomials (see § 2.5), leads to the quantum Smoluchowski equation for the quasi-probability distribution function in configuration space, namely

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{P}{\zeta} \frac{\partial V}{\partial x} + \frac{\partial}{\partial x} (D(x)P) \right\}, \quad (6.1)$$

where $D(x)$ is the diffusion coefficient given to second order in Λ by

$$D(x) = \frac{1}{\zeta\beta} \left\{ 1 + 2\Lambda V''(x) - \frac{4\Lambda^2}{5} \left[(V''(x))^2 + 3V'(x)V^{(3)}(x) - 3\beta^{-1}V^{(4)}(x) \right] \right\}, \quad (6.2)$$

while the drift coefficient $-V'(x)/\zeta$ remains as in the classical case so that an *effective potential is not involved*. We now specialise Eq. (6.1) to the quantum Brownian motion of a particle in a ratchet potential driven by a constant force a . We consider the one-dimensional, spatially periodic, $V(x) = V(x + L)$, asymmetric potential

$$V(x) = V_0 [\sin(2\pi x/L) + b_1 \sin(4\pi x/L) + b_2 \sin(6\pi x/L)], \quad (6.3)$$

where the constant V_0 determines the barrier height and the parameters b_1 and b_2 characterise the spatial asymmetry (see Fig. 6.1). Introducing the dimensionless variables

$$\begin{aligned} 2\pi x/L &\rightarrow x, & t/\tau &\rightarrow t, & \tau &= \zeta\beta L^2/4\pi^2, \\ a\beta L/2\pi &\rightarrow a, & 8\pi^2\Lambda/\beta L^2 &\rightarrow \Lambda, & \beta V(x) &\rightarrow V(x), & \beta V_0 &\rightarrow V_0, \end{aligned} \quad (6.4)$$

the quantum Smoluchowski equation (6.1) then becomes

$$\frac{\partial}{\partial t} P(x, t) = \frac{\partial}{\partial x} \left\{ [V'(x) - a] P(x, t) + \frac{\partial}{\partial x} [D(x) P(x, t)] \right\}, \quad (6.5)$$

where

$$V(x) = V_0 [\sin x + b_1 \sin 2x + b_2 \sin 3x], \quad (6.6)$$

and the dimensionless diffusion coefficient is

$$D(x) = 1 + \Lambda V''(x) - \frac{\Lambda^2}{5} \left\{ V''(x)^2 + 3 [V'(x) - a] V^{(3)}(x) - 3 V^{(4)}(x) \right\}. \quad (6.7)$$

Now, due to the mathematical difficulties involved, relatively little attention has been paid to ac driving forces, where the time-dependent Smoluchowski equation must be used. In contrast, Brownian-ratchet dynamics have been studied extensively using the *time-independent* Smoluchowski equation. For example, current reversals via manipulation of the ratchet profile have been studied classically for a two-state Markovian driving force, where the governing master equation consists of two coupled Smoluchowski equations [174]. Similarly, the role of quantum tunnelling and quantum reflection in the enhancement or suppression of the stationary average drift velocity of a quantum Brownian particle has been studied by Machura *et al.* [89] to first order in Λ using the quantum Smoluchowski equation of Ankerhold *et al.* [97]. There, they regard the diffusion coefficient in that equation as the leading term in the Taylor expansion of $[1 - \Lambda V''(x)]^{-1}$ in order to exclude Maxwell-demon effects. Such an assumption is unnecessary here as the Wigner approach automatically furnishes the desired expansion of the diffusion coefficient in powers of Λ [cf. Eq. (6.7)].

In order to lay the groundwork for the study of the *time-dependent* case, pertaining to the stationary ac response, one must first consider the time-independent solution of the quantum Smoluchowski equation (6.5), which, having been solved by quadratures, will then be used to calculate the average drift velocity in the *slow-switching limit* of a symmetric two state driving force. The average drift velocity is then presented in the form of a continued fraction.

6.3 Stationary average drift velocity

The dimensionless quantum Smoluchowski equation in the stationary state governing the time-independent quantum Brownian motion of a particle in the ratchet potential with a constant tilt of arbitrary amplitude a is

$$\frac{\partial}{\partial x} \left\{ [V'(x) - a] P_{st}(x) + \frac{\partial}{\partial x} [D(x) P_{st}(x)] \right\} = 0. \quad (6.8)$$

Under stationary conditions, the probability current satisfying the continuity equation

$$\partial_t P(x, t) = -\partial_x J(x, t), \quad (6.9)$$

must have the constant value $J(a)$, with the argument a indicating that the current has its origin purely in the tilt. Hence, from (6.8) the constant probability current is

$$J(a) = -[V'(x) - a] P_{st}(x) - \frac{\partial}{\partial x} [D(x) P_{st}(x)]. \quad (6.10)$$

The stationary average drift velocity of the particle $\langle \dot{x} \rangle$ (cf. Eq. (2.19) with $V'(x)$ replaced by $V'(x) - a$) is found by averaging the drift terms so that [7]

$$\langle \dot{x} \rangle = - \int_0^{2\pi} [V'(x) - a] P_{st}(x) dx, \quad (6.11)$$

or, noting Eq. (6.10), in terms of the probability current

$$\langle \dot{x} \rangle = \int_0^{2\pi} J(a) + \frac{\partial}{\partial x} [D(x) P_{st}(x)] dx. \quad (6.12)$$

Since $P_{st}(x)$ is bounded and therefore periodic [7], so that $P_{st}(x + 2\pi) = P_{st}(x)$, we ultimately have

$$\langle \dot{x} \rangle = \int_0^{2\pi} J(a) dx = 2\pi J(a). \quad (6.13)$$

Now, $P_{st}(x)$ is normalised, i.e. $\int_0^{2\pi} P_{st}(x) dx = 1$, so that following the arguments used in Ref. [7] (see Ch. 11) for the classical case we have by quadratures the analytical result for the tilt induced probability current (details are given in Appendix 6.A)

$$J(a) = \frac{1 - e^{-2\pi a}}{\int_0^{2\pi} dx D(x)^{-1} e^{-\Psi(x)} \int_x^{x+2\pi} dy e^{\Psi(y)}}, \quad (6.14)$$

where the equilibrium potential is

$$\Psi(x) = \int^x \frac{V'(y) - a}{D(y)} dy. \quad (6.15)$$

Equation (6.14) was essentially derived by Kramers [44] in the context of the classical Smoluchowski equation (see also Ref. [83]) and extended to a tilted cosine potential by Risken [7]. In like manner, the stationary probability distribution may be determined from Eq. (6.10). We thus have the bounded distribution

$$P_{st}(x) = J(a)D^{-1}(x) \frac{e^{-\Psi(x)}}{1 - e^{-2\pi a}} \int_x^{x+2\pi} e^{\Psi(y)} dy, \quad (6.16)$$

where the probability current $J(a)$ serves as a normalising constant, analogous to the inverse partition function, Z^{-1} . In the case of zero tilt ($a = 0$), where the probability current is zero, the stationary solution is simply the Wigner equilibrium distribution in configuration space, which to first order in Λ is [31]

$$P_{st}(x) = Z^{-1} e^{-V(x)} \left\{ 1 + \frac{\Lambda}{2} [V'(x)^2 - 2V''(x)] \right\}, \quad (6.17)$$

where $Z = \int_0^{2\pi} P_{st}(x) dx$ is the partition function.

Equations (6.13), (6.14), and (6.15) constitute the exact, analytical solution for the stationary average drift velocity in a potential $V(x)$ with constant driving force a . For a negative driving force one finds that $\langle \dot{x} \rangle_- (a) = \langle \dot{x} \rangle_+ (-a)$ (the subscripts denote the separate cases of positive and negative amplitude). We may thus obtain an expression for the average drift velocity in the *slow-switching limit* of a symmetric, two-state, $\{+a, -a\}$ driving force, namely

$$\langle \dot{x} \rangle_{ssl} = [\langle \dot{x} \rangle_+ (a) + \langle \dot{x} \rangle_+ (-a)] = 2\pi [J(a) + J(-a)]. \quad (6.18)$$

Quantum effects in the Brownian ratchet have been studied in this switching regime, both in the non-inertial case using the original quantum Smoluchowski equation of Ankerhold *et al.* [97] and in the inertial case via the Caldeira-Leggett master equation in phase space [165]. The right-hand side of the Caldeira-Leggett master equation is often taken to be the same [76] as that of the Fokker-Planck equation. Thus quantum effects appear in the Liouville term only, leading in the non-inertial limit to the *classical* Smoluchowski equation¹. Now, in the non-inertial case, adopting the equation of Ankerhold *et al.* [97], Machura *et al.* [89] regard the diffusion coefficient in that equation as the leading term in the Taylor expansion of $(1 - \Lambda V''(x))^{-1}$ in order that the second law of thermodynamics is not violated (see the inset of Fig 1. of Ref. [89]). Furthermore, quantum noise enters in two places, via an effective potential and via an effective diffusion coefficient defined using the Taylor series expansion above.

In contrast, in the quantum Smoluchowski equation used here the potential is the same as the classical case, while the expansion of the diffusion coefficient (6.7) in powers of

¹Unlike in the phase space master equation (2.9), where the Kramers-Moyal coefficients of the collision kernel contain both the momentum and the derivatives of the potential, ultimately leading in the non-inertial limit to the quantum Smoluchowski equation (2.15)

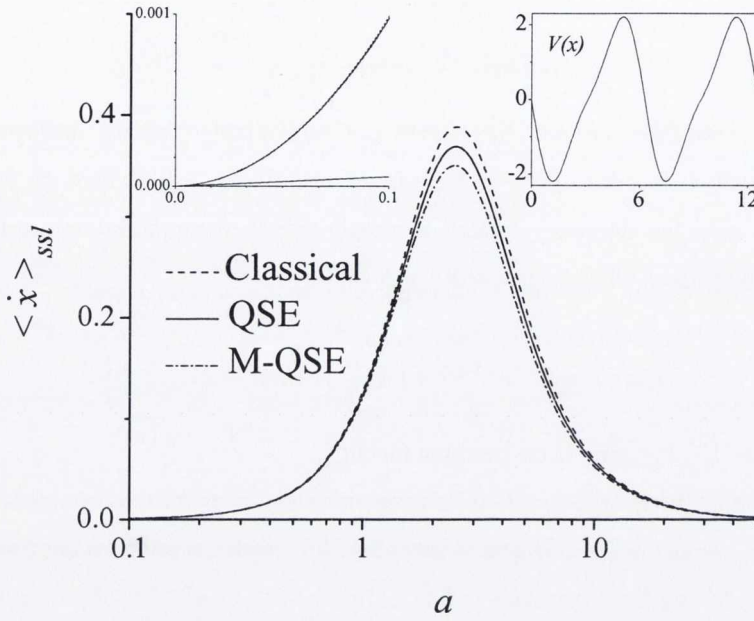


Figure 6.2: The average drift velocity in the slow switching limit $\langle \dot{x} \rangle_{ssl}$ vs. two-state driving force a for the ratchet potential $V_0 = -2$, $b_1 = 0.25$ and $b_2 = 0$ (see right inset). The quantum case ($\Lambda = 0.02$) for the quantum Smoluchowski equation (6.8) and that of Ref. [89] is shown along with the classical case ($\Lambda = 0$). In all cases there is zero probability current (no Maxwell-demon behaviour) at zero tilt (see left inset).

Λ is a consequence of the perturbation theory solution. Thus, the unphysical *net* particle-current at zero tilt is automatically eliminated. This is exemplified by the graph of the stationary average drift velocity in the slow-switching limit $\langle \dot{x} \rangle_{ssl}$ vs. the amplitude of the two-state driving force (tilt) a , plotted in Fig. 6.2 for the ratchet potential $V_0 = -2$, $b_1 = 0.25$ and $b_2 = 0$ (see right inset) by means of Eqs. (6.13), (6.14) and (6.15). For comparison both the classical result ($\Lambda = 0$) and the prediction of Machura *et al.* [89] to first order in Λ only are included. It is immediately apparent that, besides eliminating the undesirable Maxwell-demon behaviour (see left inset), the quantum Smoluchowski equation used here results in a smaller reduction in the average drift velocity due to quantum effects than that of Ref. [89]. By way of illustration of the convergence of the perturbation theory in Λ , Fig. 6.3 shows for the ratchet potential $V_0 = 1$, $b_1 = 0.5$ and $b_2 = 0.5$, in which the harmonics are relatively prominent (see right inset), the dependence of the average drift velocity $\langle \dot{x} \rangle_{ssl}$ on the two state driving amplitude a for various values of the quantum parameter, $\Lambda = 0$ (curve 1, classical limit), $\Lambda = 0.02$ (curves 2) and $\Lambda = 0.04$ (curves 3). Clearly as Λ increases the higher order terms in the diffusion coefficient must

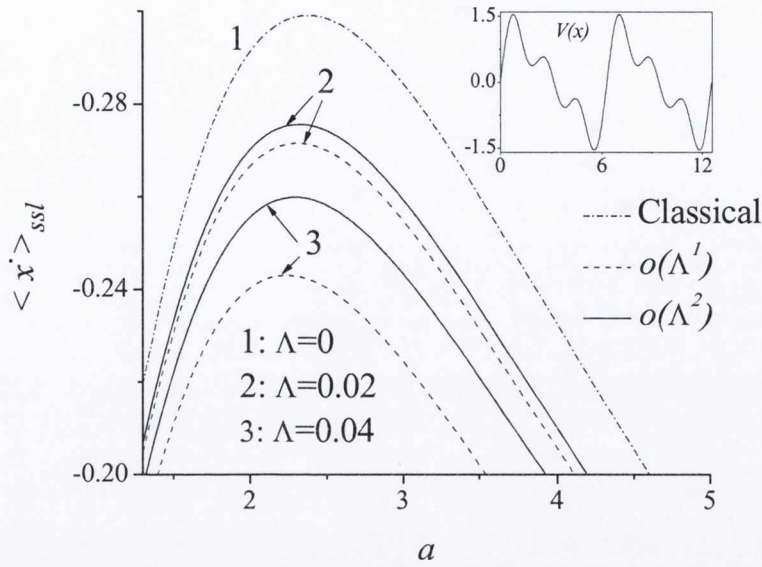


Figure 6.3: The average drift velocity in the low switching limit $\langle \dot{x} \rangle_{ssl}$ vs. two-state driving force a in the ratchet potential $V_0 = 1$, $b_1 = 0.5$ and $b_2 = 0.5$ (see inset) for various values of the quantum parameter, $\Lambda = 0$ (curve 1, classical limit), $\Lambda = 0.02$ (curves 2) and $\Lambda = 0.04$ (curves 3). Dashed and solid lines are the predictions of the quantum Smoluchowski equation to first- and second-order quantum corrections, respectively. Clearly as Λ increases the higher order terms in the diffusion coefficient must be included.

be included in order to achieve satisfactory convergence.

The stationary solution presented above in integral form has been obtained by quadratures. However, that solution may also be obtained via Fourier's theorem using continued fractions, which are particularly suited to the numerical evaluation of the Fourier coefficients. Moreover, the average drift velocity may be expressed as a linear combination of these coefficients. Continued fractions are an efficient method of obtaining the exact stationary solution for ac driving forces and have the merit that only minor alterations are required in proceeding from the time-independent stationary solution to the ac response. The time-independent solution has the Fourier expansion

$$P_{st}(x) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} C_n e^{inx}, \quad (6.19)$$

where the time-independent coefficients (characteristic function of the random variable x) are

$$C_n = \int_0^{2\pi} e^{-inx} P_{st}(x) dx = \langle e^{-inx} \rangle_0, \quad (6.20)$$

and the zero subscript denotes averaging over the stationary distribution $P_{st}(x)$. For ease of presentation, the continued fraction governing the solution of the quantum Smoluchowski equation (6.8) is written to first order in Λ only. Thus, substituting the Fourier expansion Eq. (6.19) into Eq. (6.8), the recurrence relation of the C_n to first order in Λ is

$$\begin{aligned} (ia + n)C_n - \frac{1}{2}iV_0 [(1 + n\Lambda)C_{n+1} + (1 - n\Lambda)C_{n-1}] \\ - ib_1V_0 [(1 + 2n\Lambda)C_{n+2} + (1 - 2n\Lambda)C_{n-2}] \\ - \frac{3}{2}ib_2V_0 [(1 + 3n\Lambda)C_{n+3} + (1 - 3n\Lambda)C_{n-3}] = 0. \end{aligned} \quad (6.21)$$

The solution of this seven-term recurrence relation for the Fourier coefficients via matrix continued fractions is given in Appendix 6.B. By orthogonality, using Eq. (6.11) the stationary average drift velocity of the particle $\langle \dot{x} \rangle_0$ is then given by the following linear combination of Fourier coefficients

$$\langle \dot{x} \rangle_0 = a - V_0 \text{Re} [C_1 + 2b_1C_2 + 3b_2C_3]. \quad (6.22)$$

6.4 Linear ac response of the quantum Brownian ratchet

Essentially, the same continued fraction as that resulting from Eq. (6.21) may be used to study quantum effects in the frequency dependence of the average drift velocity of the Brownian ratchet. Thus, we suppose that the ratchet is driven (in addition to the tilt a) by an unbiased ac force of amplitude a' and dimensionless angular frequency ω . Hence, the time-dependent distribution $P(x, t)$ is required. This may again be expanded as the complex Fourier series

$$P(x, t) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} c_n(t) e^{inx}, \quad (6.23)$$

where the Fourier coefficients which determine the characteristic function of the displacement x are

$$c_n(t) = \int_0^{2\pi} e^{-inx} P(x, t) dx.$$

Substituting Eq. (6.23) into Eq. (6.5), the $c_n(t)$ are found to satisfy the following ordinary differential-recurrence relation to first order in Λ

$$\begin{aligned}
\frac{d}{dt}c_n(t) + (ian + n^2)c_n(t) - \frac{inV_0}{2} [(1 + n\Lambda)c_{n+1}(t) + (1 - n\Lambda)c_{n-1}(t)] \\
- inb_1V_0 [(1 + 2n\Lambda)c_{n+2}(t) + (1 - 2n\Lambda)c_{n-2}(t)] \\
- \frac{3}{2}inb_2V_0 [(1 + 3n\Lambda)c_{n+3}(t) + (1 - 3n\Lambda)c_{n-3}(t)] = 0. \quad (6.24)
\end{aligned}$$

Equation (6.24) reduces to the previous time-independent recurrence relation (6.21) by simply omitting the time derivative. Moreover, it is essentially similar to the recurrence relation governing the quantum Brownian motion of a particle in a tilted cosine potential. The solution of that problem has recently been obtained in the context of quantum effects in the impedance of a Josephson junction [120, 173] and long ago in the classical limit [175, 176].

We now specialise Eq. (6.24) (valid for arbitrary driving amplitude a') to small amplitudes such that $a' \ll 1$. Hence the ratchet is only weakly perturbed, eliminating the phase modulation effects arising from the term $ianc_n(t)$ in Eq. (6.24), which gives rise to an infinite number of harmonics in the ac response and frequency dependence of the dc response [177]. This procedure allows one to evaluate its *linear* response, which may be extracted from Eq. (6.24) via perturbation theory in the oscillatory part a' of the tilt parameter as follows. We make the perturbation expansion (which implicitly assumes that all transients due to the imposition of the ac driving force have died away and that harmonics of that force are no longer generated)

$$c_n(t) = C_n + a'c_n(\omega)e^{i\omega t} + \dots, \quad n = 0, \pm 1, \pm 2, \dots \quad (6.25)$$

where the *stationary* coefficients C_n constitute the zeroth order of perturbation theory and satisfy the time-independent recurrence relation (6.21). Moreover, the particular Fourier coefficient $c_0(\omega) = 0$, since $c_0(t) = 1$ and $C_0 = 1$. Substituting Eq. (6.25) into the recurrence relation (6.24), with the replacement $a \rightarrow a + a'e^{i\omega t}$ and keeping only terms linear in the perturbation a' , we have the *forced* recurrence relation for the Fourier amplitudes, namely

$$(ia + n + i\omega/n)c_n(\omega) - \frac{1}{2}iV_0 [(1 + n\Lambda)c_{n+1}(\omega) + (1 - n\Lambda)c_{n-1}(\omega)] \quad (6.26)$$

$$-ib_1V_0 [(1 + 2n\Lambda)c_{n+2}(\omega) + (1 - 2n\Lambda)c_{n-2}(\omega)] \quad (6.27)$$

$$- \frac{3}{2}ib_2V_0 [(1 + 3n\Lambda)c_{n+3}(\omega) + (1 - 3n\Lambda)c_{n-3}(\omega)] = -iC_n. \quad (6.28)$$

In Appendix 6.C, the solution of the forced recurrence relation (6.26) via matrix continued fractions is presented, noting that all the stationary solution coefficients C_n are involved in

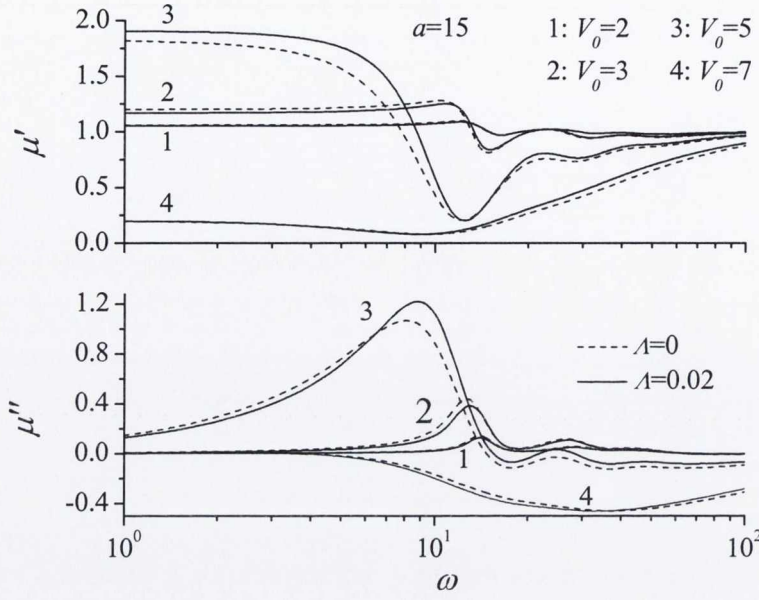


Figure 6.4: The real and imaginary parts of the linear dynamic mobility $\mu = \mu' - i\mu''$ vs. angular frequency ω in the ratchet potential $b_1 = 0.5$ and $b_2 = 0.5$ (see inset of Fig. 6.3) for various values of the barrier height $V_0 = 2$ (curves 1), $V_0 = 3$ (curves 2), $V_0 = 5$ (curves 3) and $V_0 = 7$ (curves 4), and the constant tilt $a = 15$. The classical (dashed lines, $\Lambda = 0$) and quantum (solid lines, $\Lambda = 0.02$) cases are shown.

the linear approximation. Recalling that the averaged dynamical equation in the presence of a weak ac force is

$$\langle \dot{x} \rangle_0 + \langle \dot{x} \rangle_1 = a + a' e^{i\omega t} - \langle \partial_x V \rangle_0 - \langle \partial_x V \rangle_1,$$

where the zero subscript on the angular brackets denotes the average in the absence of the ac force, and the subscript 1 the portion of the average which is linear in a' , one has

$$\langle \dot{x} \rangle_1 = \mu(\omega) a' e^{i\omega t},$$

where $\mu = \mu' - i\mu''$ is the linear dynamic mobility given via orthogonality by the linear combination of Fourier amplitudes

$$\mu(\omega) = 1 - \frac{V_0}{2} \{c_1(\omega) + c_1^*(-\omega) + 2b_1 [c_2(\omega) + c_2^*(-\omega)] + 3b_2 [c_3(\omega) + c_3^*(-\omega)]\}, \quad (6.29)$$

where $c_n(\omega) = c_{-n}^*(-\omega)$ and the asterisk denotes complex conjugate.

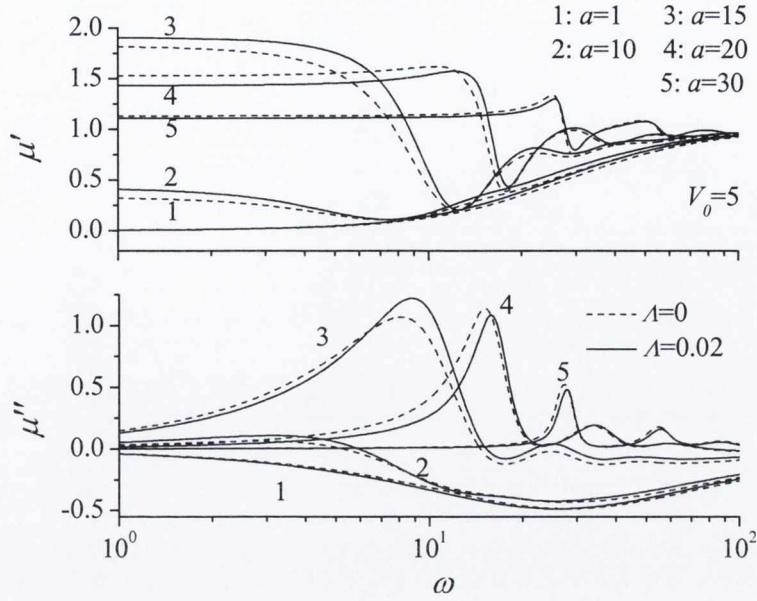


Figure 6.5: The real and imaginary parts of the linear dynamic mobility $\mu = \mu' - i\mu''$ vs. ω in the ratchet potential $V_0 = 5$, $b_1 = 0.5$ and $b_2 = 0.5$ for various values of the tilt $a = 1$ (curves 1), $a = 10$ (curves 2), $a = 15$ (curves 3), $a = 20$ (curves 4) and $a = 30$ (curves 5). The classical (dashed lines, $\Lambda = 0$) and quantum (solid lines, $\Lambda = 0.01$) cases are shown.

The real and imaginary parts of $\mu(\omega)$ given by Eq. (6.29) as a function of frequency are plotted for various values of the barrier height parameter V_0 in Fig. 6.4 and for various values of the tilt a in Fig. 6.5. In Fig. 6.4 the curves show a pronounced minimum in $\mu'(\omega)$ and maximum in $\mu''(\omega)$ accompanied by subsidiary minima and maxima at higher frequencies. The quantum effects, which increase the height of the maxima and shift them to higher frequencies (as in the related problem of the impedance of the Josephson junction, see Chapter 4), are most pronounced for moderate barrier heights $V_0 = 5$. They may be ascribed to dissipative tunnelling at high temperatures near the top of a barrier created by the ratchet potential, effectively reducing the barrier height and representing a decrease in the damping factor. The quantum effects are smaller for the barriers created by the second and third harmonics of the potential and appear at higher frequencies. This behaviour is replicated in Fig. 6.5, where the mobility is plotted for various values of the tilt. Again, as is the experience with the Josephson junction, quantum effects are most prominent at moderate tilts, causing the principal maximum in the imaginary part to shift to higher frequencies with increasing tilt.

6.5 Nonlinear response of the quantum Brownian ratchet

In the previous section, the quantum Brownian ratchet with arbitrary tilt perturbed by a weak alternating force $a'e^{i\omega t}$ so that $a' \ll 1$ was considered. Hence the response is linear in the first order of perturbation in a' . In order to calculate the frequency response of the ratchet for *arbitrary* driving amplitude a' , we must consider the nonlinear solution. Since we are again concerned with the stationary response, where the driving force has been applied for a very long time, we may ignore transient effects and seek a solution independent of the initial conditions. Thus, we make the temporal Fourier expansion

$$c_n(t) = \sum_{k=-\infty}^{\infty} c_n^k(\omega) e^{ik\omega t}, \quad (6.30)$$

where the infinite sum in k accounts for the *infinite* number of harmonics of the stimulus produced by the *nonlinear* characteristics of the Brownian ratchet and the Fourier coefficients have the property $c_n^k(\omega) = c_{-n}^{k*}(-\omega) = c_{-n}^{-k*}(\omega)$, because $P(x, t)$ must be real. The harmonic generating property of the nonlinear response is particularly obvious if one simply regards Eq. (6.24) as a differential equation for a linear time-varying system forced by the recurring terms. The integrating factor thus involves a time-varying double transcendental function, which causes phase modulation of the successive approximations solution. This has been illustrated in detail in Ref. [178] in connection with the classical treatment of the Josephson junction in the zero capacitance limit. We remark that the frequency dependence of the dc term is more or less a universal phenomenon in nonlinear systems driven by alternating forces, occurring in systems as diverse as the Josephson junction, ring-laser gyros, superparamagnetic nanoparticles [82], and the Kerr-effect response of dipoles in a mean field potential [179]. In ratchets, the frequency dependence is due to the ever prevailing modulation of the static characteristics resulting in loss of phase locking, e.g. the well known Shapiro steps in the frequency-dependent dc current-voltage characteristic of the Josephson junction [180]. However, the frequency-dependent dc response of electric dipoles is inherently simpler than that of the ratchet because the integrating factor in the sense mentioned above is essentially time-invariant. The effect of the nonlinearity in this case is to give rise to *amplitude* rather than *phase* modulation [177].

By substituting Eq. (6.30) into Eq. (6.24) and letting the tilt $a \rightarrow a + a' \cos \omega t$, we have the dual-index recurrence relation for the Fourier amplitudes $c_n^k(\omega)$, viz.

$$\begin{aligned}
& (ia + n + ik\omega/n) c_n^k(\omega) + \frac{1}{2}ia' [c_n^{k+1}(\omega) + c_n^{k-1}(\omega)] \\
& - \frac{1}{2}iV_0 [(1 + n\Lambda)c_{n+1}^k(\omega) + (1 - n\Lambda)c_{n-1}^k(\omega)] \\
& - ib_1V_0 [(1 + 2n\Lambda)c_{n+2}^k(\omega) + (1 - 2n\Lambda)c_{n-2}^k(\omega)] \\
& - \frac{3}{2}ib_2V_0 [(1 + 3n\Lambda)c_{n+3}^k(\omega) + (1 - 3n\Lambda)c_{n-3}^k(\omega)] = 0,
\end{aligned} \tag{6.31}$$

where n and k are integers varying from $-\infty$ to ∞ , $c_0^0(\omega) = 1$ and $c_0^k(\omega) = 0$ ($k > 0$). The recurrence relation (6.31) above is given in matrix continued fraction form in Appendix 6.D, where supermatrices will now be involved as a result of the dual-indices n and k . Finally, from Eq. (6.11) (replacing a with $a + a' \cos \omega t$) the average drift velocity $\langle \dot{x} \rangle$ in the presence of an alternating force $a' \cos \omega t$ is given by

$$\langle \dot{x} \rangle = a + a' \cos \omega t - \frac{1}{2\pi} \int_0^{2\pi} V'(x) \sum_{n=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} c_n^k(\omega) e^{ik\omega t} e^{inx} dx.$$

Substituting the explicit form of the potential, Eq. (6.6), and using orthogonality we have

$$\begin{aligned}
\langle \dot{x} \rangle = & a + a' \cos \omega t - \frac{V_0}{2} \sum_{k=-\infty}^{\infty} e^{ik\omega t} [c_1^k(\omega) + c_{-1}^k(\omega) \\
& + 2b_1c_2^k(\omega) + 2b_1c_{-2}^k(\omega) + 3b_2c_3^k(\omega) + 3b_2c_{-3}^k(\omega)],
\end{aligned}$$

which may be expanded as

$$\begin{aligned}
\langle \dot{x} \rangle = & a - V_0 \operatorname{Re} [c_1^0(\omega) + 2b_1c_2^0(\omega) + 3b_2c_3^0(\omega)] \\
& + \left\{ 1 - \frac{V_0}{a'} [c_1^1(\omega) + c_{-1}^1(\omega) + 2b_1c_2^1(\omega) + 2b_1c_{-2}^1(\omega) + 3b_2c_3^1(\omega) + 3b_2c_{-3}^1(\omega)] \right\} \frac{a'}{2} e^{i\omega t} \\
& + \left\{ 1 - \frac{V_0}{a'} [c_1^{-1}(\omega) + c_{-1}^{-1}(\omega) + 2b_1c_2^{-1}(\omega) + 2b_1c_{-2}^{-1}(\omega) + 3b_2c_3^{-1}(\omega) + 3b_2c_{-3}^{-1}(\omega)] \right\} \frac{a'}{2} e^{-i\omega t} \\
& + \frac{V_0}{2} \sum_{k=2}^{\infty} \left\{ e^{ik\omega t} [c_1^k(\omega) + c_{-1}^k(\omega) + 2b_1c_2^k(\omega) + 2b_1c_{-2}^k(\omega) + 3b_2c_3^k(\omega) + 3b_2c_{-3}^k(\omega)] \right. \\
& \left. + e^{-ik\omega t} [c_1^{-k}(\omega) + c_{-1}^{-k}(\omega) + 2b_1c_2^{-k}(\omega) + 2b_1c_{-2}^{-k}(\omega) + 3b_2c_3^{-k}(\omega) + 3b_2c_{-3}^{-k}(\omega)] \right\} \tag{6.32}
\end{aligned}$$

The first line of Eq. (6.32) represents the frequency-dependent dc term $\langle \dot{x} \rangle_{dc}$, corresponding to the stationary frequency-independent response Eq. (6.22). The next two lines represent the response at the fundamental frequency and although ostensibly of the same form as the *linear* dynamic mobility Eq. (6.29), differ in principle from it because each Fourier component now contains contributions from all other harmonics (which arise on account of the nonlinear behaviour, see Ref. [177]). The remaining two lines represent the infinite number of harmonics of the driving signal, generated by nonlinearity.

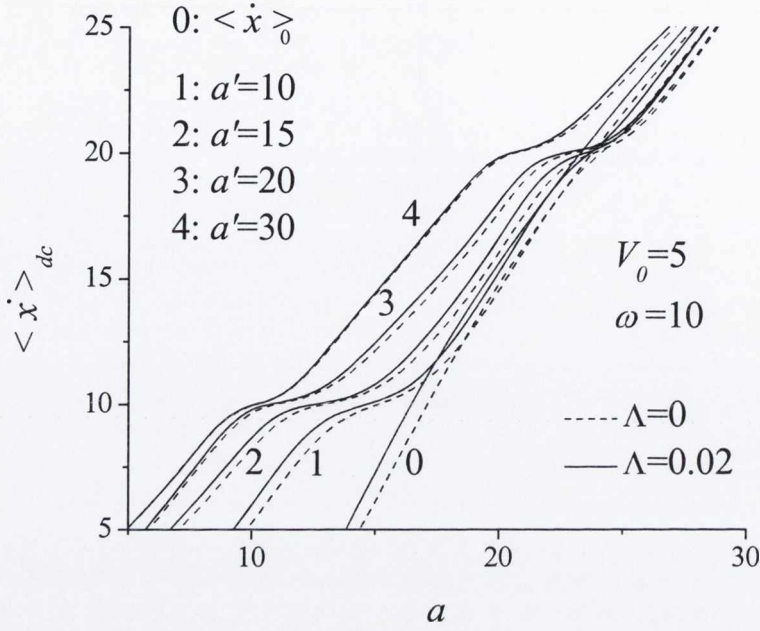


Figure 6.6: The frequency-dependent dc term of the average drift velocity $\langle \dot{x} \rangle_{dc}$ vs. the tilt a in the ratchet potential $V_0 = 5$, $b_1 = 0.5$ and $b_2 = 0.5$ for various values of the ac driving amplitude $a' = 10$ (curves 1), $a' = 15$ (curves 2), $a' = 20$ (curves 3) and $a' = 30$ (curves 4) for fixed frequency $\omega = 10$. The Shapiro steps (curves 1-4) appear as a result of phase modulation due to nonlinear effects, in contrast to the frequency-independent average drift velocity $\langle \dot{x} \rangle_0$ (curve 0) plotted using Eq. (6.22). The classical (dashed lines, $\Lambda = 0$) and quantum (solid lines, $\Lambda = 0.02$) cases are shown.

The frequency dependence of dc term $\langle \dot{x} \rangle_{dc}$ for various values of the driving amplitude a' is plotted as a function of the tilt a in Fig. 6.6 and as a function of the frequency ω in Fig. 6.7. In Fig. 6.6, the well known Shapiro steps (curves 1-4) familiar in the dc current/voltage characteristics of a Josephson junction for strong ac driving are illustrated. The steps appear as a result of phase modulation due to nonlinear effects and represent loss of phase locking (phase slips) at harmonics of the ac driving force. This result is in marked contrast to the frequency-independent average dc drift velocity Eq. (6.22) (curve 0) where the steps do not exist. The quantum effects are most pronounced, as with the previous results [120, 173] of the Josephson junction, for relatively small values of the driving force (although strong enough to cause nonlinear behaviour) becoming almost imperceptible for very large driving forces, where they tend to be masked by the nonlinearity. In Fig. 6.7, the frequency response of the ac-induced average dc mobility is shown. The quantum effects again tend to enhance the ac-induced dc mobility in comparison with the classical case.

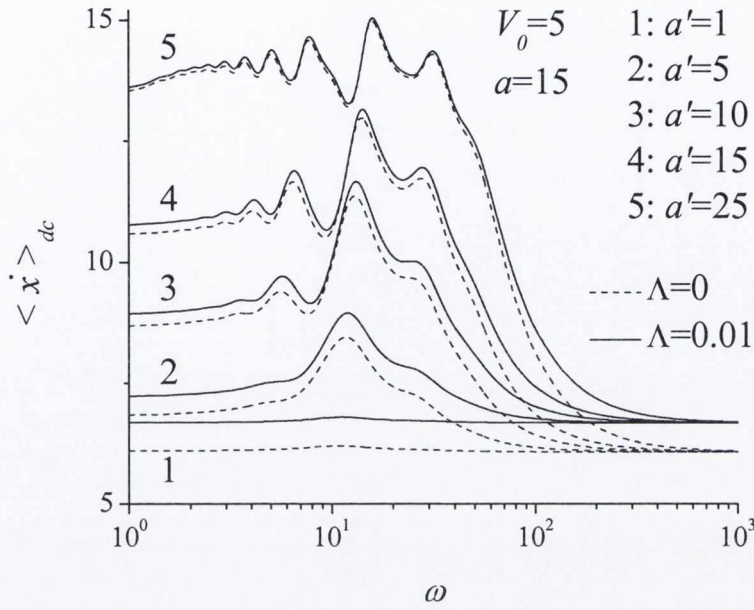


Figure 6.7: The frequency-dependent dc term of the average drift velocity $\langle \dot{x} \rangle_{dc}$ vs. angular frequency ω in the ratchet potential $V_0 = 5$, $b_1 = 0.5$ and $b_2 = 0.5$ for various values of the ac driving amplitude $a' = 1$ (curves 1), $a' = 5$ (curves 2), $a' = 10$ (curves 3), $a' = 15$ (curves 4) and $a' = 25$ (curves 5), and the constant tilt $a = 15$. The classical (dashed lines, $\Lambda = 0$) and quantum (solid lines, $\Lambda = 0.01$) cases are shown.

They are most pronounced at frequencies corresponding to the ac-induced peaks in the dc response increasing the effective peak mobility for moderate driving due to the reduction in damping, arising from high temperature dissipative tunnelling near the top of a barrier. The quantum effects also cause slower falloffs of the dc response and again become very small as the amplitude of the driving force is increased due to the masking effects of the nonlinearity (compare curves 1 and 5 of Fig. 6.7). The behaviour at the peak frequencies seems to be entirely consistent with the effective reduction in damping due to tunnelling (mentioned above), resulting in increased mobility, so enhancing the peaks just as in the Josephson junction. The same behaviour is evident in the imaginary part of the nonlinear mobility at the fundamental frequency of the driving force, where once again the maxima in the spectra are enhanced with the quantum effects being most pronounced for moderate driving as shown in Fig. 6.8.

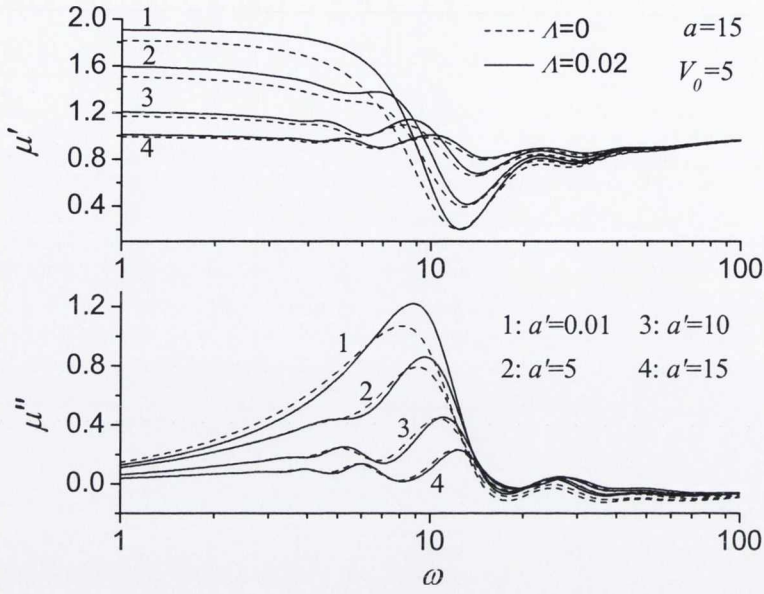


Figure 6.8: The real and imaginary parts of the *nonlinear* dynamic mobility $\mu = \mu' - i\mu''$ vs. angular frequency ω in the ratchet potential, $V_0 = 5$, $b_1 = 0.5$ and $b_2 = 0.5$ for various values of the stimulus amplitude $a' = 0.01$ (curves 1), $a' = 5$ (curves 2), $a' = 10$ (curves 3) and $a' = 15$ (curves 4), and the constant tilt $a = 15$. The classical (dashed lines, $\Lambda = 0$) and quantum (solid lines, $\Lambda = 0.02$) cases are shown. In the limit of $a' \ll 1$ the linear response is reproduced, i.e. curves 1 correspond exactly to curves 3 of Fig. 6.4.

6.6 Conclusions

The quantum Smoluchowski equation of Coffey *et al.* may be used to calculate the average drift velocity of a quantum ratchet for wide ranges of the barrier height, tilt and ac driving parameters. It appears that quantum effects reduce the average drift velocity in the slow switching limit of a two-state driving force in comparison to the classical case. In general, as far as the frequency response is concerned, the quantum effects modify the spectra of the mobility. The origin of this phenomenon appears to be due a reduction of the barrier height, representing a decrease in the damping factor and thus an increase in the dynamic mobility (due to high temperature tunnelling near the top of the barrier) over the corresponding classical results for a given bias. Furthermore, in accordance with previous experience [120, 173] concerning the ac response of the Josephson junction, the quantum effects are most pronounced for moderate ac driving forces, generally diminishing with increasing ac amplitude as they now tend to be masked by the extreme nonlinear behaviour. A most interesting additional feature of the nonlinear frequency-dependent dc response

to a strong ac driving force, in both the quantum and classical cases, is the appearance of Shapiro-like steps [178, 180] (due to loss of phase locking at harmonics of the driving force) in the average dc drift velocity versus tilt characteristic. This phenomenon is exactly analogous to the Shapiro steps [180] in the dc current/voltage characteristics of the Josephson junction for strong ac driving and should be amenable to experimental verification as a universal feature of the dc response associated with strong ac driving of particles in tilted periodic potentials.

6.A Stationary probability current

One must first obtain the equilibrium potential $\Psi(x)$. Integrating Eq. (6.8) once w.r.t. x , one finds

$$\frac{V'(x) - a}{D(x)} D(x) P_{st}(x) + \frac{\partial}{\partial x} [D(x) P_{st}(x)] = 0. \quad (6.33)$$

where the fraction $D(x)/D(x)$ has been included so that (6.33) appears in *standard* form. Thus, this first-order, linear, differential, homogeneous equation has the formal solution

$$D(x) P_{st}(x) = N e^{-\Psi(x)}, \quad (6.34)$$

where the integration factor (known in this context as the equilibrium potential) is

$$\Psi(x) = \int^x \frac{V'(y) - a}{D(y)} dy. \quad (6.35)$$

Now, in general the probability current (6.9) can be written in terms of the potential (6.35) viz.

$$J(x, t) = -e^{-\Psi(x)} \frac{\partial}{\partial x} \left[e^{\Psi(x)} D(x) P(x, t) \right]. \quad (6.36)$$

This is easily checked by directly substituting (6.35). Hence, in the stationary state, $J(x, t) = J(a)$, $P(x, t) = P_{st}(x)$ we have

$$J(a) = -e^{-\Psi(x)} \frac{\partial}{\partial x} \left[e^{\Psi(x)} D(x) P_{st}(x) \right]. \quad (6.37)$$

This is simply Eq. (6.10) written in terms of Eq. (6.35). Dividing both sides by $\exp[-\Psi(x)]$ and integrating w.r.t. x over an arbitrary period $(x, x + 2\pi)$ yields

$$J(a) = - \frac{|e^{\Psi(x)} D(x) P_{st}(x)|_x^{x+2\pi}}{\int_x^{x+2\pi} e^{\Psi(x)} dx}.$$

Since $P_{st}(x) = P_{st}(x + 2\pi)$, $\forall x$, evaluating the nominator yields²

$$J(a) = D(x)P_{st}(x) \frac{e^{\Psi(x)} - e^{\Psi(x+2\pi)}}{\int_x^{x+2\pi} e^{\Psi(x)} dx}.$$

From Eq. (6.35) we have $\Psi(x + 2\pi) = \Psi(x) - 2\pi a$ so that

$$J(a) = P_{st}(x) \frac{1 - e^{-2\pi a}}{D(x)^{-1} e^{-\Psi(x)} \int_x^{x+2\pi} e^{\Psi(x)} dx}.$$

Finally, multiplying both sides by the denominator, integrating between 0 and 2π , and using the fact that the distribution is normalised, namely $\int_0^{2\pi} P_{st}(x) dx = 1$, yields the result

$$J(a) = \frac{1 - e^{-2\pi a}}{\int_0^{2\pi} dx D(x)^{-1} e^{-\Psi(x)} \int_x^{x+2\pi} dy e^{\Psi(y)}}, \quad (6.38)$$

where the equilibrium potential is given by Eq. (6.35).

6.B Stationary solution: Matrix continued fraction solution of Eq. (6.21)

The recurrence relation for the C_n may be represented as the seven-term recurrence relation

$$\begin{aligned} q_n C_n + q_n^+ C_{n+1} + q_n^- C_{n-1} + 2b_1 q_{2n}^+ C_{n+2} + 2b_1 q_{2n}^- C_{n-2} \\ + 3b_2 q_{3n}^+ C_{n+3} + 3b_2 q_{3n}^- C_{n-3} = 0, \end{aligned} \quad (6.39)$$

where $q_n = ia + n$ and $q_n^\pm = -iV_0(1 \pm n\Lambda)/2$. By introducing the column vectors C_n (which are in general complex)

$$C_{\pm n} = \begin{pmatrix} C_{\pm 3n} \\ C_{\pm(3n-1)} \\ C_{\pm(3n-2)} \end{pmatrix}, \quad n > 1,$$

with $C_0 = (1)$ and the property $C_{-n} = C_n^*$, Eq. (6.39) may be rewritten in terms of the inhomogeneous and homogeneous matrix three-term recurrence relations

$$Q_1^- C_0 + Q_1 C_1 + Q_1^+ C_2 = -FC_1^* \quad (n = 1), \quad (6.40)$$

²The diffusion coefficient $D(x)$ is also periodic in 2π .

$$\mathbf{Q}_n^- \mathbf{C}_{n-1} + \mathbf{Q}_n \mathbf{C}_n + \mathbf{Q}_n^+ \mathbf{C}_{n+1} = 0 \quad (n > 1), \quad (6.41)$$

where the matrices $\mathbf{Q}_n$ and $\mathbf{Q}_n^\pm$ are given by

$$\begin{aligned} \mathbf{Q}_n &= \begin{pmatrix} q_{3n} & q_{3n}^- & 2b_1 q_{2(3n)}^- \\ q_{3n-1}^+ & q_{3n-1} & q_{3n-1}^- \\ 2b_1 q_{2(3n-2)}^+ & q_{3n-2}^+ & q_{3n-2} \end{pmatrix}, \\ \mathbf{Q}_n^+ &= \begin{pmatrix} 3b_2 q_{3(3n)}^+ & 2b_1 q_{2(3n)}^+ & q_{3n}^+ \\ 0 & 3b_2 q_{3(3n-1)}^+ & 2b_1 q_{2(3n-1)}^+ \\ 0 & 0 & 3b_2 q_{3(3n-2)}^+ \end{pmatrix}, \\ \mathbf{Q}_n^- &= \begin{pmatrix} 3b_2 q_{3(3n)}^- & 0 & 0 \\ 2b_1 q_{2(3n-1)}^- & 3b_2 q_{3(3n-1)}^- & 0 \\ q_{3n-2}^- & 2b_1 q_{2(3n-2)}^- & 3b_2 q_{3(3n-2)}^- \end{pmatrix}, \end{aligned}$$

with $\mathbf{Q}_1^-$ and $\mathbf{F}$ defined as

$$\mathbf{Q}_1^- = \begin{pmatrix} 3b_2 q_9^- \\ 2b_1 q_4^- \\ q_1^- \end{pmatrix}, \quad \mathbf{F} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 3b_2 q_6^- \\ 0 & 3b_2 q_3^- & 2b_1 q_2^- \end{pmatrix}.$$

Introducing matrices $\mathbf{S}_n = \mathbf{C}_n (\mathbf{C}_{n-1})^{-1}$ and $\Delta_n = \mathbf{S}_n (\mathbf{Q}_n^-)^{-1}$ we then have the solution of the homogeneous equation (6.41) for $\mathbf{C}_n$ ($n > 1$) in terms of the matrix continued fractions

$$\mathbf{C}_n = \Delta_n \mathbf{Q}_n^- \Delta_{n-1} \mathbf{Q}_{n-1}^- \dots \Delta_2 \mathbf{Q}_2^- \mathbf{C}_1, \quad (6.42)$$

where Δ_n is the infinite matrix continued fraction defined by the recurrence equation

$$\Delta_n = (-\mathbf{Q}_n - \mathbf{Q}_n^+ \Delta_{n+1} \mathbf{Q}_{n+1}^-)^{-1}. \quad (6.43)$$

The inhomogeneous equation (6.40) for the vector $\mathbf{C}_1$ then has solution

$$\mathbf{C}_1 = \Delta_1 (\mathbf{Q}_1^- \mathbf{C}_0 + \mathbf{F} \mathbf{C}_1^*). \quad (6.44)$$

Next, we eliminate $\mathbf{C}_1^*$ by representing the various complex vectors and matrices in terms of their real and imaginary parts $\mathbf{C}_1 = \mathbf{C}'_1 + i\mathbf{C}''_1$, $\Delta_1 \mathbf{Q}_1^- = \mathbf{S}'_1 + i\mathbf{S}''_1$, and $\Delta_1 \mathbf{F} = \mathbf{F}' + i\mathbf{F}''$, so obtaining from Eq. (6.44) simultaneous equations for the unknowns $\mathbf{C}'_1$ and $\mathbf{C}''_1$ comprising the desired column vector $\mathbf{C}_1$, namely

$$(\mathbf{I} - \mathbf{F}')\mathbf{C}'_1 - \mathbf{F}''\mathbf{C}''_1 = \mathbf{S}'_1\mathbf{C}_0, \quad (6.45)$$

$$(\mathbf{I} + \mathbf{F}')\mathbf{C}''_1 - \mathbf{F}''\mathbf{C}'_1 = \mathbf{S}''_1\mathbf{C}_0, \quad (6.46)$$

where $\mathbf{I}$ is the unit matrix. Solving Eqs. (6.45) and (6.46) for $\mathbf{C}'_1$ and $\mathbf{C}''_1$ we have in terms of known matrices

$$\mathbf{C}'_1 = [\mathbf{I} - \mathbf{F}' - \mathbf{F}''(\mathbf{I} + \mathbf{F}')^{-1}\mathbf{F}'']^{-1}[\mathbf{S}'_1 + \mathbf{F}''(\mathbf{I} + \mathbf{F}')^{-1}\mathbf{S}''_1]\mathbf{C}_0,$$

$$\mathbf{C}''_1 = [\mathbf{I} + \mathbf{F}' - \mathbf{F}''(\mathbf{I} - \mathbf{F}')^{-1}\mathbf{F}'']^{-1}[\mathbf{S}''_1 + \mathbf{F}''(\mathbf{I} - \mathbf{F}')^{-1}\mathbf{S}'_1]\mathbf{C}_0.$$

6.C Linear response: Matrix continued fraction solution of Eq. (6.26)

In like manner, the eight-term recurrence relation for the Fourier amplitudes $c_n(\omega)$, Eq. (6.26) can be rearranged as

$$\begin{aligned} z_n(\omega)c_n(\omega) + q_n^+c_{n+1}(\omega) + q_n^-c_{n-1}(\omega) + 2b_1[q_{2n}^+c_{n+2}(\omega) \\ + q_{2n}^-c_{n-2}(\omega)] + 3b_2[q_{3n}^+c_{n+3}(\omega) + q_{3n}^-c_{n-3}(\omega)] = -iC_n, \end{aligned} \quad (6.47)$$

where $z_n(\omega) = ia + n + i\omega/n$ and $q_n^\pm = -iV_0(1 \pm n\Lambda)/2$. By introducing column vectors $\mathbf{C}_n(\omega)$ and the *known* stationary (or zero order of perturbation solution) column vector $\mathbf{C}_n^0$ (as calculated in Eqs. (6.42) and (6.44))

$$\mathbf{C}_{\pm n}(\omega) = \begin{pmatrix} c_{\pm 3n}(-\omega) \\ c_{\pm 3n}(\omega) \\ c_{\pm(3n-1)}(-\omega) \\ c_{\pm(3n-1)}(\omega) \\ c_{\pm(3n-2)}(-\omega) \\ c_{\pm(3n-2)}(\omega) \end{pmatrix}, \quad \mathbf{C}_{\pm n}^0 = i \begin{pmatrix} C_{\pm 3n} \\ C_{\pm 3n} \\ C_{\pm(3n-1)} \\ C_{\pm(3n-1)} \\ C_{\pm(3n-2)} \\ C_{\pm(3n-2)} \end{pmatrix}, \quad (n > 1),$$

with $\mathbf{C}_0 = (0)$ and the property $\mathbf{C}_{-n}(\omega) = \mathbf{C}_n^*(-\omega)$, Eq. (6.47) may be written as the inhomogeneous matrix three-term recurrence relations

$$\mathbf{Q}_1\mathbf{C}_1 + \mathbf{Q}_1^+\mathbf{C}_2 = -(\mathbf{C}_1^0 + \mathbf{F}\mathbf{C}_1^*) \quad (n = 1), \quad (6.48)$$

$$\mathbf{Q}_n^- \mathbf{C}_{n-1} + \mathbf{Q}_n \mathbf{C}_n + \mathbf{Q}_n^+ \mathbf{C}_{n+1} = -\mathbf{C}_n^0 \quad (n > 1). \quad (6.49)$$

The matrices $\mathbf{Q}_n$ and $\mathbf{Q}_n^\pm$ are given by

$$\mathbf{Q}_n = \begin{pmatrix} z_{3n}(-\omega) & 0 & q_{3n}^- & 0 & 2b_1 q_{2(3n)}^- & 0 \\ 0 & z_{3n}(\omega) & 0 & q_{3n}^- & 0 & 2b_1 q_{2(3n)}^- \\ q_{3n-1}^+ & 0 & z_{3n-1}(-\omega) & 0 & q_{3n-1}^- & 0 \\ 0 & q_{3n-1}^+ & 0 & z_{3n-1}(\omega) & 0 & q_{3n-1}^- \\ 2b_1 q_{2(3n-2)}^+ & 0 & q_{3n-2}^+ & 0 & z_{3n-2}(-\omega) & 0 \\ 0 & 2b_1 q_{2(3n-2)}^+ & 0 & q_{3n-2}^+ & 0 & z_{3n-2}(\omega) \end{pmatrix},$$

$$\mathbf{Q}_n^+ = \begin{pmatrix} 3b_2 q_{3(3n)}^+ & 0 & 2b_1 q_{2(3n)}^+ & 0 & q_{3n}^+ & 0 \\ 0 & 3b_2 q_{3(3n)}^+ & 0 & 2b_1 q_{2(3n)}^+ & 0 & q_{3n}^+ \\ 0 & 0 & 3b_2 q_{3(3n-1)}^+ & 0 & 2b_1 q_{2(3n-1)}^+ & 0 \\ 0 & 0 & 0 & 3b_2 q_{3(3n-1)}^+ & 0 & 2b_1 q_{2(3n-1)}^+ \\ 0 & 0 & 0 & 0 & 3b_2 q_{3(3n-2)}^+ & 0 \\ 0 & 0 & 0 & 0 & 0 & 3b_2 q_{3(3n-2)}^+ \end{pmatrix},$$

$$\mathbf{Q}_n^- = \begin{pmatrix} 3b_2 q_{3(3n)}^- & 0 & 0 & 0 & 0 & 0 \\ 0 & 3b_2 q_{3(3n)}^- & 0 & 0 & 0 & 0 \\ 2b_1 q_{2(3n-1)}^- & 0 & 3b_2 q_{3(3n-1)}^- & 0 & 0 & 0 \\ 0 & 2b_1 q_{2(3n-1)}^- & 0 & 3b_2 q_{3(3n-1)}^- & 0 & 0 \\ q_{3n-2}^- & 0 & 2b_1 q_{2(3n-2)}^- & 0 & 3b_2 q_{3(3n-2)}^- & 0 \\ 0 & q_{3n-2}^- & 0 & 2b_1 q_{2(3n-2)}^- & 0 & 3b_2 q_{3(3n-2)}^- \end{pmatrix},$$

with $\mathbf{F}$ defined as

$$\mathbf{F} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3b_2 q_6^- \\ 0 & 0 & 0 & 0 & 3b_2 q_6^- & 0 \\ 0 & 0 & 0 & 3b_2 q_3^- & 0 & 2b_1 q_2^- \\ 0 & 0 & 3b_2 q_3^- & 0 & 2b_1 q_2^- & 0 \end{pmatrix}.$$

The solution of Eq. (6.49) (see Refs. [82, 181] for details) is given by

$$\mathbf{C}_n = \Delta_n \mathbf{Q}_n^- \mathbf{C}_{n-1} + \Delta_n \left[\mathbf{C}_n^0 + \sum_{k=1}^{\infty} \left(\prod_{p=1}^k \mathbf{Q}_{n+p-1}^+ \Delta_{n+p} \right) \mathbf{C}_{n+k}^0 \right]. \quad (6.50)$$

Noting that $\mathbf{C}_0 = (0)$, Eq. (6.48) can be solved for $\mathbf{C}_1$ yielding

$$\mathbf{C}_1 = \Delta_1 (\mathbf{C}_1^0 + \mathbf{X}_1 + \mathbf{F}\mathbf{C}_1^*), \quad (6.51)$$

where

$$\mathbf{X}_1 = \sum_{k=1}^{\infty} \left(\prod_{p=1}^k \mathbf{Q}_p^+ \Delta_{p+1} \right) \mathbf{C}_{k+1}^0.$$

Representing the complex vectors and matrices in (6.51) as $\mathbf{C}_1 = \mathbf{C}'_1 + i\mathbf{C}''_1$, $\Delta_1(\mathbf{C}_1^0 + \mathbf{X}_1) = \mathbf{C}_1^{0'} + i\mathbf{C}_1^{0''}$ and $\Delta_1\mathbf{F} = \mathbf{F}' + i\mathbf{F}''$, we can solve for $\mathbf{C}'_1$ and $\mathbf{C}''_1$ by equating coefficients to find in terms of known matrices

$$\mathbf{C}'_1 = [\mathbf{I} - \mathbf{F}' - \mathbf{F}''(\mathbf{I} + \mathbf{F}')^{-1}\mathbf{F}'']^{-1}[\mathbf{C}_1^{0'} + \mathbf{F}''(\mathbf{I} + \mathbf{F}')^{-1}\mathbf{C}_1^{0''}],$$

$$\mathbf{C}''_1 = [\mathbf{I} + \mathbf{F}' - \mathbf{F}''(\mathbf{I} - \mathbf{F}')^{-1}\mathbf{F}''']^{-1}[\mathbf{C}_1^{0''} + \mathbf{F}''(\mathbf{I} - \mathbf{F}')^{-1}\mathbf{C}_1^{0'}].$$

6.D Nonlinear response: Matrix continued fraction solution of Eq. (6.31)

As before, we represent the dual-index recurrence relation for the Fourier amplitudes as

$$\begin{aligned} z_n^k(\omega)c_n^k(\omega) + \frac{ia'}{2} [c_n^{k+1}(\omega) + c_n^{k-1}(\omega)] + q_n^+ c_{n+1}^k(\omega) \\ + q_n^- c_{n-1}^k(\omega) + 2b_1 [q_{2n}^+ c_{n+2}^k(\omega) + q_{2n}^- c_{n-2}^k(\omega)] \\ + 3b_2 [q_{3n}^+ c_{n+3}^k(\omega) + q_{3n}^- c_{n-3}^k(\omega)] = 0, \end{aligned} \quad (6.52)$$

where $z_n^k(\omega) = ia + n + ik\omega/n$ and $q_n^\pm = -iV_0(1 \pm n\Lambda)/2$. We may rewrite the above nine-term recurrence relation as a seven-term *matrix* recurrence relation

$$\begin{aligned} \mathbf{q}_n \mathbf{c}_n(\omega) + \mathbf{q}_n^+ \mathbf{c}_{n+1}(\omega) + \mathbf{q}_n^- \mathbf{c}_{n-1}(\omega) + 2b_1 [\mathbf{q}_{2n}^+ \mathbf{c}_{n+2}(\omega) \\ + \mathbf{q}_{2n}^- \mathbf{c}_{n-2}(\omega)] + 3b_2 [\mathbf{q}_{3n}^+ \mathbf{c}_{n+3}(\omega) + \mathbf{q}_{3n}^- \mathbf{c}_{n-3}(\omega)] = 0, \end{aligned} \quad (6.53)$$

where

$$\mathbf{c}_n(\omega) = \begin{pmatrix} \vdots \\ c_n^{-1}(\omega) \\ c_n^0(\omega) \\ c_n^1(\omega) \\ \vdots \end{pmatrix}, \quad \mathbf{c}_0 = \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix},$$

$$\mathbf{q}_n = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & z_n^{-1}(\omega) & ia'/2 & 0 & \cdots \\ \cdots & ia'/2 & z_n^0(\omega) & ia'/2 & \cdots \\ \cdots & 0 & ia'/2 & z_n^1(\omega) & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{q}_n^\pm = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & q_n^\pm & 0 & 0 & \cdots \\ \cdots & 0 & q_n^\pm & 0 & \cdots \\ \cdots & 0 & 0 & q_n^\pm & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

Next, we introduce the column vectors $\mathbf{C}_n$

$$\mathbf{C}_0 = (\mathbf{c}_0), \quad \mathbf{C}_{\pm n} = \begin{pmatrix} \mathbf{c}_{\pm 3n} \\ \mathbf{c}_{\pm(3n-1)} \\ \mathbf{c}_{\pm(3n-2)} \end{pmatrix}, \quad (n > 1),$$

with the property $\mathbf{C}_{-1}(\omega) = \mathbf{C}_1^*(-\omega)$ so that Eq. (6.53) may be rewritten in terms of the solvable matrix three-term recurrence relations

$$\mathbf{Q}_1^- \mathbf{C}_0 + \mathbf{Q}_1 \mathbf{C}_1 + \mathbf{Q}_1^+ \mathbf{C}_2 = -\mathbf{F} \mathbf{C}_1^* \quad (n = 1), \quad (6.54)$$

$$\mathbf{Q}_n^- \mathbf{C}_{n-1} + \mathbf{Q}_n \mathbf{C}_n + \mathbf{Q}_n^+ \mathbf{C}_{n+1} = 0 \quad (n > 1). \quad (6.55)$$

The supermatrices $\mathbf{Q}_n$ and $\mathbf{Q}_n^\pm$ are given by

$$\mathbf{Q}_n = \begin{pmatrix} \mathbf{q}_{3n} & \mathbf{q}_{3n}^- & 2b_1 \mathbf{q}_{2(3n)}^- \\ \mathbf{q}_{3n-1}^+ & \mathbf{q}_{3n-1} & \mathbf{q}_{3n-1}^- \\ 2b_1 \mathbf{q}_{2(3n-2)}^+ & \mathbf{q}_{3n-2}^+ & \mathbf{q}_{3n-2} \end{pmatrix},$$

$$\mathbf{Q}_n^+ = \begin{pmatrix} 3b_2\mathbf{q}_{3(3n)}^+ & 2b_1\mathbf{q}_{2(3n)}^+ & \mathbf{q}_{3n}^+ \\ 0 & 3b_2\mathbf{q}_{3(3n-1)}^+ & 2b_1\mathbf{q}_{2(3n-1)}^+ \\ 0 & 0 & 3b_2\mathbf{q}_{3(3n-2)}^+ \end{pmatrix},$$

$$\mathbf{Q}_n^- = \begin{pmatrix} 3b_2\mathbf{q}_{3(3n)}^- & 0 & 0 \\ 2b_1\mathbf{q}_{2(3n-1)}^- & 3b_2\mathbf{q}_{3(3n-1)}^- & 0 \\ \mathbf{q}_{3n-2}^- & 2b_1\mathbf{q}_{2(3n-2)}^- & 3b_2\mathbf{q}_{3(3n-2)}^- \end{pmatrix},$$

with $\mathbf{Q}_1^-$ and $\mathbf{F}$ defined as

$$\mathbf{Q}_1^- = \begin{pmatrix} 3b_2\mathbf{q}_9^- \\ 2b_1\mathbf{q}_4^- \\ \mathbf{q}_1^- \end{pmatrix}, \mathbf{F} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 3b_2\mathbf{q}_6^- \mathbf{f} \\ 0 & 3b_2\mathbf{q}_3^- \mathbf{f} & 2b_1\mathbf{q}_2^- \mathbf{f} \end{pmatrix}, \mathbf{q} = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & 0 & 0 & 1 & \cdots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & 1 & 0 & 0 & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

The matrix $\mathbf{f}$ in the supermatrix $\mathbf{F}$ arises because the distribution function must be real, meaning in terms of the column vectors $\mathbf{c}_n(\omega)$ that $\mathbf{c}_{-n}(\omega) = \mathbf{c}_n^*(-\omega)$, which may be rewritten as $\mathbf{c}_{-n}(\omega) = \mathbf{f}\mathbf{c}_n^*(\omega)$. Eqs. (6.54) and (6.55) are formally identical to Eqs. (6.40) and (6.41), respectively and their solutions are given in Appendix 6.B.

Chapter 7

Comparison of quantum kinetic models for Wigner's function for dissipative systems

The dynamics of quantum Brownian particles in a cosine periodic potential are studied using the phase space formalism associated with the Wigner distribution. Various kinetic models of the phase space master equation describing quantum Brownian motion are compared by evaluating the dynamic structure factor and escape rate from differential recurrence relations via matrix continued fractions in the manner customarily used for the classical Fokker-Planck equation. The results of numerical calculations of the escape rate are compared with those given analytically by the quantum-mechanical reaction rate theory solution of the Kramers turnover problem, enabling one to appraise each model.

7.1 Introduction

We have repeatedly seen that quantum dissipation, in particular the quantum Brownian motion, poses one of the most interesting and topical problems in the quantum mechanics of open systems, especially in the study of the passage to the classical limit. This has led to diverse methods for the theoretical treatment of the dynamics of quantum dissipative processes, e.g. representations in terms of the reduced density matrix [32–34, 72], path integrals [9, 10], and master equations in phase space [182, 183].

As far as the closed description of the quantum system is concerned the time evolution of the density operator $\hat{\rho}$ of a mixed quantum state is given by the Liouville-von Neumann equation (see § 1.3)

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)]. \quad (7.1)$$

In order to treat the dynamics of quantum dissipative processes, i.e. open systems, in particular quantum effects in the Brownian motion, Caldeira and Leggett [10] used the influence functional (or real-time path integral) method of Feynman and Vernon [9] to obtain an evolution equation for the relevant *reduced* density operator¹ $\hat{\rho}$. The model for the dissipative interaction of a particle with its surroundings consists of a continuum of harmonic oscillators, comprising a Boson bath, where a specific form for the product of the density of bath modes and the square of the coupling coefficient is assumed. By tracing over the bath variables, they obtain an evolution equation for $\hat{\rho}$, namely

$$\frac{\partial}{\partial t} \hat{\rho}(t) + \frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] = \frac{\gamma}{2i\hbar} [\hat{x}, \{\hat{p}, \hat{\rho}(t)\}] - \frac{\gamma m}{\beta \hbar^2} [\hat{x}, [\hat{x}, \hat{\rho}(t)]], \quad (7.2)$$

where $\{.,.\}$ denotes the anticommutator of two operators. According to Caldeira and Leggett, Eq. (7.2) is valid at relatively high temperatures and for Markovian coupling to the heat bath. This approach has resulted in a large body of work [29, 74, 76, 80], where the main objective has been to study semiclassical corrections to the theory of Brownian motion.

Now, an essential requirement for a density operator $\hat{\rho}$ is that it must be *positive definite*, i.e. $\text{Tr} \{\hat{\rho}\} \geq 0$. In other words, when transformed to the position representation it must represent the correct quantum mechanical probability for the displacements. However, as is well-known [182], solutions of the Caldeira-Leggett equation (7.2) for the reduced density operator are not guaranteed to preserve this property during time evolution,

¹As we are almost always dealing with a reduced density operator we do not distinguish it here in notation from the total or non-reduced density operator

even if they commence this way. This behaviour is in contrast to that of evolution equations which can be expressed in the Lindblad form [185]

$$\frac{\partial}{\partial t} \hat{\rho}(t) + \frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] = \sum_{n,m=1}^{N^2-1} a_{n,m} \left(L_n \hat{\rho}(t) L_m^\dagger - \frac{1}{2} \{L_m^\dagger L_n, \hat{\rho}(t)\} \right), \quad (7.3)$$

where the L_m are an arbitrary orthonormal basis of the operators on the N -dimensional Hilbert space of the system and the constants $a_{n,m}$ determine the dynamics². Equation (7.3) is the most general type of Markovian time-homogeneous master equation describing non-unitary evolution of the density operator $\hat{\rho}$, that is trace preserving and completely positive for any initial condition. However, positivity of the density operator does not in itself imply that the underlying physics is realistic. Moreover, a positive density operator does not necessarily lead to phase space quasi-distributions that lack negative basins as demonstrated by Wyatt [76]. Prompted by these considerations, Diósi [32, 33] in a more refined derivation (cf. Eq. (29) of Ref. [32]) of the Caldeira-Leggett equation (7.2) found two additional smoothing terms, rendering the time-dependent solution of the quantum master equation for the density operator $\hat{\rho}$ completely positive [182, 183], yielding the master equation

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(t) + \frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] &= \frac{\gamma}{2i\hbar} [\hat{x}, \{\hat{p}, \hat{\rho}(t)\}] - \frac{\gamma m}{\beta \hbar^2} [\hat{x}, [\hat{x}, \hat{\rho}(t)]] \\ &\quad - \frac{\gamma \beta}{12m} [\hat{p}, [\hat{p}, \hat{\rho}(t)]] - \frac{\gamma \Omega \beta}{6\pi} [\hat{x}, [\hat{p}, \hat{\rho}(t)]], \end{aligned} \quad (7.4)$$

where Ω is regarded as a cutoff frequency for the harmonic bath. In deriving equation (7.4), three conditions are placed on the parameters: (i) the bath response time $1/\Omega$ is short compared to characteristic system times; (ii) weak coupling to the reservoir $\gamma \gg \Omega$; (iii) moderate to high temperature $\hbar\beta\Omega \geq 1$ [76].

Starting from a microscopic model, a further approach to quantum Brownian motion has been furnished by Vacchini and Hornberger [34, 186]. Considering the quantum dynamics of a single particle in a dilute, ideal gas as described by the quantum linear Boltzmann equation [187], they obtain in the diffusive limit³ the density operator evolution equation [186]

²The coefficient matrix $a_{n,m}$ must be positive to ensure that the equation is trace preserving and completely positive.

³A similar reduction occurs on taking the diffusive limit of the classical linear Boltzmann equation to obtain the Klein-Kramers equation

$$\frac{\partial}{\partial t} \hat{\rho}(t) + \frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] = \frac{\gamma}{2i\hbar} [\hat{x}, \{\hat{p}, \hat{\rho}(t)\}] - \frac{\gamma m}{\beta \hbar^2} [\hat{x}, [\hat{x}, \hat{\rho}(t)]] - \frac{\gamma \beta}{16m} [\hat{p}, [\hat{p}, \hat{\rho}(t)]] . \quad (7.5)$$

Equation (7.5) is almost identical to the master equation of Diósi (7.4) when $\Omega = 0$. An important feature of the approach of Vacchini and Hornberger is that the friction and diffusion coefficients, γ and D_{pp} , are uniquely specified by the details of the microscopic model, i.e. by combining the thermodynamic quantities of the gas with the relevant microscopic properties of its constituent particles, in contrast to the phenomenological considerations of the Caldeira-Leggett model [34].

Now, all of the above time evolution equations for the reduced density operator may be equivalently treated using the Wigner-Moyal phase space representation of quantum mechanics, thus allowing one to compare the predictions of each particular evolution equation using the methods [7, 80, 82] associated with the classical theory of the Brownian motion in a potential. As far as such a comparison is concerned, one should also refer to another class of kinetic models, namely *extended diffusion models*, long familiar in the kinetic theory of gases and fluids [188, 190]. In contrast to models based on a Brownian motion *Stosszahlansatz*, it is assumed in the latter that a particle moves freely in space until interrupted by *instantaneous* collisions. In other words, the duration of a collision is assumed to be much smaller than the average time between collisions. The impact approximation (i.e. the infinitesimal duration of collisions) and free motion of particles between collisions are features common to all extended diffusion models. The collisions take place at random times governed by a Poisson distribution and they randomise both the position and momentum of a particle. Extended diffusion models have been successively used for the interpretation of experimental spectra of both classical and quantum systems [191]. However, a drawback associated with them is the *ad hoc* introduction of a phenomenological parameter, namely the time between collisions. Nevertheless, if this parameter is known or can be calculated from an independent approach, such simple kinetic models may yield a reasonable description of the quantum dissipative process in the semiclassical limit.

It is the purpose of this chapter, with a view towards appraising the various models, to compare the dynamical structure factor and escape rate evaluated from the master equations proposed by Diósi [32, 33], Coffey *et al.* [31, 74, 75] and the Lorentz model (a particular case of the extended diffusion models) [188, 191]. The comparisons will be effected in the Wigner-Moyal phase space representation by considering a particle moving in the periodic potential [74]

$$V(x) = -V_0 \cos(x/x_0), \quad (7.6)$$

where x is the position of the particle and x_0 is a characteristic length. Both the classical and the quantum Brownian motion in this potential have been used for example to model diffusion in solids, pre-melting materials, films, and surfaces [192–194]. Moreover, the results for the escape rate (as adapted to periodic potentials) will also be compared with those yielded by generalising the classical solution of the Kramers turnover problem, i.e. the (universal) escape rate for all values of the dissipation, to include quantum effects as accomplished by Mel'nikov [195, 196], Pollak *et al.* [197] and Rips and Pollak [198]. In the present context of a cosine periodic potential, which differs from that of a metastable well, Georgievskii and Pollak [199] have obtained a universal expression for the quantum Kramers escape rate above the crossover temperature between tunnelling and thermal activation.

7.2 Quantum master equations in phase space

We have seen that the Wigner function of a mixed quantum state described by the density operator $\hat{\rho}$ is the phase space distribution

$$W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle x + y/2 | \hat{\rho} | x - y/2 \rangle e^{-ipy/\hbar} dy. \quad (7.7)$$

The main properties of Wigner's phase space have been presented in § 1.4. In particular, considering also the Wigner function of a pure state Eq. (1.20), if either the time evolution equation of the density operator $\hat{\rho}$ (independent of representation, e.g. the Liouville-von Neumann equation), or that equation in the coordinate representation [e.g. the Schrödinger equation of the wave function $\psi(x)$] is known, then the time evolution of the corresponding Wigner function in phase space may be found by evaluating its Wigner transform. For example, details of obtaining the phase space representation of the Liouville-von Neumann equation of a mixed state and of the Schrödinger equation of a pure state are presented in Appendices 1.B and 1.A, respectively.

Hence, as far as the Caldeira-Leggett model is concerned, the Wigner phase space representation of their density operator evolution equation (7.2) is

$$\frac{\partial W}{\partial t} + \hat{M}_W W = \gamma \frac{\partial}{\partial p} \left[pW + \frac{m}{\beta} \frac{\partial W}{\partial p} \right], \quad (7.8)$$

where $\hat{M}_W$ is the closed system evolution operator given by Eq. (2.2). Equation (7.8) is simply the master equation for the closed system augmented by the classical collision

kernel of Brownian motion, i.e. the collision kernel of the Klein-Kramers equation (1.9). If only the lowest order quantum term in $\hat{M}_W$ is considered, Eq. (7.8) is often referred to as the semiclassical version of the Klein-Kramers equation. Similarly, the phase space representation [76, 182] of Diósi's master equation (7.4) is

$$\frac{\partial}{\partial t} W + \hat{M}_W W = \gamma \frac{\partial}{\partial p} \left[pW + \frac{m}{\beta} \frac{\partial W}{\partial p} \right] + \frac{\gamma \hbar^2 \beta}{12m} \frac{\partial^2 W}{\partial x^2} + \frac{\gamma \Omega \hbar^2 \beta}{6\pi} \frac{\partial^2 W}{\partial p \partial x}. \quad (7.9)$$

Thus, in contrast to Eq. (7.8), D_{xp} and D_{xx} are no longer zero [cf. Eqs. (2.4) and (2.5)]. The phase space representation of Vacchini's equation (7.5) is then simply

$$\frac{\partial}{\partial t} W + \hat{M}_W W = \gamma \frac{\partial}{\partial p} \left[pW + \frac{m}{\beta} \frac{\partial W}{\partial p} \right] + \frac{\gamma \hbar^2 \beta}{16m} \frac{\partial^2 W}{\partial x^2}. \quad (7.10)$$

The discrepancy between the position coefficient $D_{xx} = \gamma\beta/(16m)$ above and the position coefficient $D_{xx} = \gamma\beta/(12m)$ of Diósi seems insignificant at first and one is tempted to consider the Vacchini equation as simply the Diósi equation with $\Omega = 0$. Consequently, however, the stationary solution of the Vacchini master equation can no longer be expressed as a simple perturbation solution in $\hbar^2$ with coefficients given in terms of the potential. Thus, the simple difference in the factors 16 and 12 causes the coefficients of such an expansion to be soluble only numerically. This complicates the continued fraction solution considerably so that in the present comparison, treatment of Vacchini's equation is omitted.

A particular extended diffusion model shall also be treated, namely the Lorentz or τ -approximation model [188–191]. This model is based on the assumption that collisions change the state of a particle such that the probability of finding the particle in a new state is proportional to the equilibrium Boltzmann distribution $\hat{\rho}_{st} = e^{-\beta \hat{H}_0} / \text{Tr} \{ e^{-\beta \hat{H}_0} \}$. Thus a time evolution equation of the Lorentz model in the single relaxation time approximation can be written as

$$\frac{d}{dt} \hat{\rho}(t) + \frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] = -(\hat{\rho}(t) - \hat{\rho}_{st})/\tau, \quad (7.11)$$

where τ is the phenomenological parameter, characterising relaxation processes. Consequently, the phase space evolution equation for the Lorentz model is

$$\partial_t W + \hat{M}_W W = -(W - W_{st})/\tau, \quad (7.12)$$

where W_{st} is the Wigner stationary (i.e. the canonical) distribution function satisfying $\hat{M}_W W_{st} = 0$. Equation (7.11) describes relaxation of the density operator $\hat{\rho}$ to $\hat{\rho}_{st}$ with

relaxation time τ , which is the mean time between collisions. Thus interpretation of the collision kernel of Eq. (7.11) on the microscopic level is as follows. Collisions change the state (coordinates and momenta) of a particle such that the probability of finding the particle in a new state is proportional to the canonical distribution $\hat{\rho}_{st}$.

Finally, as discussed in detail in Chapter 2, by postulating the Wigner equilibrium distribution $W_{st}(x, p)$ as the stationary solution of the Kramers-Moyal expansion truncated at the second term, Coffey *et al.* [31] obtained the semiclassical master equation

$$\frac{\partial W}{\partial t} + \hat{M}_W W = \gamma \frac{\partial}{\partial p} \left[pW + \frac{m}{\beta} \frac{\partial W}{\partial p} \right] + \frac{\gamma \beta \hbar^2}{12} V''(x) \frac{\partial^2 W}{\partial p^2}. \quad (7.13)$$

Here, only terms of order $\hbar^2$ are included, although the method may be carried on to any order in $\hbar^2$ (see § 2.2).

7.3 Stationary distributions

Now, Coffey *et al.* [31, 75] have imposed the Wigner distribution W_{st} as the equilibrium solution of Eq. (7.13). Clearly the distribution W_{st} is also a stationary solution of the Lorentz model Eq. (7.12). On the other hand, in the master equation of Diósi [32, 33] the phase space stationary distribution must be calculated by setting $\dot{W} = 0$.

We proceed by making the following rescaling to the normalised variables [74]

$$\begin{aligned} x/x_0 &\rightarrow x, & p\eta/mx_0 &\rightarrow p, & t/\eta &\rightarrow t, \\ \eta\gamma &\rightarrow \gamma, & \eta\Omega/\pi &\rightarrow \Omega, & \beta V(x) &\rightarrow V(x), \\ \eta &= \sqrt{\beta m x_0^2/2}, & g &= \beta V_0, & \Lambda &= \beta^2 \hbar^2/(48\eta^2). \end{aligned}$$

We then have from Eqs. (7.9) and (7.13)

$$\frac{\partial W}{\partial t} = -p \frac{\partial W}{\partial x} + \frac{1}{2} \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \frac{\gamma}{2} \frac{\partial}{\partial p} \left[2pW + \frac{\partial W}{\partial p} \right] + DW, \quad (7.14)$$

where the dimensionless potential is $V(x) = -g \cos x$. Equation (7.14) represents the classical Klein-Kramers equation written in terms of normalised variables plus a quantum correction term DW . It follows that for the Diósi kinetic model

$$DW = \Lambda \left(-\frac{1}{4} \frac{\partial^3 V}{\partial x^3} \frac{\partial^3 W}{\partial p^3} + 2\gamma \frac{\partial^2 W}{\partial x^2} + 4\gamma \Omega \frac{\partial^2 W}{\partial p \partial x} \right), \quad (7.15)$$

while that of the Coffey *et al.* kinetic model is

$$DW = \Lambda \left(-\frac{1}{4} \frac{\partial^3 V}{\partial x^3} \frac{\partial^3 W}{\partial p^3} + \gamma \frac{\partial^2 V}{\partial x^2} \frac{\partial^2 W}{\partial p^2} \right). \quad (7.16)$$

The stationary solution of Eq. (7.14) with the correction given by Eq. (7.16) is the Wigner distribution function

$$W_{st}(x, p) = Z^{-1} e^{-p^2 - V} \left\{ 1 + \Lambda \left[(V')^2 - 3V'' + 2p^2 V'' \right] \right\}, \quad (7.17)$$

where the partition function is

$$Z = \sqrt{\pi} \int_0^{2\pi} \left[1 + \Lambda (V'(x))^2 - 2\Lambda V''(x) \right] e^{-V(x)} dx = Z_{cl} [1 - \Lambda g I_1(g)/I_0(g)], \quad (7.18)$$

where $Z_{cl} = 2\pi^{3/2} I_0(g)$ is the classical partition function and $I_v(z)$ is the modified Bessel function of the first kind of integer order. This solution is of course *independent* of the dissipation. On the other hand, as may be verified by direct substitution into the time-independent version of Eq. (7.14) with the correction given by Eq. (7.15), the stationary solution $W_D(x, p)$ of the Diósi model *depends* on the dissipation and is given by

$$W_D(x, p) = Z_D^{-1} e^{-p^2 - V} \left\{ 1 + \Lambda \left[(V')^2 - 3V'' + 2p^2 V'' + 4\gamma(\gamma + 2\Omega)V - 4p\gamma V' \right] \right\}, \quad (7.19)$$

where

$$\begin{aligned} Z_D &= \sqrt{\pi} \int_0^{2\pi} \left\{ 1 + \Lambda \left[(V'(x))^2 - 2V''(x) + 4\gamma(\gamma + 2\Omega)V(x) \right] \right\} e^{-V(x)} dx \\ &= Z_{cl} [1 - \Lambda(1 + 4\gamma(\gamma + 2\Omega))g I_1(g)/I_0(g)]. \end{aligned} \quad (7.20)$$

In the zero dissipation limit, $\gamma \rightarrow 0$ (closed systems), the Diósi distribution $W_D(x, p)$ becomes the Wigner distribution $W_{st}(x, p)$.

7.4 Solution of the time-dependent master equation

The foregoing discussion refers to the time-independent solutions of the master equations. We now consider time-dependent solutions. To investigate the process whereby the particle traverses the periodic potential we must obtain the nonperiodic solution [7, 74] of Eq. (7.14). Thus we make the *Ansatz*

$$W(x, p, t) = \int_{-1/2}^{1/2} w(k, x, p, t) e^{-ikx} dk, \quad (7.21)$$

where w is periodic in x with period 2π and it is assumed [7] that the wave vector k is restricted to the first Brillouin zone, $-1/2 \leq k \leq 1/2$. The periodic function w can then

be expanded in a Fourier series in the positions x and in orthogonal Hermite functions $e^{-p^2} H_n(p)$ in the momentum p , viz. [7, 74, 193]

$$w(k, x, p, t) = \frac{e^{-p^2 + (g/2) \cos x}}{2\pi^{3/2}} \sum_{n=0}^{\infty} \sum_{q=-\infty}^{\infty} \frac{c_{n,q}(k, t)}{\sqrt{2^n n!}} H_n(p) e^{-iqx}. \quad (7.22)$$

By substituting Eqs. (7.21) and (7.22) into Eq. (7.14), we find by orthogonality, after some algebra involving the recurrence relations of the Hermite polynomials, that the Fourier coefficients $c_{n,q}(k, t)$ for the Diósi model satisfy the following differential recurrence relation

$$\begin{aligned} & \frac{d}{dt} c_{n,q} + \gamma [n + (2(q+k)^2 - g^2/4) \Lambda] c_{n,q} \\ &= i\Lambda g \sqrt{n(n-1)(n-2)/8} (c_{n-3,q+1} - c_{n-3,q-1}) \\ &+ i\sqrt{\frac{n+1}{2}} \left[(q+k) c_{n+1,q} - \frac{g}{4} (c_{n+1,q+1} - c_{n+1,q-1}) \right] \\ &+ i\sqrt{\frac{n}{2}} \left[(q+k) (1 + 8\Omega\gamma\Lambda) c_{n-1,q} + \frac{g}{4} (1 - 8\Omega\gamma\Lambda) (c_{n-1,q+1} - c_{n-1,q-1}) \right] \\ &+ \gamma\Lambda g \left[\left(q+k + \frac{1}{2} \right) c_{n,q+1} - \left(q+k - \frac{1}{2} \right) c_{n,q-1} - \frac{g}{8} (c_{n,q+2} + c_{n,q-2}) \right], \quad (7.23) \end{aligned}$$

while for the model of Coffey *et al.*

$$\begin{aligned} & \frac{d}{dt} c_{n,q} + \gamma [n c_{n,q} - \Lambda g \sqrt{n(n-1)} (c_{n-2,q+1} + c_{n-2,q-1})] \\ &= i\sqrt{n/2} [(q+k) c_{n-1,q} + g (c_{n-1,q+1} - c_{n-1,q-1}) / 4] \\ &+ i\sqrt{(n+1)/2} [(q+k) c_{n+1,q} - g (c_{n+1,q+1} - c_{n+1,q-1}) / 4] \\ &+ i\Lambda g \sqrt{n(n-1)(n-2)/8} (c_{n-3,q+1} - c_{n-3,q-1}). \quad (7.24) \end{aligned}$$

For the Lorentz model, Eq. (7.12), the Fourier coefficients $c_{n,q}(k, t)$ satisfy the differential recurrence relation

$$\begin{aligned} & \frac{d}{dt} c_{n,q} = -\tau^{-1} (c_{n,q} - c_{n,q}(0)) \\ &+ i\sqrt{n/2} [(q+k) c_{n-1,q} + g (c_{n-1,q+1} - c_{n-1,q-1}) / 4] \\ &+ i\sqrt{(n+1)/2} [(q+k) c_{n+1,q} - g (c_{n+1,q+1} - c_{n+1,q-1}) / 4] \\ &+ i\Lambda g \sqrt{n(n-1)(n-2)/8} (c_{n-3,q+1} - c_{n-3,q-1}). \quad (7.25) \end{aligned}$$

The foregoing differential recurrence relations in two indices may now be arranged (details are given in Appendix 7.A) as matrix three-term recurrence relations in a single index.

These recurrence relations can be solved in terms of matrix continued fractions [74, 193]. Thus one may evaluate quantities of interest such as the dynamic structure factor, etc.

7.5 Dynamic structure factor

The intermediate scattering function $S(k, t)$, i.e. the characteristic function of the displacement of the particle as it wanders through the wells, can be evaluated in Fourier series form as [74]

$$S(k, t) = \left\langle e^{ik[x(t) - x(0)]} \right\rangle_0 = \sum_{q=0}^{\infty} a_q c_{0,q}(k, t), \quad (7.26)$$

where $e^{ikx(t)} = e^{V(x(t))/2} \sum_{q=0}^{\infty} a_q e^{i(q+k)x(t)}$ and the angular brackets denote equilibrium ensemble averages. By using the orthogonality properties of the circular functions $\{e^{iqx}\}$, we have from Eq. (7.26), in terms of the modified Bessel functions, the Fourier coefficients

$$a_q = \frac{1}{2\pi} \int_0^{2\pi} e^{-iqx - V(x)/2} dx = I_{|q|}(g/2). \quad (7.27)$$

Thus we ultimately have for the structure factor, which is simply the one sided Fourier transform of the intermediate scattering function,

$$\tilde{S}(k, \omega) = \sum_{q=0}^{\infty} I_{|q|}(g/2) \tilde{c}_{0,q}(k, \omega). \quad (7.28)$$

Hence, one can calculate the decay rate $\Gamma \approx \tau^{-1}$ as the inverse of the average longest relaxation time of the system, which is defined as follows [74]. The intermediate scattering function $S(k, t)$ can be approximately represented at long times as the single exponential $S(k, t) = h(k)e^{-t/\tau(k)}$ or in the frequency domain as the Lorentzian

$$\tilde{S}(k, \omega) = \frac{h(k)}{i\omega + \tau^{-1}(k)}. \quad (7.29)$$

Thus τ^{-1} , as a function of the wave number, can be extracted as

$$\tau(k) = \lim_{\omega \rightarrow 0} \frac{\tilde{S}(k, 0) - \tilde{S}(k, \omega)}{i\omega \tilde{S}(k, \omega)}. \quad (7.30)$$

Hence, we have for the average decay rate

$$\tau^{-1} = 2 \int_0^{1/2} \tau^{-1}(k) dk. \quad (7.31)$$

We remark that the average jump rate takes into account that in a periodic potential (which is of course multistable) the particle having escaped a particular well may again be trapped due to thermal fluctuations in another well. Moreover, jumps of either a single lattice spacing or of many lattice spacings are possible. Thus the escape rate in a periodic potential is called the jump rate [193]. The foregoing result pertains to the kinetic models of Diósi, Vacchini and of Coffey *et al.*, allowing us to estimate the average longest relaxation time for these. On the other hand for the Lorentz kinetic model, which has nothing to do with Brownian motion *per se*, the dynamic structure factor $\tilde{S}(k, \omega)$ can also be approximated by

$$\tilde{S}_L(k, \omega) \approx \frac{h(k)}{i\omega + \tau^{-1}}. \quad (7.32)$$

However, the quantity τ in this instance is regarded as a phenomenological parameter and in order to determine it we use Mel'nikov's estimate [195–199] of the greatest relaxation time, based on the theory of the Brownian motion.

7.6 Mel'nikov's equation for the greatest relaxation time

As we have briefly alluded to, Mel'nikov [195, 196] has extended his solution of the classical Kramers turnover problem, which is of course based on the theory of the classical Brownian motion, to include quantum effects in a semiclassical way. Thus its quantum generalisation should be consistent with the Caldeira-Leggett model and so should reproduce the results of numerical calculations of the escape rate from it. He effected the generalisation by simply inserting [195] the quantum mechanical transmission factor for a parabolic barrier into the classical integral equation for the energy distribution function yielded by the Wiener-Hopf method in the Kramers turnover region. In the approximation of Ohmic damping, he was then able to write a universal formula for the quantum rate Γ^M valid for all values of damping above the crossover temperature between tunnelling and thermal activation

$$\Gamma^M = \Gamma_{\text{IHD}} \Upsilon. \quad (7.33)$$

Here Γ_{IHD} is the quantum escape rate from an isolated well in the intermediate to high damping (IHD) region ($\gamma \geq 1$) and Υ is the quantum depopulation factor. Later, Rips and Pollak [198], following earlier work of Pollak *et al.* [197], gave a consistent solution of the quantum Kramers turnover problem, demonstrating how the Mel'nikov universal Eq. (7.33) can be obtained without his *ad hoc* interpolation between the weak and strong

damping regimes. Finally, Georgievskii and Pollak [199] treated the escape rate problem in a periodic cosine potential, which is qualitatively different from that for a metastable well because the periodic potential is multistable, showing that the quantum depopulation factor in Eq. (7.33) is given by the integral

$$\Upsilon = 4 \int_0^1 \sin^2(\pi k) F(k) dk. \quad (7.34)$$

The function $F(k)$ is (in our notation)

$$F(k) = \exp \left\{ \frac{a \sin a}{\pi} \int_{-\infty}^{\infty} \ln \left[\frac{1 - e^{-2R(x)}}{1 + e^{-2R(x)} - 2e^{-R(x)} \cos(2\pi k)} \right] \frac{dx}{\cosh(2ax) - \cos a} \right\},$$

$$R(x) = \frac{\pi\gamma}{\sqrt{3\Lambda}} \int_{-\infty}^{\infty} \frac{\cosh(\sqrt{\Lambda}y) - \cos(2\sqrt{\Lambda}xy)}{y \sinh(\sqrt{\Lambda}y) \cosh^2[\pi y/(2\sqrt{6g})]} dy.$$

Here $a = \sqrt{3\Lambda} (\sqrt{\gamma^2 + 2g} - \gamma)$ and $\delta = 8\gamma\sqrt{2g}$ is the dimensionless classical action associated with the path along the top of the barrier [201]. In the classical limit [195] $R(x) \rightarrow \delta (x^2 + 1/4)$, we have $F_M(k) = e^{\sigma(k,\delta) - \sigma(0,2\delta)/2}$, where

$$\sigma(k, \delta) = 2 \sum_{n=1}^{\infty} n^{-1} \operatorname{erfc} \left(\sqrt{n\delta}/2 \right) \cos(2\pi nk).$$

These classical equations may also be used for the quantum depopulation factor if absolute accuracy is not required. Furthermore, in calculating the escape rate in the IHD limit only, for the cosine potential given by Eq. (7.6), it is sufficient [74] to consider the escape rate from an isolated well. The IHD quantum escape rate Γ_{IHD} from such a well is [31, 74]

$$\Gamma_{\text{IHD}} = \frac{\Xi}{2\pi\eta} \left(\sqrt{\gamma^2 + 2g} - \gamma \right) e^{-2g}, \quad (7.35)$$

where

$$\Xi = 1 + \beta^2 \hbar^2 (\omega_c^2 + \omega_a^2)/24 + \dots = 1 + 2g\Lambda + \dots \quad (7.36)$$

is the quantum correction factor and $\omega_c = \sqrt{|V''(x_c)|/m} = \omega_a = \sqrt{V''(x_a)/m}$ are the saddle and well angular frequencies. We remark that in Eq. (7.36) we have taken into account only the leading quantum correction term. For Ohmic damping, the correction factor Ξ is [72, 105]

$$\Xi = \prod_{n=1}^{\infty} \frac{\omega_a^2 + (2\pi n/\hbar\beta)^2 + 2\pi n\gamma/\hbar\beta}{-\omega_c^2 + (2\pi n/\hbar\beta)^2 + 2\pi n\gamma/\hbar\beta}. \quad (7.37)$$

However, if the conditions $\hbar\gamma\beta \ll 2\pi$ and $g\Lambda \ll 1$ are fulfilled and if only leading quantum correction terms (of order $\hbar^2$) are taken into account, Eq. (7.37) reduces to Eq. (7.36) [72]. Hence, equation (7.36) is in full agreement with the results predicted by quantum Transition State Theory, where Ξ is defined as

$$\Xi = \frac{\omega_c \sinh(\hbar\beta\omega_a/2)}{\omega_a \sin(\hbar\beta\omega_c/2)} = 1 + 2g\Lambda + \dots \quad (7.38)$$

The form of Eq. (7.36) appears to be consistent with the Coffey *et al.* conception of a quantum Brownian particle as embedded in a classical bath with the quantum effects in the bath-particle interaction arising via the dependence of the diffusion coefficient on the derivatives of the potential in the quantum master equation. Equation (7.33), combined with Eqs. (7.35) and (7.36), now yields Mel'nikov's estimate of the inverse of the greatest average relaxation time for the cosine potential. We remark that comprehensive reviews of applications and developments of Kramers escape rate theory have been given by Mel'nikov [195], Hänggi *et al.* [202], Coffey *et al.* [203], and Pollak and Talkner [204].

7.7 Results and discussion

The inverse stationary distribution for the Diósi kinetic model vs. the position x for different values of the momentum p is shown in Fig. 7.1. Clearly, the Diósi stationary distribution agrees with the Wigner function $W_{st}(x, p)$ only for small damping $\gamma < 0.1$. For large γ , the deviation from $W_{st}(x, p)$ is significant. In the classical limit $\Lambda \rightarrow 0$, both quantum stationary distributions become the classical Maxwell-Boltzmann distribution.

The real and imaginary parts of the normalised dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$ vs. the dimensionless frequency $\eta\omega$ for various values of damping $\gamma = 0.5, 5$, and 20 are presented in Fig. 7.2 for the various quantum kinetic models. The results for the Lorentz extended diffusion model, with the relaxation time calculated from Mel'nikov's Eq. (7.33), are shown along with the classical results ($\Lambda = 0$) for comparison. Clearly the quantum corrections predicted by both the kinetic model of Coffey *et al.* and the Lorentz model (with Mel'nikov's relaxation time as parameter) differ only by a few percent from the classical theory based on the Klein-Kramers equation. This is of course consistent with an almost classical treatment of the problem [184]. The predictions from the equation of Diósi for high cutoff frequency $\Omega = 1000$, on the other hand, exhibit a pronounced deviation from the classical results. In particular, in Fig. 7.2(a) the negative excursions in the real part of the dynamic structure factor are reminiscent of a resonance absorption which becomes more and more pronounced as the dissipative coupling to the bath is increased.

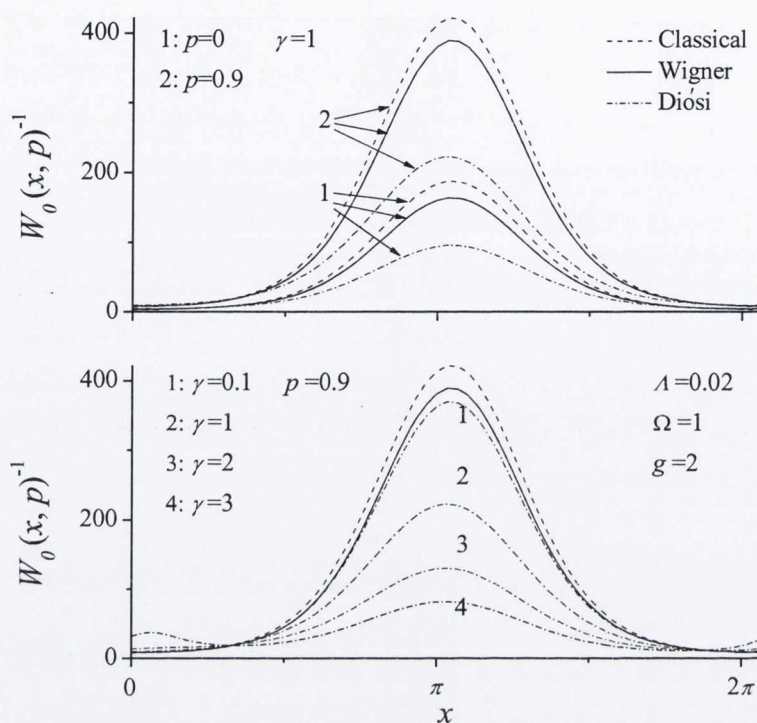


Figure 7.1: Inverse stationary distribution of the Diósi (dash-dotted lines) kinetic model, Eq. (7.19) with $\Omega = 1$, vs the coordinate x for different values of the momentum $p = 0$, $p = 0.9$ and damping parameter $\gamma = 0.1$, $\gamma = 1$, $\gamma = 2$, and $\gamma = 3$ with $g = 2$ and $\Lambda = 0.02$. The inverse Wigner stationary distribution (solid lines) and the classical Maxwell-Boltzmann distribution (dashed lines), $\Lambda = 0$ are also shown.

The same behaviour is reflected in the imaginary part, where for large dissipation the behaviour is symptomatic of a resonant peak, rather than the Lorentzian behaviour associated with the other models.

Turning now to the greatest relaxation time, shown in Fig. 7.3 as a function of the normalised dissipative coupling γ , it is apparent that the quantum behaviour of the numerical solution of Eq. (7.24) (resulting from the model of Coffey *et al.*) is closely followed by the quantum reaction rate theory solution embodied in Eqs. (7.33) and (7.34). Moreover, the latter solutions are consistent with the expected lowering of the potential barrier due to quantum effects, anticipated by Wigner [60] on the basis of his generalisation of classical TST to quantum mechanics. The equation of Diósi (for $\Omega \ll 1$) agrees with the quantum reaction rate theory results only for small damping $\gamma < 0.1$. However, for $\gamma > 0.1$ the Diósi equation (for $\Omega \ll 1$), predicts a result at variance with quantum TST, whereby the quantum mechanical effects *increase* rather than *decrease* the greatest relaxation time

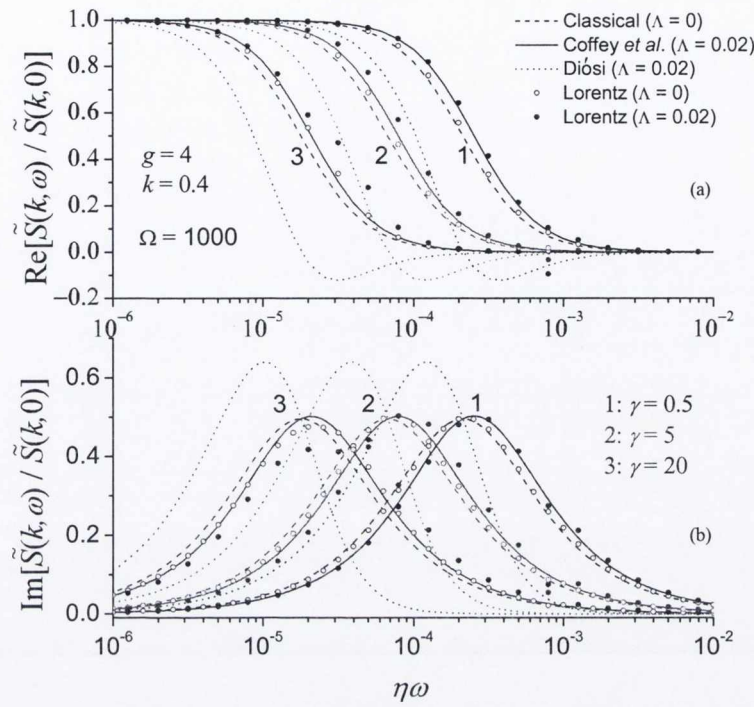


Figure 7.2: The real and imaginary parts of the normalised dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$ vs $\eta\omega$ for various values of the damping parameter $\gamma = 0.5, 5, 20$, the barrier parameter $g = 4$ and the wave number $k = 0.4$. Solid and dashed lines: the matrix continued fraction solution with $\Lambda = 0.02$ and $\Lambda = 0$ (classical case), respectively. Closed and open circles: Lorentz model. Dotted lines: Diósi model with $\Lambda = 0.02$ and $\Omega = 1000$.

over that of the classical system. Indeed, for a cutoff frequency $\Omega \neq 0$, Diósi's equation is unable to reproduce even qualitatively the expected behaviour for any region of damping.

Although the Caldeira-Leggett master equation (7.2) has not been treated here, the escape as calculated from that master equation to first order in $\hbar^2$ has been discussed in detail in Ref. [74]. There the Caldeira-Leggett master equation also predicts an *increase* rather than *decrease* of the greatest relaxation time. Thus the result is also at variance with quantum TST, although the deviation is not in any way as pronounced as in the Diósi model. The semiclassical Klein-Kramers equation retains the quantum term to first order in the quantum parameter in the *conservative* term. However, it is assumed [76] that the *collision* term is still given by the classical Fokker-Planck operator, although it is quite evident from the discussion given by Caldeira and Leggett that retention of the quantum term in the conservative part of their equation (5.14) is inconsistent with retaining the classical Fokker-Planck operator on the right-hand side of that equation. The dependence of the diffusion coefficient on the derivatives of the potential arising from the imposition of the

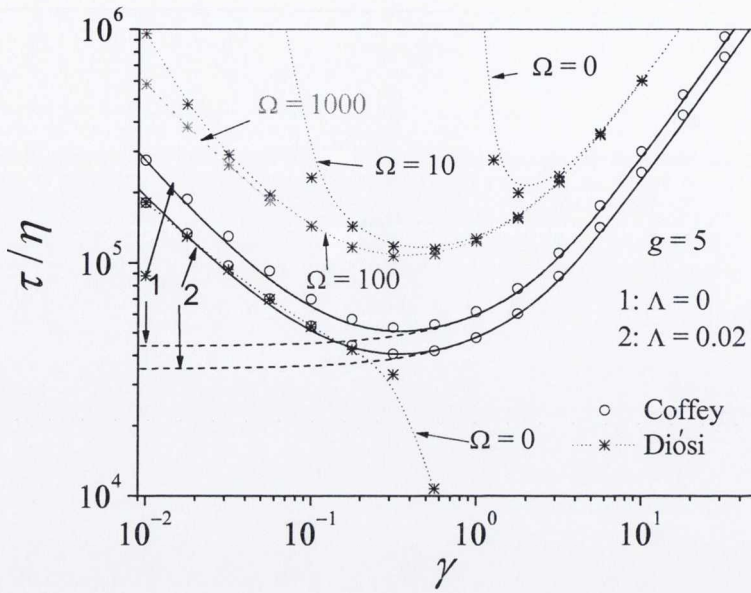


Figure 7.3: Longest relaxation time τ/η vs γ for the barrier parameter $g = 5$. Solid lines: the universal Eq. (7.33) for $\Lambda=0$ (curve 1) and $\Lambda=0.02$ (curve 2). Dashed lines: the IHD equation (7.35) for $\Lambda=0$ (curve 1) and $\Lambda=0.02$ (curve 2). Open circles: the matrix continued fraction solution of Eq. (7.24). Symbols: the matrix continued fraction solution of the Diósi master equation (7.23) for $\Omega = 0, 10, 100, 1000$.

Wigner stationary distribution is crucial. If this dependence is not taken into account, e.g. regarding the diffusion coefficient as constant (cf. Ref. [73]), the characteristic lowering of the barrier produced by the quantum tunnelling near the top of the barrier cannot be reproduced, neither can one regain the results of quantum reaction rate theory [60, 197–199]. The results of these calculations suggest that mere positivity of the density operator does not in itself guarantee solutions which are consistent with the predictions of quantum mechanical reaction rate theory, which is to be regarded as a benchmark solution.

To conclude, using the master equation in the phase space representation, quantum effects in the Brownian motion in a cosine periodic potential for various kinetic models, grounded in different physical assumptions, have been evaluated. The comparison uses the techniques previously developed for the classical Fokker-Planck equation [7, 82], facilitating a simple treatment, which allows one to study the interplay of tunnelling, thermal fluctuations, and dissipation in the quantum Brownian motion. In particular, quantum effects in the relevant dynamical quantities and the influence of quantum tunnelling on their high temperature behaviour have been evaluated in semiclassical fashion. The Diósi master equation for $\Omega \ll 1$ and the Coffey *et al.* master equation yield similar results for low

damping $\gamma < 0.1$. The Coffey *et al.* and Lorentz kinetic models also provide a reasonable description of the quantum dissipative process for $\gamma > 0.1$, unlike the Diósi model, which fails for $\gamma < 0.1$ or indeed for all damping when $\Omega \neq 0$.

As a final remark, recall that in the Coffey *et al.* kinetic model, the equilibrium Wigner function $W_{st}(x, p)$ for vanishing damping ($\gamma \rightarrow 0$) has been used to determine the explicit form of the Kramers-Moyal coefficients D_p, D_{pp}, D_{px} . However, as mentioned in Chapter 2, it is known [78] that the equilibrium state in general may deviate from the canonical distribution $\hat{\rho}_{st}$; the latter describes the thermal equilibrium of the system in the weak coupling and high temperature limits only. Hence, the stationary distribution may also differ from the canonical distribution $W_{st}(x, p)$; in particular, it may depend on the damping [78]. For a periodic potential, the damping dependence of the stationary distribution is unknown. Thus the conditions, under which the stationary distribution may be approximated by the Wigner distribution $W_{st}(x, p)$ are important in establishing a possible range of validity for the Coffey *et al.* model embodied in Eq. (7.13). Certainly, the model may be used in the high temperature limit because the stationary distribution then always reduces to $W_{st}(x, p)$. Moreover, one would expect that the master Eq. (7.13) is a reasonable approximation for the kinetics of a quantum Brownian particle in a periodic potential $V(x)$, when $\beta\hbar\gamma \ll 1$. The extension of the approach of Coffey *et al.* to spin dynamics governed by the $SU2$ rotation group (rather than the Heisenberg-Weyl group of translations), which contains the same assumption concerning the canonical distribution as the equilibrium distribution, can also be used to calculate [205] the integral relaxation time of the magnetisation, etc. The ensuing results are in exact agreement with those predicted by alternative methods such as the quantum Hubbard operator representation of the evolution equation for the spin density matrix [206, 207].

7.A Matrix continued fraction solution of Eqs. (7.23)- (7.25)

We seek perturbation solutions of Eqs. (7.23) and (7.24) in the form $c_{n,q} = c_{n,q}^0(k, t) + \Lambda c_{n,q}^1(k, t)$. Thus, we introduce the column vectors $C_n^0(t)$ and $C_n^1(t)$

$$C_n^0(t) = \begin{pmatrix} \vdots \\ c_{n-1,-1}^0(k, t) \\ c_{n-1,0}^0(k, t) \\ c_{n-1,1}^0(k, t) \\ \vdots \end{pmatrix}, \quad C_n^1(t) = \begin{pmatrix} \vdots \\ c_{n-1,-1}^1(k, t) \\ c_{n-1,0}^1(k, t) \\ c_{n-1,1}^1(k, t) \\ \vdots \end{pmatrix}.$$

Now, by seeking a perturbation solution as $\mathbf{C}_n(t) = \mathbf{C}_n^0(t) + \Lambda \mathbf{C}_n^1(t)$, Eqs. (7.23) and (7.24) can be rearranged in the zero and first order of perturbation theory as the set of matrix *three-term* recurrence equations

$$\frac{d}{dt} \mathbf{C}_n^0(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}^0(t) - \gamma(n-1) \mathbf{C}_n^0(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^0(t), \quad (7.39)$$

$$\frac{d}{dt} \mathbf{C}_n^1(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}^1(t) - \gamma(n-1) \mathbf{C}_n^1(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^1(t) + \mathbf{C}_n^0(t), \quad (7.40)$$

where

$$\mathbf{Q}_n^\pm = i \sqrt{\frac{n}{2} - \frac{1 \mp 1}{4}} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & k-1 & \mp g/4 & 0 & \cdots \\ \cdots & \pm g/4 & k & \mp g/4 & \cdots \\ \cdots & 0 & \pm g/4 & k+1 & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

The vector $\mathbf{R}_n^0(t)$ for the Diósi kinetic model is then

$$\mathbf{R}_n^0(t) = \mathbf{s}_n \mathbf{C}_{n-1}^0(t) + \mathbf{p}_n \mathbf{C}_n^0(t) + \mathbf{r}_n \mathbf{C}_{n-3}^0(t),$$

while for the model of Coffey *et al.*

$$\mathbf{R}_n^0(t) = \mathbf{q}_n \mathbf{C}_{n-2}^0(t) + \mathbf{r}_n \mathbf{C}_{n-3}^0(t),$$

where $s_n = 8\Omega\gamma\sqrt{1-1/n}\mathbf{Q}_n^+$,

$$\mathbf{q}_n = \gamma g \sqrt{(n-1)(n-2)} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & 1 & 0 & 1 & \cdots \\ \cdots & 0 & 1 & 0 & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{r}_n = ig \sqrt{\frac{(n-1)(n-2)(n-3)}{8}} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & -1 & 0 & 1 & \cdots \\ \cdots & 0 & -1 & 0 & \cdots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{P}_n = \gamma \begin{pmatrix} \ddots & & \ddots & & \ddots & & 0 & & \ddots \\ \ddots & -(2(k-1)^2 - g^2/4) & g(k-1/2) & & -g^2/8 & & 0 & & \ddots \\ \ddots & -g(k-1/2) & -(2k^2 - g^2/4) & & g(k+1/2) & & \ddots & & \ddots \\ 0 & -g^2/8 & -g(k+1/2) & & -(2(k+1)^2 - g^2/4) & & \ddots & & \ddots \\ \ddots & 0 & \ddots & & \ddots & & \ddots & & \ddots \end{pmatrix}.$$

The initial conditions follow from the stationary distribution in phase space. The initial conditions $c_{n,q}(0) = c_{n,q}^0(0) + \Lambda c_{n,q}^1(0)$ are evaluated as

$$c_{n,q}(0) = \frac{1}{\sqrt{2^n n!}} \int_{-\infty}^{\infty} \int_0^{2\pi} H_n(p) e^{iqx+V(x)/2} W_0(x, p) dx dp.$$

For the classical Boltzmann distribution, $c_{n,q}^0(0) = 0$, ($n > 0$) and

$$c_{0,q}^0(0) = \sqrt{\pi} Z_{cl}^{-1} \int_0^{2\pi} e^{iqx-V(x)/2} dx = 2\pi^{3/2} Z_{cl}^{-1} I_{|q|}(g/2).$$

Thus, $\mathbf{C}_1^0(0) \neq 0$ and $\mathbf{C}_n^0(0) = 0$, ($n \geq 2$). The first order perturbation initial conditions $c_{n,q}^1(0)$ differ from model to model. For that of Coffey *et al.*, they are

$$\begin{aligned} c_{0,q}^1(0) &= \sqrt{\pi} Z^{-1} \int_0^{2\pi} [(V'(x))^2 - 2V''(x)] e^{iqx-V(x)/2} dx \\ &= -2\pi^{3/2} Z_{cl}^{-1} [(2q)^2 - gI_1(g)/I_0(g)] I_q(g/2), \end{aligned}$$

$$c_{2,q}^1(0) = \sqrt{2\pi} Z_{cl}^{-1} \int_0^{2\pi} V''(x) e^{iqx-V(x)/2} dx = \frac{g}{\sqrt{2}} (c_{0,q+1}^0(0) + c_{0,q-1}^0(0)),$$

so that the vector initial conditions are $\mathbf{C}_1^1(0) \neq 0$, $\mathbf{C}_2^1(0) = 0$, $\mathbf{C}_3^1(0) \neq 0$. For the Diósi model, they are

$$\begin{aligned} c_{0,q}^1(0) &= \frac{\sqrt{\pi}}{Z_{cl}} \int_0^{2\pi} dx e^{iqx-V/2} \left[V'^2 - 2V'' + 4\gamma(\gamma + 2\Omega)V + (1 + 4\gamma(\gamma + 2\Omega))g \frac{I_1(g)}{I_0(g)} \right] \\ &= -\frac{2\pi^{3/2}}{Z_{cl}} \left\{ \left[4q^2 - (1 + 4\gamma(\gamma + 2\Omega))g \frac{I_1(g)}{I_0(g)} \right] I_q(g/2) \right. \\ &\quad \left. + 2\gamma(\gamma + 2\Omega)g [I_{q+1}(g/2) + I_{q-1}(g/2)] \right\}, \end{aligned}$$

$$\begin{aligned} c_{1,q}^1(0) &= -2\sqrt{2\pi} Z_{cl}^{-1} \gamma \int_0^{2\pi} dx V'(x) e^{iqx-V(x)/2} \\ &= -i4(2\pi)^{3/2} Z_{cl}^{-1} q\gamma I_q(g/2), \end{aligned}$$

$$\begin{aligned}
c_{2,q}^1(0) &= \sqrt{2\pi} Z_{cl}^{-1} \int_0^{2\pi} V''(x) e^{iqx - V(x)/2} dx \\
&= \frac{g}{\sqrt{2}} (c_{0,q+1}^0(0) + c_{0,q-1}^0(0)),
\end{aligned}$$

and the vector initial conditions are $C_1^1(0) \neq 0$, $C_2^1(0) \neq 0$, $C_3^1(0) \neq 0$. All other vectors are zero, i.e. $C_n^1(0) = 0$, ($n \geq 4$).

Taking the Laplace transform of Eqs. (7.39) and (7.40), namely $\tilde{C}_n^0(s) = \int_0^\infty C_n^0(t) e^{-st} dt$, and applying the general matrix method of solution of three-term recurrence equations [195, 201, 202], we have the zero-order vectors

$$\tilde{C}_1^0(s) = \Delta_1(s) C_1^0(0),$$

$$\tilde{C}_n^0(s) = S_n^- \tilde{C}_{n-1}^0(s) = S_n^- S_{n-1}^- \dots S_2^- \Delta_1(s) C_1^0(0), \quad (n \geq 2),$$

and the first-order vectors

$$\tilde{C}_1^1(s) = \Delta_1(s) \left[\left(C_1^1(0) + \tilde{R}_1^0(s) \right) + \sum_{j=1}^{\infty} \left[\prod_{k=1}^j Q_k^+ \Delta_{k+1}(s) \right] \left(C_{j+1}^1(0) + \tilde{R}_{j+1}^0(s) \right) \right],$$

$$\begin{aligned}
\tilde{C}_n^1(s) &= \Delta_n(s) Q_n^- \tilde{C}_{n-1}^1(s) \\
&+ \Delta_n(s) \left[\left(C_n^1(0) + \tilde{R}_n^0(s) \right) + \sum_{j=1}^{\infty} \left[\prod_{k=1}^j Q_{n+k-1}^+ \Delta_{n+k}(s) \right] \left(C_{n+j}^1(0) + \tilde{R}_{n+j}^0(s) \right) \right],
\end{aligned}$$

where $S_n^- = \Delta_n(s) Q_n^-$, $S_n^+ = Q_{n-1}^+ \Delta_n(s)$, and the matrix continued fraction $\Delta_n(s)$ is defined by the recurrence equation

$$\Delta_n(s) = \{ [s + \gamma(n-1)] \mathbf{I} - Q_n^+ \Delta_{n+1}(s) Q_{n+1}^- \}^{-1}.$$

Taking account of the initial conditions, the expression for $\tilde{C}_1^1(s)$ simplifies to

$$\tilde{C}_1^1(s) = \Delta_1(s) \left(C_1^1(0) + \tilde{R}_1^0(s) \right) + \Delta_1(s) S_2^+ \left(C_2^1(0) + \tilde{R}_2^0(s) \right) + \Delta_1(s) S_2^+ S_3^+ [C_3^1(0) + \mathbf{F}],$$

where

$$\mathbf{F} = \tilde{R}_3^0(s) + S_4^+ [\tilde{R}_4^0(s) + S_5^+ [\tilde{R}_5^0(s) + \dots]].$$

For the Lorentz model, Eq. (7.25) can be rearranged as

$$\frac{d}{dt} \mathbf{C}_n^0(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}^0(t) - \tau^{-1} \mathbf{C}_n^0(t) + \tau^{-1} \mathbf{C}_1^0(0) \delta_{n,1} + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^0(t),$$

$$\frac{d}{dt} \mathbf{C}_n^1(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}^1(t) - \tau^{-1} \mathbf{C}_n^1(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^1(t) + \tau^{-1} \mathbf{C}_1^1(0) \delta_{n,1} + \tau^{-1} \mathbf{C}_3^1(0) \delta_{n,3} + \mathbf{R}_n^0(t),$$

where $\mathbf{R}_n^0(t) = \mathbf{r}_n \mathbf{C}_{n-3}^0(t)$. The above equations have the following solution for the zero- and first-order vectors

$$\tilde{\mathbf{C}}_1^0(s) = [1 + (s\tau)^{-1}] \Delta'_1(s) \mathbf{C}_1^0(0),$$

$$\tilde{\mathbf{C}}_n^0(s) = \mathbf{S}_n'^- \tilde{\mathbf{C}}_{n-1}^0(s) = (1 + (s\tau)^{-1}) \mathbf{S}_n'^- \mathbf{S}_{n-1}'^- \dots \mathbf{S}_2'^- \Delta'_1(s) \mathbf{C}_1^0(0), \quad (n \geq 2),$$

$$\tilde{\mathbf{C}}_1^1(s) = (1 + (s\tau)^{-1}) \Delta'_1(s) \mathbf{C}_1^1(0) + \Delta'_1(s) \mathbf{S}_2'^+ \mathbf{S}_3'^+ [(1 + (s\tau)^{-1}) \mathbf{C}_3^1(0) + \mathbf{F}],$$

where $\mathbf{S}_n'^- = \Delta'_n(s) \mathbf{Q}_n^-$, $\mathbf{S}_n'^+ = \mathbf{Q}_{n-1}^+ \Delta'_n(s)$, $\mathbf{F} = \mathbf{S}_4'^+ [\tilde{\mathbf{R}}_4^0(s) + \mathbf{S}_5'^+ [\tilde{\mathbf{R}}_5^0(s) + \dots]]$, and the matrix continued fraction $\Delta'_n(s)$ is defined by the recurrence equation

$$\Delta'_n(s) = \{ [s + \tau^{-1}] \mathbf{I} - \mathbf{Q}_n^+ \Delta_{n+1}(s) \mathbf{Q}_{n+1}^- \}^{-1}.$$

Chapter 8

Conclusion

Quantum Brownian motion is a rich and vast topic encompassing myriad approaches from path integral solutions and projection operator techniques to quantum linear Boltzmann equations and Lindblad master equations. In this thesis, the recent semiclassical approach to quantum Brownian motion of Coffey *et al.*, based on the mapping of quantum operators in Hilbert space to a classically meaningful representation space, namely Wigner's quasi-phase space (x, p) , has been studied in detail. This approach has its origin in Wigner's method of obtaining corrections to the classical equilibrium Maxwell-Boltzmann distribution. Following closely the Markovian theory of classical Brownian motion, Coffey *et al.* propose coupling the Wigner-Moyal equation to a classical heat bath or collision kernel in the form of a Kramers-Moyal expansion truncated at the second term, just as in the classical theory. Assuming frequency-independent damping, the Kramers-Moyal coefficients may then be determined using the equilibrium Ansatz (i.e. imposing the Wigner equilibrium distribution of the closed system as the stationary distribution of the open system), yielding position- and momentum-dependent coefficients¹. The result is a semiclassical master equation for the reduced Wigner function in quasi-phase space valid in the weak coupling and high temperature limits.

Using the master equation of Coffey *et al.*, quantum effects in the non-inertial Brownian motion of a particle in a one dimensional tilted cosine potential have been treated. In particular, the quantum Smoluchowski equation (QSE) associated with the master equation has been applied to the linear dynamics of a point Josephson junction (RSJ model). For small values of the quantum parameter, the junction's characteristics may be calculated using a three-term scalar recurrence relation, essentially similar to that encountered in the

¹This result had been anticipated as early as 1958 by Zwanzig [53]

classical solution. Thus, considering only the leading order correction term, one may obtain analytic formulae very similar to those of the classical case. A simple comparison of the predictions the QSE with those of another form of the QSE, in which the drift as well as the diffusion coefficient is altered [97], has also been presented. As demonstrated in the dc characteristics of the junction, the latter equation predicts unphysical results such as a negative resistance for zero voltage and negative differential resistance. Subsequently, the supposition that quantum effects should appear in the diffusion coefficient alone has been accepted in publications [79, 172] and in recent books [72, 110].

Quantum effects in the response of the Josephson junction to an ac current of arbitrary amplitude (nonlinear response) have also been treated, allowing one to treat important features of the dc and ac characteristics, absent in the small signal response (linear response), e.g. the Shapiro steps. Essentially, the effect of the quantum correction is to enhance the peaks and troughs in the response, i.e. to enhance the nonlinear dynamics of the junction. However, as the ac stimulus is increased, this quantum enhancement is soon dominated by the nonlinearity itself, thus masking the quantum effects. A similar enhancement of the peaks and troughs, in addition to their shift toward higher frequencies, occurs in the frequency response of the average voltage across the junction. With regard to the continued fraction solution of the QSE, unlike the linear response, treatment of the nonlinear response required the introduction of supermatrices to solve a recurrence relation in two indices.

In application of the QSE to quantum Brownian motion in a double well potential, the distribution function is expanded in a set of non-periodic orthonormal basis functions, namely the Hermite polynomials. Including terms only to first order in the quantum parameter, one obtains a nine-term recurrence relation (this is however more tractable than the fifteen-term recurrence relation associated with the full phase space relation [75]). This nine-term recurrence relation, is reduced to a set of matrix three-term recurrence relations, representing the classical relation forced by the first-order quantum terms. Subsequently, the spectrum of the position correlation function and the integral and effective relaxation times has been calculated via matrix continued fractions, yielding quantum effects in the linear dynamic susceptibility in agreement with predictions of quantum reaction rate theory in the high damping limit, constituting a novel result.

The quantum Smoluchowski equation has also been applied to the non-inertial Brownian motion of a particle in a ratchet potential. Here, the full power of semiclassical methods of solution, in particular quadratures and the continued fraction method, has been demonstrated in calculating the stationary, linear, and nonlinear response of a quantum Brownian

ratchet to a constant driving force, small ac driving force, and arbitrarily large ac driving force, respectively. Ratchet potentials afford very rich nonequilibrium dynamics, not least the alluring possibility of extracting a net particle current from symmetrical driving. The stationary average drift velocity for a constant force has been obtained in analytical form to any order in Planck's constant and applied to a symmetric two state driving force. Quantum effects in the linear and nonlinear response of the Brownian ratchet bare a striking resemblance in behaviour to the Josephson junction. In particular, the appearance of Shapiro steps in the nonlinear response of the frequency-dependent dc term of the average drift velocity mimics the nonlinear response of the Josephson junction, with the quantum effects most pronounced for relatively small values of the driving force.

A comparison of the semiclassical master equation of Coffey *et al.* with the master equations of various kinetic models describing quantum Brownian motion, namely the master equation of Diósi [32] and the Lorentz model has been presented by considering the complete (inertial) quasi-phase space dynamics of the quantum Brownian particle in a simple cosine potential. The results for the escape rate have been compared with those given analytically by the quantum reaction rate theory solution of the Kramers turnover problem, which is to be regarded as a benchmark solution. While good agreement between the analytical results and the predictions of the Coffey *et al.* equation is obtained for all damping, agreement with the predictions of the Diósi equation is obtained for low damping and very low bath cutoff-frequency only. For large values of the cutoff frequency, the Diósi equation fails to reproduce even qualitatively the analytical results for the escape rate, yielding similar behaviour to that of the Caldeira-Leggett equation [74]. This suggests that mere positivity of the density operator does not in itself guarantee solutions, which are consistent with the predictions of quantum reaction rate theory. Moreover, it appears to be essential that the position coefficient D_{pp} must not remain as in the classical Brownian motion. In order to reproduce for all damping the characteristic lowering of the barrier (produced by quantum tunnelling near the top of the barrier), the coefficient must become a function of the derivatives of the potential. Finally, reflecting on the quantum-classical correspondence, the comparison of semiclassical master equations with quantum master equations obtained from purely quantum mechanical considerations provides significant insight into understanding the interplay of classical and quantum phenomena in dissipative systems. In this respect, the long-sought-after "quantum Boltzmann equation" and its limiting forms, such as quantum Brownian motion and pure collisional decoherence, are of great interest and may be considered as benchmarks for the purpose of establishing a comprehensive theory of quantum dissipative systems.

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