QUASIPROBABILITY DENSITY DIFFUSION EQUATIONS FOR THE QUANTUM BROWNIAN MOTION IN A POTENTIAL

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.

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To Niamh, with all my love.

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Abstract

Wigner's [E. P. Wigner*, Phys. Rev.,* 1932, **40**, 749] representation of the density operator as a *c*-number quasiprobablity distribution in phase space allowing quantum mechanical averages involving the density matrix to be calculated as phase space averages just as classical averages originally used by him to obtain quantum mechanical corrections to classical thermodynamic equilibrium i.e. to the Maxwell-Boltzmann distribution so applying to closed quantum systems is extended to open quantum systems comprising a canonical ensemble of Brownian particles in a potential. This is accomplished via an idea of Gross and Lebowitz [E. P. Gross and J. L. Lebowitz, *Phys. Rev.* 1956, **104,** 1528]. They suggested that using Wigner's representation the connection between classical and quantum collision kernels, (i.e. in classical mechanics the Stosszahlanzatz describing the bath-particle interaction in the open system in the Boltzmann equation for the single particle distribution function) is much more transparent than in the density operator formalism. Moreover the quantum kernel should closely correspond to the classical one. Hence the idea developed in this Thesis that in the quantum Brownian motion the collision term in a quantum master equation in Wigner's representation should be described by a Kramers–Moyal like expansion truncated at the second term (leading of course in the classical limit to the Fokker-Planck equation) as in the classical Brownian motion. Imposition of the Wigner equilibrium distribution as the stationary solution of this equation (which is akin to the Fokker-Planck equation) in the manner used by Einstein [A. Einstein, in R. H. Fürth, Ed., *Investigations on the Theory of the Brownian Movement*, Methuen, London, 1926; reprinted Dover, New York, 1954] used to calculate diffusion coefficients in the Fokker-Planck equation by imposing the Maxwell-Boltzmann distribution as the stationary distribution then leads to the most important results of this Thesis. Namely the diffusion coefficients in the master equation become functions of the quantum parameter and the derivatives of the potential. Moreover all the solution techniques (matrix continued fractions etc) developed for the Fokker-Planck equation carry over to the quantum case as is illustrated by calculating the reaction rate and dynamical structure factor of a particle in a periodic cosine potential where the results are in agreement with those predicted by quantum reaction rate theory.

Contents

CHAPTER I

Introductory concepts: reasons for the development of a theory of quantum Brownian motion

The classical theory of dissipation based on the Brownian motion (representing the heat bath degrees of freedom) of a particle in a potential is ubiquitous in many areas of applied mathematics, theoretical physics and chemistry, particularly those aspects of nonequilibrium statistical mechanics and fluid mechanics dealing with the nature of metastable states and the rates at which these states decay. (The classical theory is summarized in Chapter II). Typical examples from statistical mechanics are current-voltage characteristics of Josephson junctions, the rate of condensation of a supersaturated vapour, dielectric and Kerr effect relaxation in liquids and nematic liquid crystals, dynamic light scattering, chemical reaction rate theory in condensed phases, superparamagnetic relaxation, polymer dynamics, nuclear fission and fusion and so on [1-4]. All these phenomena in one way or another depend on the nucleation and growth of some characteristic disturbance within a metastable system, e.g., condensation of a saturated vapour is initiated by the formation of a sufficiently large droplet of the liquid. If this droplet is big enough it will be more likely to grow than to dissipate and will bring about condensation of the entire sample [2].

In many cases particularly at low temperatures a theory of dissipation based on the classical Brownian motion (which is a particular *Stosszahlansatz* for the Boltzmann equation describing the evolution of the *single* particle distribution function i.e. the *reduced* distribution function in phase space) may be inadequate because it ignores quantum effects. Quantum noise arising from quantum fluctuations is also of importance in nanoscale and biological systems. We mention [3] the noise assisted tunnelling and transfer of electrons and quasi-particles. The characteristics of such quantum noise vary strongly as a function of

temperature and at high temperatures a crossover to Johnson-Nyquist noise which is essentially governed by the classical Brownian motion takes place.

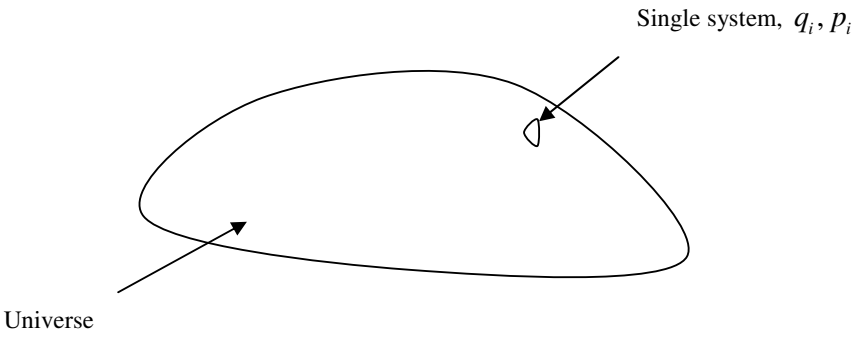

Figure I.I. The classical dynamics of a collection of *N* particles where *N* is of the order of 10^{23} say, is described by the Liouville equation [1] in the 6*N* phase space (***q***,***p***) where ***q****(t)* and ***p****(t)* denote the collection of 3*N* positions and 3*N* momenta. The Liouville equation describes the time evolution of the phase space density of representative points ρ (***q***,***p***) (it is simply a statement of the fact that the representative points are conserved and stream along the constant energy trajectories in phase space) and is

$$\frac{D\rho}{Dt} \equiv \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

$$\{\rho, \mathrm{H}\} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} \right)$$

where $\{\rho, H\}$ is the Poisson bracket, *H* is the Hamiltonian and the large *D*'s denote the hydrodynamical derivative. It is a purely dynamical theorem first given by Joseph Liouville in 1838. Boltzmann's idea (1872) was essentially to replace the entire system of 10^{23} degrees of freedom by a single (tagged) system of 3 degrees of freedom interchanging energy with the rest of universe or heat bath, i.e. the effect of the remaining $10^{23} - 3$ degrees of freedom is represented by collisions (this is the *Stosszahlansatz*) so that for the tagged system $\frac{D\rho}{Dt}$ is no longer zero and the (***q***,***p***) for the universe is now reduced to (q_s, p_s) for the single system, ρ is then the reduced or single particle distribution function which obeys the famous Boltzmann equation describing the evolution of the single particle distribution function from an initial state. Since the hydrodynamical derivative is no longer zero the trajectories of the single system in the (q_s,p_s) phase space exhibit energy diffusion and no longer purely stream. This idea is due to Boltzmann and comes from his

attempt to show that whatever the initial state of a gas the Maxwell-Boltzmann distribution must ultimately set in. Later Einstein (1905) used these concepts to great effect to explain the Brownian motion using the Fokker-Planck equation which is a particular form of the Boltzmann equation when the collisions are frequent, but weak. The whole procedure is remarkably well illustrated in the following paragraph from *Statistical Physics* II*, Nonequilibrium Statistical Mechanics,* by R. Kubo, M. Toda and N. Hashitsume, 2nd edition Berlin Springer-Verlag, 1991:

"We have emphasized repeatedly that the fundamental logic structure of statistical physics is the derivation of the laws of physics by introducing different stages of coarse graining from microscopic laws. By proceeding a step further, our description is made even cruder than the previous one by partial contraction of information. This contraction is a projection of the object onto a certain cross section of our understanding. Here the problem is to find the appropriate way of describing of the projected process.

For example, the stochastic process called Brownian motion is the projection of the microscopic motion of a colloid particle and all the molecules of the surrounding liquid onto the dimension of the motion of the colloid particle only. Furthermore, if the motion is projected onto the displacement then it becomes a diffusion process of the Brownian particle.

The complete dynamical description of *N* gaseous molecules confined in a box is made in terms of their position and momentum variables given as functions of time *t*. If the molecular positions are not observable, then the projected motion is described by the stochastic evolution of the distribution function $f(p_1, p_2, ..., p_N, t)$. The equation governing this evolution is called a master equation. It should furthermore be possible to discover the probability $f_1(r, p, t)$ of finding a molecule with momentum *p* and position *r* at time *t*. This is largely contracted information and useful in describing the pas only extremely crudely.

When a colloid particle is much larger and heavier than molecules of the surrounding liquid, the projected process becomes an ideal Brownian motion which is Gaussian and Markovian."

Yet another aspect of the subject which has come to the fore in recent years is the quantum mechanics of macroscopic quantum variables such as the decay of a zero voltage state in a biased Josephson junction, flux quantum transitions in a SQUID [4] and the possible reversal by quantum tunnelling of the magnetization of a single domain ferromagnetic particle as used to store data. Such particles typically comprise 10^4-10^5 spins acting in unison so that the magnetization is a

macroscopic quantum object. It has been conjectured by Bean and Livingston [5,6] that the magnetization may reverse (so losing the stored information) by quantum tunnelling through the particle internal magnetocrystalline anisotropy barrier as well as by the conventional mechanism of thermally agitated jumping over the barrier [1,7] which is in this context is called Néel relaxation [8]. More precisely by this tunnelling they mean the possibility of transitions of the magnetic moment at absolute zero of temperature from a state of complete alignment to a state of zero overall magnetization, due to the moment tunnelling through the barrier. It is thus immediately apparent that the Brownian motion plays a vital role in information and communications technology as well as in fundamental issues of applied mathematics and theoretical physics such as the existence of quantum tunnelling on a macroscopic scale. One may also remark in the context of macroscopic quantum tunnelling (which is a mesoscale quantum phenomenon) that substantial experimental data on magnetic relaxation now exists [8] at mK temperatures the analysis of which is severely hampered by the lack of an appropriate theory of quantum dissipation which could predict for example the relaxation behaviour as a function of spin size.

All these considerations necessitate the development of a theory of quantum Brownian motion both for translation (particles) and rotation (spins) particularly a theory which addresses directly the issue of the quantum-classical correspondence [9,10] in terms of a quantum analogue of the classical Fokker-Planck equation (which is a particular form of the Boltzmann equation describing the classical Brownian motion where the *Stosszahlansatz* is that the collisions ensuing from the bath-particle interaction are frequent but weak) describing the classical Brownian motion. Such an evolution equation will allow system parameters such as the Kramers escape rate [1] (in magnetic relaxation the inverse of the time of reversal of the magnetization), correlation times, susceptibilities, etc., to be calculated in terms of the eigensolutions of that equation in a manner analogous to those of the Fokker-Planck equation. Moreover, it would be possible to compare asymptotic solutions for parameters such as escape rates yielded by reaction rate theory with the corresponding quantities calculated from such a quantum master equation. For example, in the classical case, the smallest nonvanishing eigenvalue of the Fokker-Planck equation yields the exact Kramers escape rate. Thus the range of validity of the various asymptotic expressions in

different damping regimes for that quantity may be accurately established [1,11-13]. **Wigner's [14] (*c*-number) representation of quantum statistical mechanics in terms of phase space distributions (via [15] direct classical analogues of the relevant quantum operators and quantities so that the expectation values of physical variables may be expressed via phase space integration as rapidly converging expansions in Planck's constant $\hbar$), is an ideal starting point for the formulation of semiclassical quantum master equations (akin to the Fokker-Planck equation) governing almost classical systems constituting quantum mechanics on the mesoscale.**

Now the treatment of the Brownian motion in terms of diffusion (Fokker-Planck) equations by Einstein, Kramers, etc. which is essentially based on a single particle phase space distribution function describing the time evolution of the swarm of moving phase space points and which with the aid of modern computing techniques [1,16] allows one to evaluate various physical parameters ignores quantum effects. If one wishes to include these, however, in a diffusion equation treatment, a difficulty immediately arises, namely one cannot speak, because of the uncertainty principle, [14] of a particle having *simultaneously a well defined position and momentum* i.e. in the quantum world the concept of a *precise* phase point has no meaning. In other words it is impossible to ascertain the position of a system in phase space more accurately than to say that it is in a volume of the order of $\hbar^n$, where n is the number of degrees of freedom and $\hbar$ is Planck's constant [17] or experimentally it is ultimately impossible to make the measurements necessary to establish the classical trajectory. It follows therefore that one cannot define as in classical statistical mechanics a probability that the particle has a *particular position* and a *particular momentum* i.e. a joint probability distribution of the canonical variables. Hence one cannot define a true phase space probability distribution for a quantum mechanical particle emphasising the need for a different representation than the classical moving phase point. Nevertheless functions of the canonical variables as we have introduced in the last paragraph instead of the more usual Heisenberg and Schrödinger representations, bearing some resemblance to phase space distribution functions namely *quasiprobability* (not everywhere necessarily positive with the occurrence of "negative probability" being closely related to the

impossibility of simultaneously measuring canonical variables) *distribution functions* have proven [14,18] very useful in quantum mechanical systems as they provide insights into the connection between classical and quantum mechanics allowing one to express quantum mechanical averages in a form which is very similar to that of classical averages. Thus they are ideally suited to the study of the quantum-classical correspondence as is well illustrated by the following remarks of Baker [17] and Stratonovich [19]; Baker: "The large-scale experimental validity of classical mechanics tells us that quantum theory must, in some sense, correspond closely to classical mechanics. We have altered the classical concept of a moving point in phase space to that of a quasi-probability distribution which changes in time. This distribution is imagined to be concentrated about the classical point, so that a crude measurement will be unable to differentiate between the two theories. To ensure this correspondence, we use the statement which actually seems to be given by experiments – on the average, Hamilton's canonical equations hold*";* Stratonovich: "The statistical nature of quantum theory is manifested in the process of physical "measurement." From this it follows that the "pre-observation" state of a quantum system, which exists before the "measurement" and is independent of it (one can speak of such a state, to be understood in a definite sense), is a statistical state.

In the classical theory the "pre-observation" state of a statistical system is described by distribution functions in a certain space (we denote this space by M). We assume that in the quantum theory such a "pre-observation" state is described by distribution functions in this same "representation" space M, which accordingly has a classical meaning. But owing to the fact that a quantum "measurement" is more complicated than a macroscopic measurement, and is inevitably associated with an integral operation in the representation space, in contrast to the classical situation, negative values of the distribution function are possible at particular points of this space. The "representation distributions" of course do not give an entirely classical interpretation of quantum theory, but they provide a basis for that interpretation of the quantum theory which has maximum closeness to classical ideas and thus has the greatest physical-intuitive meaning."

The first of these quasiprobability distributions was introduced by Wigner [14] in 1932 in order to study in semiclassical fashion quantum corrections to the Maxwell-Boltzmann distribution of classical statistical mechanics which *inter alia*

elucidated the role played by tunnelling effects at high temperatures in reaction rate theory [14,18]. The Wigner distribution function was meant to be a reformulation, using the concept of a quasi-probability distribution in *phase space*, of Schrödinger's wave mechanics which describes quantum states of functions in *configuration space*. Thus the Wigner function is of particular use in the statistical mechanics of closed systems (i.e., systems with zero dissipation to the heat bath) as effectively it allows one to consider quantum corrections up to $O\left(\hbar^{2N}\right)$ to the classical distribution function, i.e., the quantum-classical correspondence. Hence, Wigner's formulation originally given for translational motion of a particle provides a basis for mesoscale quantum mechanics. The corresponding phase space representation for spin systems was given by Stratonovich in 1956 [19] who introduced the Wigner quasiprobability density function on the surface of the unit sphere in the phase space of orientations i.e. the polar and azimuthal angles (ϑ,φ). By way of background we remark that Wigner [14] originally arrived at his quasiprobability density *W(x,p)* for translational motion of a particle in phase space (x,p), which is the quasiprobability representation of the density operator simply by requiring that, the marginal distributions of *W(x,p)* should yield the correct quantum mechanical probability densities for the position x and momentum p of the particle with Hamiltonian $\hat{H}=\hat{p}^2/2m+V(\hat{x})$ in phase space. He thus established in a more or less heuristic manner a one to one correspondence [20] between the quantum state $|\psi\rangle$ in the particle Hilbert space and a real phase space function $W(x,p)$ which is also called the Wigner transform. Later Moyal [21] discovered a much more general formulation of representation space distributions where he showed that on introducing a characteristic function operator $\hat{M}(\tau,\theta)=\exp\left[i\left(\tau\hat{p}+\theta\hat{x}\right)\right]$ of the position and momentum that the Weyl correspondence rule between *c*-numbers and operators can be inverted via the Wigner transform from an operator in the Hilbert space to a function in the phase space. This is now known as the Moyal quantization and was originally applied to particles with symmetries described by the Heisenberg-Weyl group. Stratonovich [19] on the other hand in attempting to generalize the Moyal quantization to spins governed by the SU(2) rotation group in the representation space of polar angles (the quasiprobability density function

$W(\vartheta,\varphi)$ is entirely analogous to *W(x,p)* for the Heisenberg-Weyl group except that certain differences arise because of the angular momentum commutation relations [19]) discovered a linear bijective mapping (cf. Eqs. 1-3 of [19]) between operators on the Hilbert space and functions in representation space. This mapping [22] satisfies a number of physically intuitive properties, covariance and tracing being the two most important, and essentially replaces Moyal's characteristic function operator. Thus representation space distributions can be determined (see Chapter IV) via this bijective map from the general definition of a representation distribution using the symmetry properties of the underlying group, e.g., the translational Wigner function $W(x,p)$ is derived [19] by applying the principles of homogeneity and equivalence of directions.

We further remark that extensive computer simulations of Wigner distributions have been carried out by Filinov et al. [23] using molecular dynamics. These simulations are very useful in so far as they provide "experimental" benchmarks for the verification of quantum reaction rate theory and analytic solutions derived from quantum master equations.

Now in the classical Brownian motion a particle constitutes an *open* system, i.e., it may interchange energy with its surroundings and so dissipation is involved. An elegant attempt to include quantum effects in this context was made by Caldeira and (Nobel Laureate) Leggett in 1983 [24]. They showed how nonequilibrium effects could be included in Wigner's approach by regarding a Brownian particle as bilinearly coupled to a large number of harmonic oscillators in thermal equilibrium at temperature T as in the method of Pollak [25]. The oscillators represent the normal modes of the bath or environment. Quantization of the bath oscillators then leads to a semiclassical quantum master equation governing the time dependent Wigner distribution function in phase space. This equation resembles the classical Fokker-Planck equation, thus as shown by the author and his collaborators [26] a representation of the solution as matrix continued fractions in the frequency domain may again be used. Hence asymptotic formulae for quantum escape rates etc. can be compared with the exact solutions just as in the classical case and ranges of validity of the approximate solutions can be delineated. An important difference however is that in order for the Wigner equilibrium phase space distribution to be the stationary distribution, the diffusion

coefficient in the Fokker-Planck like master equation arising from the truncation of a Kramers-Moyal expansion at the second order term *must become a function of the derivatives of the potential* as noted in [26]. In the classical theory of the Brownian motion the Kramers-Moyal expansion is simply a differential representation of the Chapman-Kolmogorov integral equation describing the evolution of the transition probability for a Markov process. Truncation at the second term in the Kramers-Moyal expansion is possible for the Gaussian white noise characteristic of the Brownian motion because the higher order statistical moments may be all expressed as powers of the second moment [1]. In assuming a second order truncation of a Kramers-Moyal expansion in the quantum case we are in effect following the remark of Baker above "that quantum theory must in some sense correspond closely to classical mechanics…"

Up to the present, little in the nature of detailed solutions of semiclassical master equations describing quantum Brownian motion in external potentials has appeared in the literature. A notable exception is the Brownian motion of a quantum harmonic oscillator which has been treated by Agarwal [27] and others (see, e.g., refs. [28,29] and references cited therein). However, recently García-Palacios and Zueco [30,31] have proposed an effective approach to the solution of the master equation for the quantum Brownian motion in an anharmonic potential $V(x)$. They proceed by assuming that a Kramers-Moyal expansion of an integral equation for the transition probability exists just as in the classical case and that the expansion may again by truncated at the second term. However unlike the work described in the present Thesis they regard the diffusion coefficients as constant with the consequence that when the resulting master equation is applied to the calculation of quantum corrections to the Kramers escape rate their calculation is unable to predict the lowering of the potential barrier due to quantum effects as first identified by Wigner in his quantum transition state theory based on the Wigner function for the closed system which incorporates quantum effects into the Maxwell-Boltzmann statistics. Nevertheless their work is valuable in so far as their ideas suggest how Brinkman's representation (see Chapter II) of the classical Fokker-Planck equation as a partial differential recurrence relation in configuration space [32] and its associated solution methods based on matrix continued fractions arising from the choice of a suitable spatial

basis for the observables [1,16] could be also extended to the quantum regime. This has been successfully accomplished for the first time by the author and his collaborators for the particular case of a periodic cosine potential [26].

Moreover, analytical solutions for various quantum parameters such as escape rates available from quantum rate theory (which has been extensively verified via computer quantum molecular dynamic simulations [23]) have been compared with those obtained from the solution of quantum master equation for this potential. Both solutions essentially agree with each other indicating that our approach via a semiclassical quantum master equation is likely to be fruitful in the future.

In a general sense one may remark that the problem of quantum effects in the translation and rotational Brownian motion is significant at a fundamental scientific level, and in information and communication theory particularly because its solution will elucidate the role played by dissipative quantum tunnelling in the various quantum relaxation processes as well as providing a basis for a theory of macroscopic quantum tunnelling for which the semiclassical approach is ideally suited. The problem of macroscopic quantum tunnelling in spin systems is especially important in the context of information storage by means of magnetic nanoparticles. These constitute single domain ferromagnetic particles consisting of one giant spin of amount $10^4 - 10^5$ Bohr magnetons. Such particles may reverse their magnetization in classical fashion because the magnetization may escape due to thermal agitation over the internal anisotropy potential barrier of the particle with consequent loss of the information stored. It is, however, possible that the magnetization may also tunnel through the anisotropy potential barrier which is an example of macroscopic quantum tunnelling as a giant spin is involved. The existence or otherwise of this phenomenon may only be verified by having a theory of quantum spin relaxation in an anisotropy potential, the simplest example of which is uniaxial anisotropy with a transverse field applied. If a solution of this problem were available one could pinpoint the crossover temperature between reversal by thermal agitation and quantum tunnelling and its possible implications for information storage at low temperatures. We remark that this problem has been studied experimentally in some detail [8]. However, analysis of the

experimental data is hampered by the lack of an adequate theory. See for example [33,34]

In the context of the spin relaxation we should also mention the problem of molecular nanomagnets [35] where the effect of spin size is all-important. In fact one can show experimentally [8] the size effects in the magnetization dynamics and hysteresis loops in going from multi-domain magnetic nanoparticles to molecular clusters. Hence a theoretical method for predicting the magnetization evolution as a function of spin size which would come from extending Stratonovich's formulation of the Wigner function for spins to include dissipation would be extremely useful particularly to major players in the magnetic recording industry such as Seagate, BASF etc. Finally the Wigner function has extensive practical applications in signal processing, filtering, and engineering (time-frequency analysis), since time and frequency constitute a pair of Fourier-conjugate variables just like the x and p pair of phase space. We mention bioengineering, acoustics, speech analysis, vision processing, turbulence microstructure analysis, radar imaging, seismic data analysis, quantum optics, quantum computing and so on [36].

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CHAPTER II

Summary of the classical theory of the Brownian motion

As a background to the development of semiclassical master equations for the quantum Brownian motion it is first necessary to summarize the classical theory. We shall accomplish this first by means of an introductory section outlining in brief the main developments and from that we shall select for a detailed description those parts that are necessary for the development of a quantum theory.

II.I Early developments of the classical Brownian motion

The commonest example of the Brownian motion is the rapid haphazard perpetual motion (*Schwankung*) of a pollen grain in a colloidal suspension,

Figure II.I. Trajectory of a Brownian particle.

first reported in a meticulous series of observations by the botanist Robert Brown in 1828 [1]. The motion was theoretically explained by Einstein in 1905 [1,2-7] in terms of a discrete time random walk in the diffusion limit of a very large number of microscopic steps with the *same* variance each taking on average the *same* microscopic time and is mathematically [1,4] a consequence of the central limit theorem of probability theory, the only random variable being the direction of the walker. Thus Einstein was able to write down a probability density diffusion equation in configuration space governing the time evolution of the concentration of the Brownian particles. Hence he was able to calculate the mean square

displacement of a Brownian particle regarded as a sphere in terms of the viscous drag (given by Stokes' law) imposed by the surroundings, the absolute temperature and the time between successive observations of the displacement of the particle. Einstein envisaged the motion in physical terms as an inescapable consequence of the second law of thermodynamics and as incontrovertible evidence for the existence of atoms as later (1908) verified experimentally by Perrin [1,2]. He used Einstein's formula in order to determine Avogadro's number and obtained satisfactory agreement with the accepted value. Einstein's theory which ignores the inertia of the particle and its subsequent extensions which are listed below effectively allow one to construct a classical theory of dissipative phenomena.

The most significant extensions which are of physical interest [1,2-7] are due to Smoluchowski (1906, who treated the non inertial Brownian motion in an external potential, such as that due to gravity), Langevin (1908, who proceeded from the Newtonian equation of motion of the particle augmented by stochastic terms imposed by the surroundings so rederiving Einstein's results (in the non inertial limit) and so must be regarded as the founder of the subject of stochastic differential equations; he essentially considered the position and momentum of the particle as random variables), Debye (1913, who considered the non inertial rotational Brownian motion of a rigid rotator in the presence of an applied alternating electric field for the purpose of explaining dielectric relaxation of polar molecules at high frequencies), Ornstein (1917, who included the inertia of the Brownian particle in the formula for the mean square displacement), Klein (1921, who gave a probability density diffusion equation (Klein-Kramers equation) for the evolution of the joint probability density function of the positions and momenta of an assembly of Brownian particles in phase space in the presence of an external potential so that inertial effects could be included exactly), Kramers (1940, who treated noise activated escape over a potential barrier due to the Brownian motion and so was able to predict the influence of solvent friction on the transmission coefficient) [1,2,3,7], Doob (1942, who showed [7] that the proper interpretation of the Langevin equation was as an integral equation leading *inter alia* to the Itô and Stratonovich interpretations of that equation [6]), Brinkman [8] (1956, who formulated the Klein-Kramers equation in the presence of an arbitrary potential as a partial differential recurrence relation in

configuration space), and Risken [6] (1983, who developed effective matrix continued fraction algorithms for the exact solution of Brinkman's recurrence relation using matrix methods based on a Heisenberg-like formulation of the solution of the problem. This is described in Section II.IV below. We summarize Einstein's theory of the Brownian motion as follows [4].

II.II Einstein's theory of the Brownian motion

Einstein's theory of the Brownian motion [1,4] is based on the notion that the Brownian particle - a large particle such as a pollen grain suspended in a colloidal suspension executes a discrete time random walk. The walk is due to the very large number of impacts of the surrounding molecules on the Brownian grain. In other words the displacement of the Brownian particle is a *sum of random variables, each having arbitrary distributions*. We suppose that the density of random walkers in an element $x \to x + dx$ at time t is f. After a discrete time τ has elapsed we consider a neighbouring element of the same size situated at x' (τ is supposed so large that the motion of the random walker is independent of its motion at time $t \pm \tau$ yet τ is supposed very small compared to the observation time intervals). We next suppose that the probability of a walker entering from a neighbouring element to x' is:

$$\phi(x - x', \tau) = \phi(\Delta, \tau) \tag{2.1}$$

with:

$$\phi(-\Delta, \tau) = \phi(\Delta, \tau) \tag{2.2}$$

since we have an unbiased random walker. Summing over all neighbouring elements we then have:

$$f(x, t + \tau) = \int_{-\infty}^{\infty} f(x + \Delta, t)\phi(\Delta, \tau) d\Delta . \tag{2.3}$$

The above integral equation, called the *Smoluchowski integral equation* [1], is a particular form of the *Boltzmann equation* introduced by Boltzmann in 1872 [1] in order to demonstrate that whatever the initial distribution of an assembly of molecules in phase space, the ultimate result would be the Maxwell-Boltzmann distribution. Eq. (2.3) provides [1] a complete analogue of the Boltzmann equation when molecules of the medium can collide only against fixed centres or other molecules that have a given velocity distribution. Eq. (2.3) must be solved for f given an initial distribution for f. Also a "mechanism" or physical cause

(*stosszahlansatz*) for the random process must be given i.e. $\phi(\Delta,\tau)$ must be specified - here we specify ϕ by imagining that the random walker moves along the x-axis in such a way that in each step it can move either Δ to the right or Δ to the left, the duration of each step being τ, moreover, each individual random walker executes a motion which is independent of the motion of all other walkers in the system. Finally the motion of a random walker at a particular instant is independent of the motion of the random walker at any other instant (the random walker has no memory) that is the motion at time $t\pm\tau$ is *statistically independent* of the motion at time *t*.

Equation (2.3) can however equally well be written by Taylor's theorem as:

$$\begin{aligned}\sum_{n=0}^{\infty}\frac{\tau^n}{n!}\frac{\partial^n f}{\partial t^n} &= \sum_{n=0}^{\infty}\left(\frac{\int_{-\infty}^{\infty}\Delta^n\phi(\Delta,\tau)d\Delta}{n!}\right)\frac{\partial^n f}{\partial x^n} \\ &= \sum_{n=0}^{\infty}\frac{\left\langle\Delta^{2n}\right\rangle}{(2n)!}\frac{\partial^{2n} f}{\partial x^{2n}}\end{aligned} \tag{2.4}$$

by the definition of an average. Moreover, on account of Eq. (2.2)

$$\left\langle\Delta^{2n+1}\right\rangle = 0\,. \tag{2.5}$$

Equation (2.4) which is the simplest form of the Kramers-Moyal [1] expansion is entirely equivalent to the Smoluchowski integral equation. Now let us suppose that Δ and τ approach zero (extremely small displacements in infinitesimally short times) in such a way that:

$$\lim_{\substack{\Delta\to 0\\ \tau\to 0}}\frac{\left\langle\Delta^2\right\rangle}{2\tau} = D \tag{2.6}$$

and let us further suppose that all terms (τ^2) and (τ^4) and higher vanish in Eq. (2.4) then that equation formally goes over into the diffusion equation:

$$\frac{\partial f}{\partial x} = D\frac{\partial^2 f}{\partial x^2} \tag{2.7}$$

where:

$$f dx = f(x,t\,|\,x_0,t_0)dx \tag{2.8}$$

is the conditional probability that the random walker is in $x \to x + dx$ at time t given that it was at x_0 at time t_0. The neglect of the higher order terms in $\langle \Delta^{2n} \rangle$ as $\tau \to 0$ may be justified as follows. We recall that the probability distribution $\phi(\Delta, \tau)$ of the elementary displacements in time τ arises from the continual buffeting of the random walker by the very large number of impacts by the molecules of the surrounding medium. Thus the resulting displacement Δ of the walker is the sum of the elementary displacements arising from the molecular collisions (supposed statistically independent) which take place in time τ so that the central limit theorem of probability theory applies. The central limit theorem may be stated as follows [1]; let $\{\xi_i\}$ be a sequence of n independent random variables each having arbitrary distributions, then the sum:

$$\xi = \frac{\xi_1 + \xi_2 + \ldots + \xi_n}{\sqrt{n}} \tag{2.9}$$

approaches a normally distributed random variable (in this case Δ) as $n \to \infty$. Furthermore, if ξ_i has mean zero and variance $\langle \xi_i^2 \rangle = \sigma_i^2 < \infty$ then ξ has mean zero and variance σ^2 where:

$$\sigma^2 = \frac{1}{n} \sum_{i=1}^{n} \sigma_i^2 \,. \tag{2.10}$$

The elementary displacement Δ is a centred Gaussian random variable thus

$$\langle \Delta^{2n} \rangle = (2n-1)!! \langle \Delta^2 \rangle^n \,. \tag{2.11}$$

Equation (2.11) when combined with Eq. (2.4) is the justification for the neglect of the higher order terms in the Kramers-Moyal expansion. The fundamental solution of Eq. (2.7) also called the Green function or propagator is:

$$f(x, t \,|\, x_0, t_0) = \frac{1}{\sqrt{4\pi D |t - t_0|}} e^{-\frac{[x(t) - x(t_0)]^2}{4D|t - t_0|}} \tag{2.12}$$

which is a centred Gaussian distribution with variance:

$$\sigma^2 = \langle [x(t) - x(t_0)]^2 \rangle = 2D|t - t_0| \tag{2.13}$$

Equation (2.12) defines the *Wiener process* [1] that is the probability distribution of the displacements of the Brownian particle. We note two important points, σ is not mean square differentiable so that the velocity of a Brownian

particle cannot exist. Wiener proved that the realisations (sample paths) $[x(t) - x_0]$ of the Brownian process are almost everywhere continuous but nowhere differentiable. Moreover, Eqs. (2.6) and (2.13) are the same which is an indication of the *self-similar nature* of the Brownian process. Meaning that any given magnification (subject of course to physical limits such as distances of the order of the mean free path of a molecule) the Brownian motion trajectories appear on average to be the same, that is, the trajectory of a given Brownian particle is a *random fractal* [2] (*dilation invariant object*). The scaling of the steps or segments of the trajectory with magnification defines the *fractal dimension* which in this case according to the right side of Eq. (2.13) is 2.

To continue, Einstein essentially by considering the Brownian motion of a particle in a potential $V(x)$ and requiring that ultimately the Maxwell-Boltzmann distribution should prevail determined the diffusion coefficient D so finding the famous formula:

$$\left\langle [x(t) - x(t_0)]^2 \right\rangle = \frac{2kT}{\zeta} |t - t_0|. \tag{2.14}$$

In writing Eq. (2.14) it is assumed that the viscous drag on the particle is given by Stokes' Law. ζ is the drag coefficient. Equation (2.14) which connects the mean square fluctuations in the displacement of the Brownian particle with the dissipative coupling to the heat bath is essentially the fluctuation-dissipation theorem. Equation (2.7) in the presence of a potential $V(x)$ which reads:

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial f}{\partial x} + \frac{f}{\zeta}\frac{\partial V}{\partial x} \right) \tag{2.15}$$

is called the *Smoluchowski differential equation*, usually abbreviated to just the Smoluchowski equation. Notice that the second term arises from Stokes' law essentially as follows because the drift current is $\mathbf{J}_{dr} = f\mathbf{v}$, where $\mathbf{v} = \dfrac{\mathbf{F}}{\zeta}$ and $\mathbf{F}$ is the applied force of potential $V(x)$. The diffusion Eq. (2.15) then follows from the continuity equation $\dfrac{\partial f}{\partial t} = -\text{div}\mathbf{J}$ where $\mathbf{J} = \mathbf{J}_{dr} + \mathbf{J}_{diff}$, $\mathbf{J}_{diff} = -D\dfrac{\partial f}{\partial x}$ is the diffusion current by requiring that *at equilibrium* the total current $\mathbf{J}$ must vanish, in other words the drift current is exactly balanced by the diffusion current. This method of calculating diffusion coefficients due to Einstein will be extended to the quantum case in Chapter VI where the Maxwell-Boltzmann distribution in the

potential well will be replaced by the Wigner stationary distribution and the ensuing alterations to the collision term which causes the diffusion coefficient to become a function of the derivatives of the potential will be calculated. In many problems notably in curvilinear coordinates the drift and diffusion coefficients are functions of the coordinates because of the metrics involved.

In 1908 Perrin [1,2] successfully calculated the Avogadro number from observations of the mean square displacement of a Brownian particle so confirming Eq. (2.14).

We remark that Einstein's approach to the Brownian motion is based on statistical assumptions of a general nature, not fixed to a specific model [2]. On the other hand Smoluchowski's investigations which yielded essentially the same results, were published some months later than Einstein's. He considered (in the spirit of Boltzmann) a detailed kinetic model namely collisions of hard spheres as well described by Mazo [2]. Unlike Einstein whose theory is essentially statistical and follows from the central limit theorem, Smoluchowski used the dynamics of the particle motion in a specific dynamic way. The link between the two methods was provided by Langevin in 1908. His idea was [1,2] that a suspended particle in a fluid is acted upon by forces due to the molecules of the solvent. This force can be expressed as a sum of its average value and a fluctuation about this average value. Thus Langevin's starting point is the Newtonian equation:

$$m\frac{dv}{dt}+\zeta v=\lambda(t),\quad \frac{dx}{dt}=v \tag{2.16}$$

in which the fluctuating force $\lambda(t)$ has the following properties

$$\langle\lambda(t)\rangle=0 \tag{2.17}$$

$$\langle\lambda(t_1)\lambda(t_2)\rangle=2kT\zeta\delta(t_1-t_2) \tag{2.18}$$

(δ denoting the Dirac-delta function) where the angular braces denote the statistical average of λ over its realizations. Moreover Isserlis's theorem [1] concerning averages of products of Gaussian random variables must be satisfied namely that in an even number of observations everywhere time average is ensemble average

$$\begin{aligned}\overline{F(t)F(t')} &= \overline{F(t)F(t+\tau)} \\ &=< F(t)F(t+\tau) > \\ &= \lim_{T'\to\infty}\frac{1}{T'}\int_0^{T'} F(t)F(t+\tau)\,d\tau\end{aligned} \tag{2.19}$$

$$\begin{aligned}\langle \lambda_1\lambda_2...\lambda_{2n}\rangle &\equiv \langle \lambda(t_1)\lambda(t_2)...\lambda(t_{2n})\rangle \\ &= \sum\prod_{k_i<k_j}\langle \lambda(t_{k_i})\lambda(t_{k_j})\rangle,\end{aligned} \tag{2.20}$$

where the sum is over all distinct products of expectation value pairs, each of which is formed by selecting n pairs of subscripts from $2n$ subscripts. For example, when $n=2$, we have

$$\langle \lambda_1\lambda_2\lambda_3\lambda_4\rangle = \langle \lambda_1\lambda_2\rangle\langle \lambda_3\lambda_4\rangle + \langle \lambda_1\lambda_3\rangle\langle \lambda_2\lambda_4\rangle + \langle \lambda_1\lambda_4\rangle\langle \lambda_2\lambda_3\rangle$$

In general, from the theory of permutations and combinations, there will be $(2n)!/(2^n n!)$ such distinct pairs. We also have for an odd number of observations

$$\begin{aligned}\langle \lambda(t_1)\lambda(t_2)...\lambda(t_{2n+1})\rangle &\equiv \langle \lambda_1\lambda_2...\lambda_{2n+1}\rangle \\ &= 0.\end{aligned}$$

Isserlis's theorem also known Wick's theorem allows the truncation of the Kramers-Moyal expansion after the second term as it automatically shows that all the higher order terms are of order of τ^2 and higher (cf the notation following Eq. (2.6)). Equation (2.16) (which is the equation of motion of the random variables x and v) when averaged over the realizations of the phase path (x,v) then yields (for convenience setting $t_0 = 0$)

$$\langle [x(t)-x(0)]^2\rangle = \frac{kTm}{\zeta^2}\left(\frac{\zeta|t|}{m} - 1 + e^{-\frac{\zeta|t|}{m}}\right) \tag{2.21}$$

(a result actually obtained for the first time by Ornstein in 1918 [2].) Equation (2.21) is mean square differentiable, so that the velocity of the Brownian particle now exists, is equivalent to Einstein's result only at times well in excess of m/ζ, the frictional time. The reason for this is [2] that Einstein worked only in the configuration space of the Brownian particle, he did not actually introduce the velocity of the particle except in so far as to demonstrate that for the pollen particles he envisaged, the time scales were so long that the last two terms in Eq. (2.21) were negligible. This assumption is equivalent to stating that the particles

thermalize exceedingly rapidly. By working in the complete phase space [2] Langevin was also able to find the velocity relaxation.

Einstein's treatment of the Brownian motion introduces an external force of potential $V(x)$ only in a virtual sense in order to calculate the diffusion coefficient. The gist of his argument being that the introduction of a potential well causes a Maxwell-Boltzmann distribution to be set up in the well which must then render the collision term in the Fokker-Planck equation zero. The well is necessary in order to have a stationary solution, because for a free Brownian particle no stationary solution exists. The introduction of a virtual force renders Einstein's analysis more complicated for the beginner than either that of Smoluchowski who includes the well explicitly or Langevin who obtains the constant in his rapidly fluctuating random force by arguing that a Maxwellian distribution of the velocities sets in almost immediately which is true for large particles such as pollen grains.

In general the form of the Fokker-Planck equation for diffusion in one dimension under the influence of an external force is

$$\frac{\partial f(y,t\,|\,x)}{\partial t} = -\frac{\partial}{\partial y}\Big[D^{(1)}(y,t) f(y,t\,|\,x)\Big] + \frac{\partial^2}{\partial y^2}\Big[D^{(2)}(y,t) f(y,t\,|\,x)\Big] \tag{2.22}$$

where $D^{(1)}$ is the drift coefficient and $D^{(2)}$ is the diffusion coefficient. Throughout this Chapter we will specify the distribution by f and we shall distinguish the various distribution functions by quoting their arguments. Clearly Smoluchowski's differential Eq. (2.15) is a special case of Eq. (2.22).

Since in general we will be dealing with the multivariable form of the Fokker-Planck equation, it is necessary to quote the form of that equation for many dimensions characterized by a set of random variables $\{\boldsymbol{\xi}\} = \{\xi_1, \cdots \xi_n\}$. The multivariable form of the Fokker-Planck equation [6] is with $f = f(\{\mathbf{y}\}, t\,|\,\{\mathbf{x}\})$, $\{\mathbf{y}\}$ denoting a set of realisations of the random variables $\{\boldsymbol{\xi}\}$:

$$\frac{\partial f(\mathbf{y},t)}{\partial t} = -\sum_i \frac{\partial}{\partial y_i}\Big[D_i^{(1)}(\mathbf{y},t) f(\mathbf{y},t)\Big] + \frac{1}{2}\sum_{k,l}\frac{\partial^2}{\partial y_k \partial y_l}\Big[D_{k,l}^{(2)}(\mathbf{y},t) f(\mathbf{y},t)\Big]. \tag{2.23}$$

For simplicity, let us suppose that the process is characterised by a state vector **y** having only two components (y_1, y_2) (these, for example, could be the realisations of the position and velocity of a Brownian particle), and so the two variable Fokker-Planck equation written in full is assuming that the 2 dimensional Kramers-Moyal expansion is truncated at the second term,

$$\frac{\partial f}{\partial t} = -\sum_{i=1}^{2} \frac{\partial}{\partial y_i}\left[D_i^{(1)} f\right] + \frac{1}{2}\sum_{k,l}\frac{\partial^2}{\partial y_k \partial y_l}\left[D_{k,l}^{(2)} f\right] \qquad (2.24)$$

or

$$\begin{aligned}\frac{\partial f}{\partial t} = &-\frac{\partial}{\partial y_1}\left[D_1^{(1)} f\right] - \frac{\partial}{\partial y_2}\left[D_2^{(1)} f\right] + \frac{1}{2}\frac{\partial^2}{\partial y_1^2}\left[D_{1,1}^{(2)} f\right] \\ &+ \frac{1}{2}\frac{\partial^2}{\partial y_1 \partial y_2}\left[D_{1,2}^{(2)} f\right] + \frac{1}{2}\frac{\partial^2}{\partial y_2 \partial y_1}\left[D_{2,1}^{(2)} f\right] + \frac{1}{2}\frac{\partial^2}{\partial y_2^2}\left[D_{2,2}^{(2)} f\right].\end{aligned} \qquad (2.25)$$

In general, $D_{1,2}^{(2)} = D_{2,1}^{(2)}$ so that

$$\begin{aligned}\frac{\partial f}{\partial t} = &-\frac{\partial}{\partial y_1}\left[D_1^{(1)} f\right] - \frac{\partial}{\partial y_2}\left[D_2^{(1)} f\right] \\ &+ \frac{1}{2}\frac{\partial^2}{\partial y_1^2}\left[D_{1,1}^{(2)} f\right] + \frac{1}{2}\frac{\partial^2}{\partial y_2^2}\left[D_{2,2}^{(2)} f\right] + \frac{\partial^2}{\partial y_1 \partial y_2}\left[D_{1,2}^{(2)} f\right],\end{aligned} \qquad (2.26)$$

where the various drift and diffusion coefficients are

$$D_i^{(1)} = \lim_{\Delta t \to 0}\frac{\overline{\Delta y_i}}{\Delta t}, \quad D_{i,j}^{(2)} = \lim_{\Delta t \to 0}\frac{\overline{\Delta y_i \Delta y_j}}{\Delta t}, \quad (i, j = 1, 2). \qquad (2.27)$$

A particular example of this is the Langevin equation for a free Brownian particle which may be represented as the system describing the random motion of the phase point $(x(t), v(t))$

$$\frac{dx}{dt} = v, \quad \frac{dv}{dt} = -\gamma v + \frac{\lambda(t)}{m} \qquad (2.28)$$

with

$$\begin{aligned}\langle \lambda(t) \rangle &= 0, \\ \langle \lambda(t_1)\lambda(t_2) \rangle &= 2m\gamma kT\delta(t_1 - t_2).\end{aligned}$$

This equation may be used to calculate the drift and diffusion coefficients as follows. We have writing the Langevin equation in terms of infinitesimals over a small time Δt for the first drift coefficient

$$D_1^{(1)} = \lim_{\Delta t \to 0}\frac{\overline{\Delta y_1}}{\Delta t} = \lim_{\Delta t \to 0}\frac{\overline{\Delta x}}{\Delta t} = v \qquad (2.29)$$

which follows from the fact that the average of the noise is zero.

Now, the change in velocity in a small time Δt is

$$\Delta v \approx -\gamma v \Delta t + \frac{1}{m}\int_{t}^{t+\Delta t} F(t')dt' .$$

Thus the second drift coefficient $D_2^{(1)}$ is

$$D_2^{(1)} = \lim_{\Delta t \to 0} \frac{\overline{\Delta v}}{\Delta t} = -\gamma v . \tag{2.30}$$

Likewise, the diffusion coefficients $D_{1,1}^{(2)}(x,v)$ and $D_{1,2}^{(2)}(x,v)$ are

$$\begin{aligned} D_{1,1}^{(2)}(x,v) &= \lim_{\Delta t \to 0} \frac{\overline{(\Delta x)^2}}{\Delta t} \\ &= \lim_{\Delta t \to 0} \frac{\overline{v^2 (\Delta t)^2}}{\Delta t} \\ &= 0 \end{aligned} \tag{2.31}$$

because the numerator is obviously of order $(\Delta t)^2$. In like manner

$$\begin{aligned} D_{1,2}^{(2)}(x,v) &= \lim_{\Delta t \to 0} \frac{\overline{\Delta x \Delta v}}{\Delta t} \\ &= \lim_{\Delta t \to 0} \frac{\overline{v \Delta t \Delta v}}{\Delta t} \\ &= \lim_{\Delta t \to 0} \overline{-\gamma v^2 \Delta t + v \int_{t}^{t+\Delta t} \frac{F(t')}{m} dt'} \\ &= 0 \end{aligned} \tag{2.32}$$

because $\overline{F(t)} = 0$. In order to evaluate the second diffusion coefficient

$$D_{2,2}^{(2)}(x,v) = \lim_{\Delta t \to 0} \frac{\overline{(\Delta v)^2}}{\Delta t} \tag{2.33}$$

consider

$$\begin{aligned} (\Delta v)^2 = \gamma^2 v^2 (\Delta t)^2 &- \frac{2\gamma v \Delta t}{m} \int_{t}^{t+\Delta t} F(t')dt' \\ &+ \frac{1}{m^2} \int_{t}^{t+\Delta t} \int_{t}^{t+\Delta t} F(t')F(t'')dt'dt''. \end{aligned} \tag{2.34}$$

The first term on the right-hand side of Eq. (2.34) is of order $(\Delta t)^2$, the second term vanishes on averaging, and

$$\int_t^{t+\Delta t}\int_t^{t+\Delta t}\overline{F(t')F(t'')}dt'dt'' = 2D\int_t^{t+\Delta t}\int_t^{t+\Delta t}\delta(t'-t'')dt'dt'' \\ = 2D\Delta t \tag{2.35}$$

($D = \gamma kTm$), whence the diffusion coefficient is

$$D_{2,2}^{(2)}(x,v) = 2kT\gamma/m\,. \tag{2.36}$$

Thus, we obtain

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} = \gamma\left[\frac{\partial(vf)}{\partial v} + \frac{kT}{m}\frac{\partial^2 f}{\partial v^2}\right], \tag{2.37}$$

which is the desired Fokker-Planck equation describing the evolution of the probability distribution of the displacement and velocity of a free Brownian particle in phase space $(x(t), v(t))$. The left hand side of this equation corresponds to the Liouville equation for the single particle distribution function and is *the convective derivative which is no longer zero* while the right hand side is the Boltzmann collision term arising from the reduction of the many particle distribution function to a single particle one as described earlier. If an external conservative force is introduced nothing new is essentially involved and Eq. (2.37) merely becomes

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} - \frac{1}{m}\frac{dV}{dx}\frac{\partial f}{\partial v} = \gamma\left[\frac{\partial(vf)}{\partial v} + \frac{kT}{m}\frac{\partial^2 f}{\partial v^2}\right]. \tag{2.38}$$

Clearly in this case the second drift coefficient is no longer zero in the Kramers-Moyal expansion. Equation (2.38) is called the Klein-Kramers equation. It may be equally written in the phase space of positions and momenta which is more convenient for the quantum generalizations. The Klein-Kramers equation may be solved by converting it via appropriate orthogonal expansions of the phase space variables into a differential recurrence relation for the observables, i.e., the decay functions of the system as described in Section II.IV below. These may be represented [1,6] as matrix continued fractions in the frequency domain. The same representation may also be obtained directly from the Langevin equation by averaging that equation over its realizations in phase space [1]. (Recall that the Langevin equation is simply the Newtonian equation of motion of the particle augmented by a systematic frictional force proportional to the velocity of the

particle superimposed on which is a rapidly fluctuating random force both forces representing the effect of the heat bath on the particle and in the Klein-Kramers equation are represented by the collision term). The continued fraction representation has led to many exact solutions as outlined in [1,6]. In the present context one should also mention that it may be shown (see Appendix II.I) [10] that a generalized Langevin equation, i.e., the equation of motion of a Brownian particle with memory friction is equivalent to the Newtonian equation of motion of a particle moving in a potential $V(x)$ bilinearly coupled to a bath of harmonic oscillators (essentially a string or transmission line attached to the particle which serves as a schematic description of the heat bath) with a high frequency cutoff *ansatz* for the spectral density of the bath oscillators.

The particle plus harmonic oscillator heat bath (string), etc. readily lends itself to quantum generalizations. Due to the introduction of the string the number of degrees of freedom becomes essentially infinite. However, this inconvenience is compensated [11,12] by the fact that we now have a conservative dynamical system which can be quantized in the usual manner. The essential ideas go back to Lamb's [13] attempt to explain radiation damping in classical electrodynamics and Planck's (1900) inspired treatment of blackbody radiation. One of the most notable quantum generalizations based on such particle-string models is that of Caldeira and Leggett [14] yielding quantum master equations describing nonequilibrium phenomena in phase space leading to generalizations of the Wigner distribution (see Chapter VI).

II.III Klein-Kramers equation and its application to reaction rate theory

In transition state theory (TST) [15] which constitutes the simplest form of reaction rate theory (see Figure II.II below) a chemical reaction is modelled as escape of particles due to thermal agitation from a source situated at the bottom of a potential well A say over a high barrier of height ΔV situated at C which is called the transition state, the coordinate x is called the reaction coordinate.

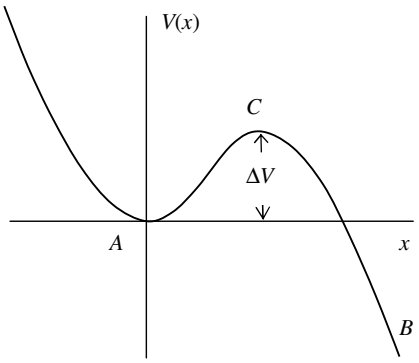

Figure II.II Single well potential function as the simplest example of escape over a barrier. Particles are initially trapped in the well near the point *A* by a high potential barrier at the point *C*. They very rapidly thermalise in the well. Due to thermal agitation however very few may attain enough energy to escape over the barrier into region *B* whence they never return.

For simplicity the particles of mass *m* are supposed having crossed the barrier never to return. This leads to the following formula [4] for the rate constant (formally defined as the current or flux of particles at the barrier divided by the population of the particles in the well)

$$\Gamma = \nu_A e^{-\frac{\Delta V}{kT}} = \frac{1}{2\pi}\sqrt{\frac{V''(x_A)}{m}}e^{-\frac{\Delta V}{kT}} \tag{2.39}$$

which was originally proposed by Arrhenius from analysis of experimental data. An elementary derivation of Eq. (2.39) is given in Chapter V. Equation (2.39) however has the flaw that the prefactor ν_A is simply the frequency of oscillation in the well (the attempt frequency) and is thus entirely independent of the dissipative coupling of the particles in the well to the surrounding heat bath. Thus escape of particles may occur in the absence of fluctuations so violating the fluctuation dissipation theorem. Another way of stating this is that in the transition state or equilibrium theory the Maxwell-Boltzmann distribution which prevails in the depths of the well is assumed to hold everywhere. This is not true near the top of the barrier due to the leaking of particles over the barrier. The problem of incorporating nonequilibrium effects which is essentially a boundary layer problem was first attacked by Kramers [16]. In 1940 he suggested that Eq.(2.39) should be replaced by:

$$\Gamma = A\nu_A e^{-\frac{\Delta V}{kT}} \tag{2.40}$$

where A is a (transmission) factor describing the dissipative coupling of the bath to the well. The aim is to calculate the transmission factor A as a function of the coupling. Kramers accomplished this by generalizing, as we have just seen, Einstein's theory of the Brownian motion to yield the complete phase space description, (i.e. Eq. (2.38) above), of the Brownian motion which is then used as a model of the dissipative coupling. The Klein-Kramers equation applies to systems, which (ignoring the bath coordinates) have a separable additive Hamiltonian of the form:

$$H = \frac{1}{2} m\dot{x}^2 + V(x) \tag{2.41}$$

and is entirely equivalent to the Langevin equation:

$$m\ddot{x} + \zeta \dot{x} + \frac{\partial V}{\partial x} = \lambda(t) \tag{2.42}$$

provided $\lambda(t)$ is Gaussian white noise. Kramers obtained asymptotic solutions for the prefactor A from Eq. (2.38) in two limiting cases. The first is called *very low damping* which may be explained as follows: Here he proceeded by rewriting Eq. (2.38) in angle-action variables (or equivalently angle-energy variables). Then he supposed that the energy trajectories form essentially closed (apart from a critical energy curve known as the separatrix on which the particle may escape) loops so that they do not differ significantly from those of the undamped librational motion in the well with energy equal to the barrier or saddle energy ΔV. Next since the motion is very lightly damped the loss of energy in one cycle of the motion is very small i.e. the energy is a *slow* variable (it is almost conserved) while the angle or phase is a *fast* variable. Thus eliminating the phase by averaging along an energy trajectory over the fast phase variable yields a diffusion equation in the energy. The solution of this energy diffusion equation ultimately leads to the escape rate for very low damping (VLD). We have:

$$\begin{aligned} \Gamma &= \nu_A \frac{\zeta}{m} \frac{J(E_c)}{kT} e^{-\frac{\Delta V}{kT}} \\ &= \gamma \frac{\omega_A}{2\pi} \frac{J(E_c)}{kT} e^{-\frac{\Delta V}{kT}} \end{aligned} \tag{2.43}$$

where

$$\gamma = \frac{\zeta}{m}$$

so that

$$A = \gamma J(E_c)$$

where $\gamma J(E_c)$ is the energy loss per cycle of the almost periodic motion along the barrier (saddle) energy trajectory, $E_c = \Delta V$ and $J(E_c)$ is the action evaluated at the barrier energy. The approximation $\nu_A J(E_c) \sim E_c = \Delta V$ may be used to render Eq. (2.43) in an even simpler form. Equation (2.43) which unlike Eq. (2.39) precludes escape without coupling to the bath holds if in Eq. (2.40) $A \ll 1$ that is when:

$$\gamma J(E_c) = \Delta E \ll kT \,. \tag{2.44}$$

Thus the energy loss per cycle of the almost periodic motion of the saddle energy trajectory is much less than the thermal energy. Kramers also obtained an asymptotic solution for the escape rate for *very high damping* (VHD) namely $\Delta E \gg kT$:

$$\Gamma = \frac{\sqrt{V''(x_A)\left|V''(x_C)\right|}}{\zeta} e^{-\frac{\Delta V}{kT}} \tag{2.45}$$

which is often written:

$$\frac{\omega_A \omega_C}{2\pi\gamma} e^{-\frac{\Delta V}{kT}} \tag{2.46}$$

so that:

$$A = \frac{\omega_C}{\gamma} \,. \tag{2.47}$$

Thus unlike the transition state theory escape is precluded for *very small* or *very large* coupling to the bath. Moreover at a certain *critical* coupling where ($\Delta E \sim kT$) a transition in the escape rate from ζ to inverse ζ dependence occurs. This region is much more difficult to treat as no small perturbation parameter exists [1,17] (see our discussion at the end of this Section). Equation (2.46) which does not include inertial effects may be determined entirely either from the Smoluchowski differential equation (for the distribution function in configuration space which neglects inertia) or from the very high friction limit of the Kramers asymptotic solution of the Klein-Kramers equation for the escape rate for $\Delta E > kT$. The asymptotic solution is valid in the so called *intermediate to high damping* case (IHD):

$$\Gamma = \frac{\omega_A}{2\pi}\left[\sqrt{1+\frac{\gamma^2}{4\omega_C^2}}-\frac{\gamma}{2\omega_C}\right]e^{-\frac{\Delta V}{kT}} \tag{2.48}$$

where intermediate damping is defined as the $\gamma = 0$ value of Eq. (2.48) which corresponds to the TST result where the transmission factor is unity.

Equation (2.48) includes inertial effects but is not valid for very small damping. In its derivation which requires linearization of the Langevin equation about the saddle point (in this one dimensional case a simple maximum) one assumes that the thermal distribution prevails almost to the top of the well. This is not true for small damping because the nonequilibrium region extends into the depths of the well far beyond the saddle point region where the Langevin equation may be linearized. It goes over into the VHD damping result for large γ. The Kramers calculation (which explains the riddle of escape in the absence of fluctuations, associated with the transition state theory) applies to mechanical systems with separable and additive Hamiltonians of the form of Eq.(2.41). It was generalized to systems of *n* degrees of freedom and non-separable Hamiltonians by Langer [1,17,18] in the IHD case he obtained:

$$\Gamma = \lambda^+ \sqrt{\frac{\det E_A}{|\det E_C|}} e^{-\frac{\Delta V}{kT}}. \tag{2.49}$$

Thus the escape rate is expressed in terms of the Hessians of the saddle and well energies and the (unstable) positive eigenvalue λ^+, of the set of noiseless Langevin equations of the system linearized about the saddle point. Equation (2.49) is extremely useful in discussions of the time of reversal of the magnetization of single domain ferromagnetic particles in non-axially symmetric potentials of the magnetocrystalline anisotropy and has been verified experimentally for such systems [19]. Furthermore Eq. (2.49) demonstrates that to calculate the escape rate all that is necessary is a knowledge of the *energy landscape* of a system which is in itself however, an extremely difficult problem. Equation (2.49) itself forms a key part of Langer's [18] general theory of the decay of metastable states and is a generalisation of Becker and Döring's (1935) calculation [1] of the rate of condensation of a supersaturated vapour. We remark that the Kramers asymptotic solutions for the escape rate may be verified by solving the Klein-Kramers equation for the smallest non vanishing eigenvalue which is directly proportional to the escape rate as it is exponentially small

compared to all the other eigenvalues. This has been accomplished for a large variety of systems by Risken [6] and Coffey et al. [1] in the context of dielectric and magnetic relaxation. λ_1 may also be calculated by averaging the Langevin equation over its realisations as described by Coffey et al. [1] and solving the resulting hierarchy of equations for the statistical averages by matrix continued fraction methods.

Kramers was however, unable to find asymptotic solutions valid in the so called *Kramers turnover region*, where the energy loss per cycle of a particle having the saddle point energy is *of the order of the thermal energy*. Here the coupling between the Liouville and dissipative terms in the Klein–Kramers equation enters so that one may no longer ignore the Liouville term as was done in his solution for the very low damping regime. (The Liouville term vanishes when averaged over the fast variable in the VLD case by the principle of the conservation of density in phase). This problem, named the Kramers turnover problem, was solved nearly 50 years later by Mel'nikov and Meshkov [20]. They gave an integral formula namely

$$\Gamma = \exp\left(\frac{1}{2\pi} \int_{-\infty}^{\infty} \ln\left[1 - e^{-\frac{\gamma I(E_C)}{kT}\left(\lambda^2 + 1/4\right)} \right] \frac{d\lambda}{\lambda^2 + 1/4} \right) \Gamma_{\mathrm{IHD}} \qquad (2.50)$$

bridging the VLD and intermediate damping (essentially the TST) asymptotic solutions simultaneously establishing a range of validity for the TST solution. Their solution [17,20,21] for the energy distribution function which is obtained by the Wiener-Hopf method is based on the Green function of an energy/action diffusion representation of the Klein-Kramers equation in the Kramers turnover region. Thence they obtain an integral called the depopulation factor, which when multiplied by the TST or intermediate damping result yields a formula which reduces to the VLD formula as the friction coefficient tends to zero so solving the Kramers turnover problem. Furthermore, Mel'nikov [11,12] (see also Meshkov and Mel'nikov [20]) established in the context of Kramers' Brownian motion model of noise assisted escape that the TST escape rate is accurate provided the ratio of the thermal energy to the barrier height is less than the ratio of the friction coefficient to the saddle angular frequency with that ratio in turn much less than unity. Now the TST or intermediate damping result is a particular case of the IHD formula provided the preceding condition is satisfied (in fact that result constitutes

the absolute lower limit of validity of the IHD solution as a function of friction). Thus they postulate from heuristic reasoning, essentially appealing to continuity that a formula valid in *all* damping regimes may be given by simply multiplying the general IHD result by the depopulation factor, i.e. Eq. (2.50). Besides their use in reaction rate theory these asymptotic solutions which hold of course only when the barrier height is significantly greater than the thermal energy are also very useful as benchmark solutions in the numerical calculation of escape reaction rates i.e. the smallest non vanishing eigenvalue for matrix continued fraction solution of the Klein-Kramers equation. They also lend themselves to quantum generalizations which we now briefly summarize as they will be used in Chapter VI.

First Mel'nikov [11,12] extended the depopulation factor method to take into account quantum effects in a semiclassical *ad hoc* way by simply inserting the quantum mechanical transmission factor for a parabolic barrier [22] into the classical integral equation for the energy distribution function yielded by the Wiener-Hopf method in the Kramers turnover region. On solving for the energy distribution function and proceeding to the VLD limit he was able to obtain an integral formula for the VLD quantum Kramers rate which at high temperatures reduces to the classical VLD result. Moreover, he gave explicit expressions for the quantum VLD rate for cubic and cosine potentials (for details see Section 3.4 of [11]). These results simplify if the potential well is assumed to be very wide so that the noise can be treated as classical; see Eqs. (15) and (16) of [12] here it is possible to give a simple analytic formula for the VLD quantum Kramers rate; see Eq. (16) of Ref. [11].

The procedure for finding the quantum VLD rate involving insertion of the quantum transmission factor into the classical integral equation in the Kramers turnover region, explicitly solving the resulting integral equation by the Wiener-Hopf method and proceeding to the VLD limit avoids an explicit quantum mechanical evolution equation. This conclusion may be drawn because the quantum TST (or in the context of Brownian motion the intermediate damping result with quantum corrections) whence the depopulation factor interpolates to the VLD regime follows from purely equilibrium considerations. In like manner, the quantum IHD rate (of which quantum TST is a particular case) may be obtained without explicit knowledge of an evolution equation as demonstrated by

Pollak [23,24] using the string-particle model. Mel'nikov's idea is also likely to be of use in obtaining the VLD result even if an explicit quantum Fokker-Planck equation in phase space is known due to the difficulty in transforming such an equation into energy/angle variables (when the diffusion coefficient becomes a function of the derivatives of the potential) in order to obtain an energy diffusion equation in the manner of Kramers. However, the *ad hoc* insertion of the parabolic barrier transmission factor requires rigorous justification. Following Mel'nikov and Meshkov [20], Grabert [25] and Pollak et al. [26] presented a complete solution of the classical Kramers turnover problem and have shown that the Mel'nikov and Meshkov universal formula can be obtained without their *ad hoc* interpolation between the weak and strong damping regimes. In the semiclassical limit, the latter theory was extended to the quantum regime by Rips and Pollak [27] where a review and comparison of the various approaches is given. We remark that comprehensive reviews of applications and developments of Kramers' reaction rate theory have been given by Hänggi et al. [28], Mel'nikov [11], Coffey et al. [17], and Pollak and Talkner [29]. These review articles provide one with a detailed theoretical description of reaction rate theory, a variety of examples of its application, relevant references, and even indicate future open problems to be tackled.

The classical Mel'nikov and Meshkov universal formula involving the depopulation factor provides an accurate approximation to the exact rate for all values of damping including the VHD, VLD, and the Kramers turnover regions as has been repeatedly verified theoretically (see, e.g., Refs. [30-36]). Furthermore, Coffey et al. [17,21] have extended the Mel'nikov method to the magnetization relaxation of single-domain ferromagnetic particles. (The magnetic relaxation differs fundamentally from that of mechanical Brownian particles because the undamped equation of motion of the magnetization of a single domain ferromagnetic particle is the gyromagnetic equation and the Hamiltonian is non separable. Thus the inertia plays no role; the part played by inertia in the mechanical system is essentially mimicked in the magnetic system by the gyromagnetic term causing the coupling or 'entanglement' of the transverse and longitudinal modes). The calculation of the longest relaxation time for various magnetocrystalline anisotropies has been accomplished in Refs. 37-40. We remark that in spite of very good overall agreement between numerical results and

the universal turnover formula a marked difference of order of 20% between numerical and analytical results in the VLD region at moderate barriers exists [30-33,36]. In order to improve the accuracy of the universal turnover formula in this region, Mel'nikov [41,42] suggested a systematic way of accounting for finite-barrier corrections. If such a correction is included, the accuracy of the universal formula is considerably improved (see, e.g., [43]). Thus, the classical Kramers turnover problem may be consider as solved despite of some open questions remaining to be clarified [29]. On the other hand in the quantum case, apart from comparisons using numerical simulations (see, e.g., Ref. [44-47]) which are essentially numerical, the quantum mechanical extensions of the Kramers theory and its various generalizations have not been verified due to the lack of a suitable master equation for the quantum Brownian motion in a potential.

II.IV Klein-Kramers equation: Representation of the master equation as partial differential relations in configuration space- Brinkman's method

In this section in view of its importance in the formulation of the quantum master equation we illustrate how the Klein-Kramers equation may be written as a partial differential recurrence relation in configuration space, which may be solved by continued fraction methods provided the form of the potential is specified.

The Klein-Kramers equation, i.e. Eq. (2.38) can be written in terms of the momentum p as (with $\beta = 1/kT$)

$$\frac{\partial f}{\partial t} + \frac{p}{m}\frac{\partial f}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial f}{\partial p} = \gamma \frac{\partial}{\partial p}\left[pf + \frac{m}{\beta}\frac{\partial f}{\partial p} \right]. \qquad (2.51)$$

In 1956 Brinkman [8] 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 $D_n(y)$ as

$$f(x,p,t) = e^{-\beta p^2/4m} \sum_{n=0}^{\infty} D_n\left(p\sqrt{\frac{\beta}{m}} \right) \varphi_n(x,t) \qquad (2.52)$$

where $\varphi_n(x,t)$ are configuration space distribution functions for $n \geq 0$. 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 [6]. In this section we proceed to calculate Brinkman's equations from the Klein-Kramers equation. In a later Chapter (VIII) we extend this calculation to the second order in perturbation theory in the square of Planck's constant.

First we recall that the harmonic oscillator functions $D_n(y)$ satisfy the recurrence relations [48]:

$$\begin{aligned} &D_{n+1}(y) - yD_n(y) + nD_{n-1}(y) = 0, \\ &\frac{dD_n(y)}{dy} + \frac{y}{2}D_n(y) - nD_{n-1}(y) = 0, \\ &\frac{dD_n(y)}{dy} - \frac{y}{2}D_n(y) + D_{n+1}(y) = 0, \end{aligned} \tag{2.53}$$

the differential equation

$$\frac{d^2D_n(y)}{dy^2} + \left(n + \frac{1}{2} - \frac{y^2}{4}\right)D_n(y) = 0, \tag{2.54}$$

and the orthogonality relation

$$\int_{-\infty}^{\infty} D_n(y)D_m(y)dy = n!\sqrt{2\pi}\delta_{m,n}, \tag{2.55}$$

where $\delta_{m,n}$ denotes Kronecker's delta. By substituting Eq. (2.52) into the classical Klein-Kramers equation, namely Eq. (2.51) , and using Eqs. (2.53)-(2.55), we have the following partial differential recurrence relation for the separation functions φ_n

$$\begin{aligned} &\frac{\partial \varphi_n}{\partial t} + n\gamma\varphi_n + \frac{1}{\sqrt{\beta m}}\left[\frac{\partial \varphi_{n-1}}{\partial x} + (n+1)\frac{\partial \varphi_{n+1}}{\partial x}\right] \\ &+\sqrt{\frac{\beta}{m}}\frac{\partial V}{\partial x}\varphi_{n-1} = 0. \end{aligned} \tag{2.56}$$

This set is now called Brinkman's hierarchy. Following Brinkman [8,49], on defining the following spatial differential operators

$$J = -\frac{1}{\gamma\sqrt{m\beta}}\left[\frac{\partial}{\partial x} + \beta\frac{\partial V(x)}{\partial x}\right], \qquad J_D = -\frac{1}{\gamma\sqrt{m\beta}}\frac{\partial}{\partial x}, \tag{2.57}$$

we find that the Brinkman hierarchy becomes the three term differential recurrence relation

$$\frac{1}{\gamma}\frac{\partial \varphi_n}{\partial t} + n\varphi_n = J\varphi_{n-1} + (n+1)J_D\varphi_{n+1}. \tag{2.58}$$

If we now take the Laplace transform over the time variables and suppose that the initial velocity distribution is Maxwellian so that $\varphi_n(x,0) = 0, \quad n > 0$, we find in the *s*-domain that Eq. (2.58) becomes the set

$$\begin{aligned} \frac{s}{\gamma}\tilde{\varphi}_0(x,s) - \frac{\varphi_0(x,0)}{\gamma} &= J_D\tilde{\varphi}_1(x,s), \\ (1+s/\gamma)\tilde{\varphi}_1(x,s) &= J\tilde{\varphi}_0(x,s) + 2J_D\tilde{\varphi}_2(x,s), \\ &\vdots \\ (n+s/\gamma)\tilde{\varphi}_n(x,s) &= J\tilde{\varphi}_{n-1}(x,s) + (n+1)J_D\tilde{\varphi}_{n-1}(x,s), \end{aligned} \tag{2.59}$$

where the tilde $\tilde{}$ denotes the Laplace transform. This set may then be solved by successive approximations to yield for the Laplace transform of the configuration space distribution

$$\begin{aligned} s\tilde{\varphi}_0(x,s) - \varphi_0(x,0) = &\frac{\gamma J_D J}{(1+s/\gamma)}\tilde{\varphi}_0(x,s) \\ &+ \frac{2\gamma J_D J_D JJ}{(2+s/\gamma)(1+s/\gamma)^2}\tilde{\varphi}_0(x,s) + \cdots. \end{aligned} \tag{2.60}$$

In the high dissipation limit, where $\gamma^{-1} \to 0$, only the leading term on the right hand side of Eq. (2.60) survives and we are left with (since $J_D J \sim O(\gamma^{-1})$)

$$s\tilde{\varphi}_0(x,s) - \varphi_0(x,0) = \gamma J_D J\tilde{\varphi}_0(x,s) \tag{2.61}$$

which on inversion to the time domain yields the Smoluchowski equation, i.e.,

$$\frac{\partial \varphi_0(x,t)}{\partial t} = \frac{kT}{\zeta}\frac{\partial}{\partial x}\left[\beta V'(x)\varphi_0 + \frac{\partial \varphi_0}{\partial x}\right] \tag{2.62}$$

($\zeta = \gamma m$). We note that Eq. (2.60) may also be formally arranged in the coordinate representation as the continued fraction of operators

$$s\tilde{\varphi}_0(x,s) - \varphi_0(x,0) = \cfrac{\gamma^2 J_D J}{s+\gamma - \cfrac{2\gamma^2 J_D J}{s+2\gamma - \cfrac{3\gamma^2 J_D J}{s+3\gamma - \cdots}}}\tilde{\varphi}_0(x,s). \tag{2.63}$$

This equation may also be written in a Heisenberg-like representation where postulating a suitable spatial basis and corresponding state vector, we may replace the spatial differential operators J_D and J by matrices (see for details [50]) so that Eq. (2.63) may be represented as a matrix continued fraction for the observables.

The matrix continued fraction approach is very convenient for the purpose of computation [1,6] and is easily extended to the quantum case [51-56].

APPENDIX II

Appendix II.I: How Wolynes' result may be derived using the harmonic version of quantal TST without using path integral methods

In this Appendix we partially rewrite a paper by Pollak [23] with derivations of the various equations of that paper. We use the notation of his paper. Let

$V^{\#}$=barrier height

$V(q)$=the potential

$\eta(t)$ = a time-dependent friction related to the zero-centered Gaussian random force $F_{ext}(t)$ by the fluctuation-dissipation relation, i.e.,

$$\left\langle F_{ext}(0) F_{ext}(t) \right\rangle = k_B T \eta(t). \tag{2.64}$$

The generalised Langevin equation is (for the classical particle)

$$M \frac{d^2 q}{dt^2} + \int_0^t \eta(t) \frac{dq(t-\tau)}{dt} d\tau + \frac{dV}{dq} = F_{ext}(t). \tag{2.65}$$

This equation may be derived from a Hamiltonian with a harmonic bath [57], i.e.

$$H = \frac{p_q^{\,2}}{2M} + V(q) + \sum_{j=1}^{N} \left\{ \frac{p_j^{\,2}}{2m_j} + \frac{1}{2} m_j \left[\omega_j x_j + \left(\frac{C_j}{m_j \omega_j} q \right) \right]^2 \right\}. \tag{2.66}$$

(See also [58].)Here (p_j, x_j) are the momenta and coordinates of the j^{th} bath oscillator whose mass and frequency are m_j and ω_j respectively. C_j couples the j^{th} bath oscillator to the system. By assuming that at time $t=0$, the bath is in thermal equilibrium, it can be shown [57] that $q(t)$ is exactly governed by Eq. (2.65) (and Eq. (2.64)) where the time-dependent friction $\eta(t)$ is

$$\eta(t) = \sum_{j=1}^{N} \frac{C_j^{\,2}}{m_j \omega_j^{\,2}} \cos(\omega_j t). \tag{2.67}$$

The spectral density of the bath $J(\omega)$ is defined as [58]

$$J(\omega) \equiv \frac{\pi}{2} \sum_{j=1}^{N} \frac{C_j^{\,2}}{m_j \omega_j} \delta(\omega - \omega_j). \tag{2.68}$$

The time-dependent friction (Eq. (2.67)) can be expressed in terms of the spectral density $J(\omega)$

$$\eta(t) = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \; d\omega. \tag{2.69}$$

To prove Eq. (2.69) we multiply Eq. (2.68) by

$$\frac{\cos \omega t}{\omega} d\omega \tag{2.70}$$

to get

$$\frac{J(\omega)}{\omega} \cos \omega t = \frac{\pi}{2} \sum_{j=1}^{N} \frac{C_j^{\,2}}{m_j \omega_j \omega} \cos \omega t \, \delta(\omega - \omega_j) \tag{2.71}$$

and integrate over all values of ω, i.e.

$$\int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \; d\omega = \frac{\pi}{2} \sum_{j=1}^{N} \frac{C_j^{\,2}}{m_j \omega_j} \int_{-\infty}^{\infty} \frac{\cos \omega t}{\omega} \delta(\omega - \omega_j) \; d\omega. \tag{2.72}$$

Using the sifting property of the delta function [59] namely

$$\int_{-\infty}^{\infty} f(t) \delta(t - a) \; dt = f(a) \tag{2.73}$$

gives us the result

$$\int_{-\infty}^{\infty} \frac{\cos \omega t}{\omega} \delta(\omega - \omega_j) \; d\omega = \frac{\cos \omega_j t}{\omega_j} \tag{2.74}$$

and from which

$$\int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \; d\omega = \frac{\pi}{2} \sum_{j=1}^{N} \frac{C_j^{\,2}}{m_j \omega_j} \cos \omega_j t \tag{2.75}$$

and therefore

$$\begin{aligned} \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \; d\omega &= \sum_{j=1}^{N} \frac{C_j^{\,2}}{m_j \omega_j} \cos \omega_j t \\ &= \eta(t). \end{aligned} \tag{2.76}$$

Once again,

$$\eta(t) = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \; d\omega.$$

"*With this notation it is possible to obtain the continuum limit for the dynamics by defining* $J(\omega)$ *as a continuous function instead of defining each* C_j *separately*" [23].

We take the Laplace transform of $\eta(t)$, i.e.

$$\mathcal{L}(\eta(t)) = \tilde{\eta}(s) = \int_0^\infty e^{-st}\eta(t)\, dt \tag{2.77}$$

which on inserting Eq. (2.69)

$$\begin{aligned}\tilde{\eta}(s) &= \frac{2}{\pi}\int_0^\infty e^{-st}\int_{-\infty}^{\infty}\frac{J(\omega)}{\omega}\cos\omega t\; d\omega\, dt \\ &= \frac{2}{\pi}\int_0^\infty\int_{-\infty}^{\infty} e^{-st}\,\frac{J(\omega)}{\omega}\cos\omega t\; d\omega\, dt.\end{aligned} \tag{2.78}$$

Now we change the order of integration and integrate with respect to *t* first

$$\begin{aligned}\tilde{\eta}(s) &= \frac{2}{\pi}\int_{-\infty}^{\infty}\int_0^\infty e^{-st}\,\frac{J(\omega)}{\omega}\cos\omega t\; dt\, d\omega \\ &= \frac{2}{\pi}\int_{-\infty}^{\infty}\frac{J(\omega)}{\omega}\left[\int_0^\infty e^{-st}\cos\omega t\; dt\right] d\omega.\end{aligned} \tag{2.79}$$

The integral (in Eq. (2.79)) is the Laplace transform of $\cos\omega t$ the result of which can be found from tables and is

$$\begin{aligned}\int_0^\infty e^{-st}\cos\omega t\; dt &\equiv \mathcal{L}(\cos\omega t) \\ &= \frac{s}{s^2+\omega^2}.\end{aligned} \tag{2.80}$$

We can also solve this integral by remembering that $\cos\omega t = \frac{1}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)$ and carrying out the integrations. Now we have

$$\tilde{\eta}(s) = \frac{2}{\pi}\int_{-\infty}^{\infty}\frac{J(\omega)}{\omega}\left(\frac{s}{s^2+\omega^2}\right) d\omega. \tag{2.81}$$

Equation (2.81) may also be written (using Eq. (2.67) and getting its Laplace transform with the result of Eq. (2.80)) as

$$\tilde{\eta}(s) = \sum_{j=1}^{N}\frac{C_j^{\,2}}{m_j\omega_j^{\,2}}\left(\frac{s}{s^2+\omega_j^{\,2}}\right). \tag{2.82}$$

We wish to calculate the quantal rate and do so by using the following methodology, namely the Hamiltonian given in Eq. (2.66) may be treated as a

quantal Hamiltonian. For a finite discrete set of oscillators one may evaluate the quantal thermal decay rate using harmonic quantum transition state theory (TST). After obtaining the TST expression one may take the continuum limit, to obtain an estimate for the quantal decay rate of a particle governed by the generalised Langevin equation.

To implement this, we must evaluate quantal partition functions at the well (q=0) and the barrier (q=$q_{\#}$). The partition functions may be evaluated via a normal mode analysis at the barrier and the well. To prepare the ground for the derivation of the rate expression we undertake the normal mode analysis. We assume that the potential may be approximated as

$$V(q) \approx \frac{1}{2} M \omega_0^{\,2} q^2 \tag{2.83}$$

in the vicinity of the well and as

$$V(q) \approx V^{\#} - \frac{1}{2} M \omega_{\#}^{\,2} (q - q_{\#})^2 \tag{2.84}$$

at the barrier. Here ω_0 is the frequency at the well and $\omega_{\#}$ is the imaginary frequency at the barrier. The harmonic approximations given in Eqs. (2.83) and (2.84) implies that the Hamiltonian in the vicinity of the well and barrier may be written in separable form as a sum of $N+1$ harmonic oscillators. This is achieved [60] by first transforming to mass-weighted coordinates

$$\begin{aligned} q' &= M^{1/2} q \\ x_j' &= m_j^{1/2} x_j \end{aligned} \tag{2.85}$$

and then diagonalizing the $(N+1)\times(N+1)$ force constant matrix defined by the second derivatives of the potential at the well and the barrier.

The Hamiltonian Eq. (2.66) with Eq. (2.83) becomes

$$\begin{aligned} H &= \frac{p_q^{\,2}}{2M} + V(q) + \sum_{j=1}^{N} \left\{ \frac{p_j^{\,2}}{2m_j} + \frac{1}{2} m_j \left[\omega_j x_j + \left(\frac{C_j}{m_j \omega_j} q \right) \right]^2 \right\} \\ &= \frac{p_q^{\,2}}{2M} + \frac{1}{2} M \omega_0^{\,2} q^2 + \sum_{j=1}^{N} \left\{ \frac{p_j^{\,2}}{2m_j} + \frac{1}{2} \left[m_j^{1/2} \omega_j x_j + \left(\frac{C_j m_j^{1/2}}{m_j \omega_j} q \right) \right]^2 \right\} \end{aligned} \tag{2.86}$$

and with Eq. (2.85) it is now

$$H = \frac{p_q^{\,2}}{2M} + \frac{1}{2}\omega_0^{\,2} q'^2 + \sum_{j=1}^{N} \left\{ \frac{p_j^{\,2}}{2m_j} + \frac{1}{2}\left[x_j'\omega_j + \left(\frac{C_j}{m_j^{1/2}\omega_j} \times \frac{q'}{M^{1/2}} \right) \right]^2 \right\} . \quad (2.87)$$

From this equation and Eq. (2.83) it is clear that the well is located at $q' = x_j' = 0$; j=1,…,N. Derivatives of H are:

$$\frac{\partial H}{\partial q'} = \omega_0^{\,2} q' + \sum_{j=1}^{N} \frac{C_j}{M^{1/2} m_j^{1/2} \omega_j} \left[x_j'\omega_j + \frac{C_j}{M^{1/2} m_j^{1/2} \omega_j} q' \right] \quad (2.88)$$

$$\frac{\partial^2 H}{\partial q'^2} = \omega_0^{\,2} + \sum_{j=1}^{N} \frac{C_j^{\,2}}{M m_j \omega_j^{\,2}} = k_{00} \quad (2.89)$$

$$\frac{\partial H}{\partial x_j'} = x_j'\omega_j^{\,2} + \frac{C_j}{M^{1/2} m_j^{1/2}} q' \quad (2.90)$$

$$\frac{\partial^2 H}{\partial x_j'^2} = \omega_j^{\,2} = k_{ii}, i = \quad (2.91)$$

and

$$\frac{\partial^2 H}{\partial x_j' \partial q'} = \frac{C_j}{M^{1/2} m_j^{1/2}} = k_{0i} = k_{i0}, i = 1, 2, ..., N . \quad (2.92)$$

The second-derivative matrix of the potential (with respect to the mass-weighted coordinates) at the well is denoted by $\underset{\sim}{K}$ and has the following structure

$$\underset{\sim}{K} = \begin{pmatrix} k_{00} & \cdots & k_{0N} \\ \vdots & \ddots & \vdots \\ k_{N0} & \cdots & k_{NN} \end{pmatrix} \quad (2.93)$$

where

$$\begin{aligned} k_{00} &= \omega_0^{\,2} + \sum_{j=1}^{N} \frac{C_j^{\,2}}{M m_j \omega_j^{\,2}} \\ k_{0i} &= k_{i0} = \frac{C_i^{\,2}}{M m_i \omega_i^{\,2}}, \; i = 0, 1, 2, ..., N \\ k_{i,j} &= 0, \; i \neq j, \; i, j = 1, 2, ..., N \end{aligned} \quad (2.94)$$

i.e.

$$\underset{\sim}{K} = \begin{pmatrix} \omega_0^2 + \sum_{j=1}^{N} \frac{C_j^2}{M m_j \omega_j^2} & \frac{C_1}{M^{1/2} m_1^{1/2}} & \frac{C_2}{M^{1/2} m_2^{1/2}} & \cdots & \frac{C_N}{M^{1/2} m_N^{1/2}} \\ \frac{C_1}{M^{1/2} m_1^{1/2}} & \omega_1^2 & 0 & \cdots & 0 \\ \frac{C_2}{M^{1/2} m_2^{1/2}} & 0 & \omega_2^2 & \cdots & 0 \\ \vdots & & & & \\ \frac{C_N}{M^{1/2} m_N^{1/2}} & 0 & 0 & \cdots & \omega_N^2 \end{pmatrix}.$$

(2.95)

We have $(N+1)$ equations and the $(N+1)$ eigenvalues of $\underset{\sim}{K}$ are denoted by λ_i^2; $i = 0,1,...,N$. The λ_i are the normal mode frequencies at the well.

(Now [61] for a general matrix $\underset{\sim}{A}$ the eigenvalue problem $\underset{\sim}{A}\underset{\sim}{x} = \lambda \underset{\sim}{x}$ which is for $\underset{\sim}{x} \neq \underset{\sim}{0}$, $(\underset{\sim}{A} - \lambda \underset{\sim}{I})\underset{\sim}{x} = \underset{\sim}{0}$. $\underset{\sim}{A} - \lambda \underset{\sim}{I}$ is singular if and only if its determinant $\det(\underset{\sim}{A} - \lambda \underset{\sim}{I})$ called the characteristic determinant of $\underset{\sim}{A}$ is zero. The resulting polynomial equation in λ is called the characteristic or secular equation of $\underset{\sim}{A}$ and its solutions are the eigenvalues $\lambda_1, \lambda_2, ..., \lambda_n$ of $\underset{\sim}{A}$.)

The secular equation for $\underset{\sim}{K}$ is

$$\left| \underset{\sim}{K} - \lambda^2 \underset{\sim}{I} \right| = 0$$

$$= \begin{vmatrix} \omega_0^2 - \lambda^2 + \sum_{j=1}^{N} \frac{C_j^2}{M m_j \omega_j^2} & \frac{C_1}{M^{1/2} m_1^{1/2}} & \frac{C_2}{M^{1/2} m_2^{1/2}} & \cdots & \frac{C_N}{M^{1/2} m_N^{1/2}} \\ \frac{C_1}{M^{1/2} m_1^{1/2}} & \omega_1^2 - \lambda^2 & 0 & \cdots & 0 \\ \frac{C_2}{M^{1/2} m_2^{1/2}} & 0 & \omega_2^2 - \lambda^2 & \cdots & 0 \\ \vdots & & & & \\ \frac{C_N}{M^{1/2} m_N^{1/2}} & 0 & 0 & \cdots & \omega_N^2 - \lambda^2 \end{vmatrix}.$$

(2.96)

This is a difficult determinant to work out. However we can rewrite this by carrying out elementary row operations and arrive at our new determinant say $\det\left(\underset{\sim}{L}\right)$ i.e.

$$\left|\underset{\sim}{L}\right| = \begin{vmatrix} \omega_0^2 - \lambda^2 + \sum_{j=1}^{N} \frac{C_j^2}{Mm_j\omega_j^2} - \sum_{j=1}^{N} \frac{C_j^2}{Mm_j\left(\omega_j^2 - \lambda^2\right)} & \frac{C_1}{M^{1/2}m_1^{1/2}} & \frac{C_2}{M^{1/2}m_2^{1/2}} & \cdots & \frac{C_N}{M^{1/2}m_N^{1/2}} \\ 0 & \omega_1^2 - \lambda^2 & 0 & \cdots & 0 \\ 0 & 0 & \omega_2^2 - \lambda^2 & \cdots & 0 \\ \vdots & & & & \\ 0 & 0 & 0 & \cdots & \omega_N^2 - \lambda^2 \end{vmatrix} \tag{2.97}$$

and from the theory of determinants, that the determinant of a real symmetric matrix is given by the products of the eigenvalues

$$\det\left(\underset{\sim}{L}\right) = \det\left(\underset{\sim}{K} - \lambda^2 \underset{\sim}{I}\right) \tag{2.98}$$

i.e.

$$\begin{aligned} \det\left(\underset{\sim}{L}\right) = &\left\{ \omega_0^2 - \lambda^2 + \sum_{j=1}^{N} \frac{C_j^2}{Mm_j\omega_j^2} - \sum_{j=1}^{N} \frac{C_j^2}{Mm_j\left(\omega_j^2 - \lambda^2\right)} \right\} \\ &\times \prod_{j=1}^{N} \left(\omega_j^2 - \lambda^2\right). \end{aligned} \tag{2.99}$$

Tidying up the term in the curly brackets of Eq. (2.99) we have

$$\det\left(\underset{\sim}{L}\right) = \left\{ \omega_0^2 - \lambda^2 \left[1 + \sum_{j=1}^{N} \frac{C_j^2}{Mm_j\omega_j^2\left(\omega_j^2 - \lambda^2\right)} \right] \right\} \prod_{j=1}^{N} \left(\omega_j^2 - \lambda^2\right). \tag{2.100}$$

Now

$$\begin{aligned} \det\left(\underset{\sim}{L}\right) &= \det\left(\underset{\sim}{K} - \lambda^2 \underset{\sim}{I}\right) \\ &= 0 \end{aligned} \tag{2.101}$$

implies that

$$\left\{ \omega_0^2 - \lambda^2 \left[1 + \sum_{j=1}^{N} \frac{C_j^2}{Mm_j\omega_j^2\left(\omega_j^2 - \lambda^2\right)} \right] \right\} = 0 \tag{2.102}$$

or

$$\prod_{j=1}^{N}\left(\omega_j^{\,2}-\lambda^2\right)=0\,. \tag{2.103}$$

The solutions of Eq. (2.103) are simply

$$\lambda^2=\omega_j^{\,2},\ \ j=1,2,...,N\,. \tag{2.104}$$

Let $\lambda_0^{\,2}$ be a solution of Eq. (2.102) i.e. $\lambda^2=\lambda_0^{\,2}$.

Now,

$$\det\left(\underset{\sim}{K}-\lambda^2\underset{\sim}{I}\right)=\left(\lambda_0^{\,2}-\lambda^2\right)\prod_{j=1}^{N}\left(\omega_j^{\,2}-\lambda^2\right) \tag{2.105}$$

and let $\lambda^2=-s^2$ so Eq. (2.105) is

$$\det\left(\underset{\sim}{K}-s^2\underset{\sim}{I}\right)=\left(\lambda_0^{\,2}-s^2\right)\prod_{j=1}^{N}\left(\omega_j^{\,2}-s^2\right). \tag{2.106}$$

This is the first part of Pollak's Eq. (13) [23]

Now Eq. (2.82) viz,

$$\tilde{\eta}(s)=\sum_{j=1}^{N}\frac{C_j^{\,2}}{m_j\omega_j^{\,2}}\left(\frac{s}{s^2+\omega_j^{\,2}}\right) \tag{2.107}$$

from which we can write

$$\omega_0^{\,2}+s^2+\left(\frac{s}{M}\right)\tilde{\eta}(s)=\omega_0^{\,2}+s^2\left[1+\sum_{j=1}^{N}\frac{C_j^{\,2}}{Mm_j\omega_j^{\,2}\left(\omega_j^{\,2}+s^2\right)}\right]. \tag{2.108}$$

The right hand side of Eq. (2.108) is the leading entry in $\underset{\sim}{L}$ with λ^2 replaced by $-s^2$. Therefore we can replace the leading term in $\underset{\sim}{L}$ by the left hand side of Eq. (2.108). Since $\det\left(\underset{\sim}{K}\right)=\lambda_1^{\,2}\lambda_2^{\,2}...\lambda_N^{\,2}$.and this is equivalent to determinant whose diagonal elements are $\lambda_1^{\,2},\lambda_2^{\,2},...,\lambda_N^{\,2}$. And so it follows that

$$\begin{aligned}\det\left(\underset{\sim}{K}+s^2\underset{\sim}{I}\right)&=\left(\lambda_0^{\,2}+s^2\right)\left(\lambda_1^{\,2}+s^2\right)\cdots\left(\lambda_N^{\,2}+s^2\right)\\&=\left(\lambda_0^{\,2}+s^2\right)\prod_{j=1}^{N}\left(\lambda_j^{\,2}+s^2\right)\end{aligned} \tag{2.109}$$

Quantal transition state theory:

The transition state theory expression for the rate of decay Γ is well known [62]:

$$\Gamma(T)=\left(\frac{k_BT}{h}\right)\frac{Z^{\#}}{Z^0}\,. \tag{2.110}$$

Here h is Planck's constant and $Z^{\#}$ and Z^{0} are the partition functions at the transition state and at reactants. At the transition state we have N real oscillators with frequencies $\lambda_j^{\#}; j=1,...,N$ and one imaginary frequency oscillator with imaginary frequency $\lambda_0^{\#}$. Therefore the quantal partition function is ($\beta=\left(k_B T\right)^{-1}$)

$$Z^{\#}=\frac{\frac{1}{2}\hbar\beta\lambda_0^{\#}}{\sin\left(\frac{1}{2}\hbar\beta\lambda_0^{\#}\right)}e^{-\beta V^{\#}}\prod_{j=1}^{N}\frac{1}{2\sinh\left(\frac{1}{2}\hbar\beta\lambda_j^{\#}\right)}. \qquad (2.111)$$

Note the well known divergence of $Z^{\#}$ at low temperatures [23]. The quantal partition function at the well is

$$Z^{0}=\frac{1}{2\sinh\left(\frac{1}{2}\hbar\beta\lambda_0\right)}e^{-\beta V^{0}}\prod_{j=1}^{N}\frac{1}{2\sinh\left(\frac{1}{2}\hbar\beta\lambda_j\right)}. \qquad (2.112)$$

Therefore the thermal decay rate, i.e. Eq. (2.110) becomes (on putting in Eqs. (2.111) and (2.112))

$$\begin{aligned}\Gamma(T)&=\frac{1}{h\beta}\times\frac{Z^{\#}}{Z^{0}}\\&=\frac{1}{h\beta}\times\frac{\frac{1}{2}\hbar\beta\lambda_0^{\#}}{\sin\left(\frac{1}{2}\hbar\beta\lambda_0^{\#}\right)}e^{-\beta V^{\#}}\prod_{j=1}^{N}\frac{1}{2\sinh\left(\frac{1}{2}\hbar\beta\lambda_j^{\#}\right)}\\&\quad\times 2\sinh\left(\frac{1}{2}\hbar\beta\lambda_0\right)e^{+\beta V^{0}}\prod_{j=1}^{N}2\sinh\left(\frac{1}{2}\hbar\beta\lambda_j\right).\end{aligned} \qquad (2.113)$$

We can write this as

$$\Gamma(T)=\left(\frac{\omega_0}{2\pi}\right)\times\left(\frac{\lambda_0^{\#}}{\omega_{\#}}\right)e^{-\beta V^{\#}}\rho \qquad (2.114)$$

where

$$\rho=\left(\frac{\omega_{\#}}{\omega_0}\right)\frac{\sinh\left(\frac{1}{2}\hbar\beta\lambda_0\right)}{\sin\left(\frac{1}{2}\hbar\beta\lambda_0^{\#}\right)}\prod_{j=1}^{N}\frac{\sinh\left(\frac{1}{2}\hbar\beta\lambda_j\right)}{\sinh\left(\frac{1}{2}\hbar\beta\lambda_j^{\#}\right)}. \qquad (2.115)$$

For very high temperatures, i.e. T –large which also implies β is small we use the following approximations: $\sinh x\approx x$ and $\sin x\approx x$ for x small. Therefore

$$\rho\approx\left(\frac{\omega_{\#}}{\omega_0}\right)\left(\frac{\lambda_0}{\lambda_0^{\#}}\right)\prod_{j=1}^{N}\frac{\lambda_j}{\lambda_j^{\#}}. \qquad (2.116)$$

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CHAPTER III

The density matrix

III.I Introduction

In classical statistical mechanics a statistical ensemble is represented by a distribution function in the phase space of the canonical variables describing the system. In quantum mechanics such a distribution function is replaced by a (statistical) density matrix denoted by ρ hereafter. The statistical density matrix was originally introduced by von Neumann in order to treat systems where there is a statistical element to the physics other than that which arises directly from quantum mechanics (where *each* particle presents a *range* of possible states unlike classical mechanics), e.g. the ensemble just mentioned whose *constituent members* (i.e. each particle) are distributed over a range of possible states. Before embarking on a general discussion of the density matrix we shall illustrate the basic concepts by considering the probability density for a *pure state*, i.e. one described by a wave function $\psi(x)$, where the quantum mechanical probability (for which there is no classical analogy) that the particle may be found between x and $x+dx$ is given by

$$\begin{aligned} P(x) &= \rho dx \\ &= \psi(x)\psi^*(x)dx. \end{aligned} \tag{3.1}$$

In the language of ensembles [1] an ensemble in a *pure state* (i.e. a state common to all members to the ensemble) can be regarded as representing an *individual* system whose exact quantum mechanical state is known. On the other hand an ensemble in an appropriate *mixed state* can be regarded as representing a system whose complete possible quantum specification is not known.

In Dirac notation the configuration space probability amplitude and its conjugate are written

$$\psi(x) = \langle x|\psi\rangle \tag{3.2}$$

and

$$\psi^*(x) = \langle \psi | x \rangle \tag{3.3}$$

so that

$$\psi(x)\psi^*(x) = \langle x | \psi \rangle \langle \psi | x \rangle = \rho(x). \tag{3.4}$$

The ket-bra operator in the middle of Eq. (3.4) is called the *density operator*

$$\hat{\rho} = |\psi\rangle\langle\psi| \tag{3.5}$$

and the position space diagonal matrix element of the operator is

$$\rho(x) = \langle x | \hat{\rho} | x \rangle \tag{3.6}$$

where $|x\rangle$ is an eigenket of the position operator $\hat{x}$.

The most didactic way of presenting the density matrix is to consider a particle in a one-dimensional box in the ground state. Here

$$\rho(x) = \frac{2}{L}\sin^2\frac{\pi x}{L} \tag{3.7}$$

by elementary quantum mechanics. In general, expressions such as Eqs. (3.1) and (3.7) may be thought of as the diagonal matrix elements of a more generalised density operator,

$$\rho(x, x') = \langle x | \hat{\rho} | x' \rangle \tag{3.8}$$

where x and x' may be thought of as continuous labels on the rows and columns of the density matrix. (A detailed explanation of the Dirac notation used in Eq. (3.8) is given at the end of Section III.IV below). For example, for an electron in the ground state of a box of length *L*, the x and x' matrix element of the density operator in position space representation is given by [2]

$$\rho(x, x') = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\sqrt{\frac{2}{L}}\sin\frac{\pi x'}{L} \tag{3.9}$$

and one may verify that the time evolution of the matrix element $\rho(x, x')$ for a particle moving in a one dimensional potential, e.g. a box of length *L*, $V(x)$ is in general in the position space representation given by [3]

$$\frac{d\langle x|\hat{\rho}|x'\rangle}{dt} = \left\{\frac{i\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x'^2}\right) - \frac{i}{\hbar}\left(V(x) - V(x')\right)\right\} \times \langle x|\hat{\rho}|x'\rangle \tag{3.10}$$

Clearly Eq. (3.9) is a steady state solution of Eq. (3.10).

According to Tolman [1] the example we have taken is a system of which we have *maximal* knowledge in so far as is allowed by quantum mechanics. Thus the system at any time of interest will be in a perfectly definite quantum state so that it may be represented by an ensemble in a pure state *each* member of the ensemble being in the *same* state as the system itself. The only uncertainties as to its properties and the only needs for taking averages will arise because of the *inherently statistical character of the quantum mechanics itself for which there is no classical analogy*. On the other hand if our knowledge of the system is less than maximal so that we represent it by an ensemble in a mixed state then the system itself might be in one of the various quantum mechanical states represented in the ensemble. Hence further uncertainties and needs for taking averages will be present of the *same kind* as encountered in the classical mechanics due to the distribution over the different states.

In order to crystallize these ideas we note (see later on in this Chapter) that for a mixed state comprising a statistical mixture [2] the density operator can be written in terms of a linear combination of density operators for a set of N eigenstates so that the x, x' matrix element of that operator is in the position representation

$$\begin{aligned} \rho(x,x') &= \langle x|\hat{\rho}|x'\rangle \\ &= \sum_{j=1}^{N} w_j \psi_j^*(x)\psi_j(x') \end{aligned} \tag{3.11}$$

where the weights w_j (characterising the distribution over the states and corresponding to the usual averaging process over the ensemble in the classical statistical mechanics) occurring in the linear combination are non negative $w_j \geq 0$ and

$$\sum_{j=1}^{N} w_j = 1 \tag{3.12}$$

which follows from the fact that ρ must be normalised. Here the density operator is

$$\begin{aligned} \hat{\rho} &= \sum_{j=1}^{N} w_j |\psi_j\rangle\langle\psi_j| \\ &= \sum_{j=1}^{N} w_j \hat{\rho}_j . \end{aligned} \tag{3.13}$$

A useful example is that given by Wyatt [2] namely the density matrix elements in position space representation for a Boltzmann (thermal) distribution at temperature T over the particle-in-a-box energy eigenstates N namely

$$\rho(x,x') = \sum_{j=1}^{N} \frac{e^{-E_j/k_B T}}{Z(T)} \sqrt{\frac{2}{L}} \sin\frac{j\pi x}{L} \sqrt{\frac{2}{L}} \sin\frac{j\pi x'}{L} \qquad (3.14)$$

in which $Z(T)$ is the partition function. For this mixed state, the probability density would be the diagonal element viz

$$\rho(x) = \sum_{j=1}^{N} \frac{e^{-E_j/k_B T}}{Z(T)} \frac{2}{L} \sin^2\frac{j\pi x}{L} \qquad (3.15)$$

Integrating this expression over the length of the box and noting the definition of the partition function namely

$$Z(T) = \sum_{j=1}^{N} e^{-E_j/k_B T} \qquad (3.16)$$

shows that ρ is normalised to unity. This corresponds in the operator representation to requiring that

$$\mathrm{Tr}\,\hat{\rho} = 1. \qquad (3.17)$$

Yet another example [4] is the Hamiltonian operator for a uniaxial paramagnet of arbitrary spin value S in a *constant* field $\mathbf{H}_0$ superimposed on a uniaxial anisotropy field which is

$$\beta\hat{H}_S = -\xi\hat{S}_Z - \sigma\hat{S}_Z^2. \qquad (3.18)$$

where $\hat{S}_Z$ is the Z-component of the spin operator $\hat{\mathbf{S}}$, σ and ξ are the dimensionless internal and external field parameters respectively. The equilibrium spin density matrix $\hat{\rho}$ is given by

$$\hat{\rho} = e^{-\beta\hat{H}_S}/Z_S\,, \qquad (3.19)$$

where $Z_S = \mathrm{Tr}\{e^{-\beta\hat{H}_S}\}$ is the partition function. Here the matrix elements $\rho_{m,m'}$ of the equilibrium spin density matrix $\hat{\rho} = e^{-\beta\hat{H}_S}/Z_S$ are

$$\rho_{m,m'} = \delta_{m,m'}\, e^{\sigma m^2 + \xi m}/Z_S\,, \qquad (3.20)$$

where the partition function Z_S is given by the finite sum $Z_S = \sum_{m=-S}^{S} e^{\sigma m^2 + \xi m}$. In general the coordinate representation of the density operator does not lend itself as easily to the calculation of quantum corrections to classical distribution functions

as the phase space representation pioneered by Wigner [5], which is discussed in Chapter IV.

III.II Systems in a pure state

In this section we will follow closely the treatment of Tolman [1] (1938) and consider a system of *f* degrees of freedom specified by coordinates $q_1 ... q_f$ which collectively we denote by *q* and we suppose that the system is in a pure state for the time being. Let us now consider the function

$$u(q) = \psi(q, t_0) \tag{3.21}$$

This is called the probability amplitude and pertains to a fixed time t_0. We can express Eq. (3.21) using generalized Fourier series as a linear combination of the eigenfunctions $u_k(q)$ which describe states characteristic of some selected observables viz

$$\psi(q, t_0) = \sum_k c_k u_k(q) \tag{3.22}$$

where the c_k are the Fourier coefficients. If we want to change to a continuous time we simply write Eq. (3.22) as

$$\psi(q, t) = \sum_k a_k(t) u_k(q) . \tag{3.23}$$

Hence by orthogonality the Fourier coefficients are given by the integral over the collection of coordinates

$$\int \psi(q, t) u_n^*(q) dq = a_n(t) . \tag{3.24}$$

A case of frequent interest is in terms of the eigenfunctions corresponding to the eigenvalues E_n of the energy. We have for an isolated system the Schrödinger equation

$$H\psi + \frac{\hbar}{i}\frac{\partial \psi}{\partial t} = 0 \tag{3.25}$$

so that with Eq. (3.23)

$$\begin{gathered} \sum_k \left[H + \frac{\hbar}{i}\frac{\partial}{\partial t} \right] a_k(t) u_k(q) = 0 \\ \sum_k \left[H a_k u_k(q) + \frac{\hbar}{i} u_k(q) \frac{da_k(t)}{dt} \right] = 0. \end{gathered} \tag{3.26}$$

For an isolated system

$$Hu_k(q) = E_k \tag{3.27}$$

because H is time independent. Hence by the orthogonality properties of the $u_k(q)$ we have that

$$a_n(t)E_n + \frac{\hbar}{i}\frac{da_n}{dt} = 0\,, \tag{3.28}$$

with solution

$$a_n(t) = c_n e^{-\frac{i}{\hbar}E_n t} \tag{3.29}$$

implying

$$\psi(q,t) = \sum_k c_k u_k e^{-\frac{i}{\hbar}E_k t}\,. \tag{3.30}$$

We may write this in more familiar Fourier like form as

$$a_k(t) = \int u_k^*(q)\psi(q,t)dq\,, \tag{3.31}$$

$$\psi(q,t) = \sum_k a_k(t)u_k(q)\,. \tag{3.32}$$

Thus the system can be specified at time t either in coordinate language by $\psi(q,t)$ or in Fourier coefficient language $a_k(t)$. Hence in the manner of Born the quantum mechanical probability of finding an individual system described by Eq. (3.32) in the characteristic state corresponding to the eigenfunction $u_n(q)$ is

$$W_n(t) = a_n^*(t)a_n(t)\,. \tag{3.33}$$

Since the system is in a pure state this expression is typical of each constituent of the ensemble. Equation (3.33) is then a Fourier representation of the quantum mechanical probability. The case where n is not necessarily equal to m can be used to define the density matrix in the Fourier representation, as we shall see shortly. We justify Eq. (3.33) as follows. We have

$$\psi\psi^* = \sum_{k,l} a_l^* a_k u_k u_l^* e^{\frac{i}{\hbar}(E_l - E_k)t}\,. \tag{3.34}$$

Now

$$\int \psi\psi^* dq = 1 \tag{3.35}$$

implies

$$\sum_l a_l^* a_l = 1 \tag{3.36}$$

or

$$\sum_l W_l = 1 . \tag{3.37}$$

Thus

$$a_l^* a_l = W_l . \tag{3.38}$$

Hence we see that W_l represents a probability arising because of a *spread in the predictions* associated with the specification of a *single* quantum mechanical state.

III.III Systems in a mixed state

We saw that in the classical statistical mechanics we represent the state of a system of *f* degrees of freedom by the position of a point in a *qp*-phase space of 2*f* dimensions, and then represent an ensemble of such systems by a 'cloud' of phase points distributed with the *density* ρ. Assuming that this density has been normalised to unity, so that we have

$$\int_\Omega \rho dq dp = 1 \tag{3.39}$$

with

$$\begin{aligned} dq &= dq_1 ... dq_f \\ dp &= dp_1 ... dp_f \end{aligned} \tag{3.40}$$

we can then calculate the mean value – for the systems in the ensemble – of any function *F(q,p)* of the coordinates and momenta with the help of the equation

$$\langle F \rangle = \int_\Omega F(q,p) dq dp . \tag{3.41}$$

Now [1] the *density matrix* with components $\rho_{n,m}$ introduced by von Neumann [6] in the quantum mechanics plays a role somewhat similar to that of the density ρ in the classical mechanics. Since the specific expression of this matrix will depend on the *particular language* or *quantum mechanical representation*, which is being used, it will be desirable to use the generalised Fourier coefficient language we have introduced above in defining the matrix. Thus let us regard the state of *each constituent system*, in an ensemble of *similar non-interacting* quantum mechanical systems, as represented by a *generalised probability amplitude* $a_n(t)$ so that

$$\psi(q,t) = \sum_k a_k(t) u_k(q) \tag{3.42}$$

where the $u(k,q)$ are any desired complete set of orthogonal, normalised eigenfunctions. Using the general $a_k(t)$ language, *the density matrix* can then be defined by its *component elements*

$$\rho_{n,m} = \frac{1}{N}\sum_{\alpha=1}^{N} a_{m\ (\alpha)}^{\ *}(t)a_{n\ (\alpha)}(t) = \left\langle\left\langle a_m^* a_n \right\rangle\right\rangle, \tag{3.43}$$

where we take a mean of the products $a_m^*(t)a_n(t)$ for all the systems of the ensemble α =1,2,…,*N,* and the order of the indices for $\rho_{n,m}$ has been chosen to agree with the convention usually made in this connection.

Since $W_n = a_n^* a_n$,

then

$$\begin{aligned} P_n = \rho_{n,n} &= \left\langle\left\langle W_n \right\rangle\right\rangle \\ &= \left\langle\left\langle a_n^* a_n \right\rangle\right\rangle. \end{aligned} \tag{3.44}$$

This is an expression for the probability that a system chosen at random from the ensemble would be found in the state *n*.

We may summarize by saying that in general the double brace will correspond to taking a mean *first over the range of possibilities presented by each member of the ensemble* (quantum mechanical average) and then *over the members of the ensemble* (ensemble average). Thus recalling that *F* must now be regarded as a quantum operator that

$$\left\langle F(q,p)\right\rangle \equiv \left\langle \hat{F} \right\rangle = \int \psi^*(q,t)\, F(q, \frac{\hbar}{i}\frac{\partial}{\partial q})\psi(q,t)dq \tag{3.45}$$

would denote the mean value of the observable *F* for a system in the quantum mechanical state ψ and

$$\left\langle\left\langle F \right\rangle\right\rangle = \frac{1}{N}\sum_{\alpha=1}^{N}\left\langle F_{(\alpha)} \right\rangle \tag{3.46}$$

would denote the mean value of that observable for the *N* systems α =1,2,…,*N* of an ensemble. We shall use the double bar, however, in the precise sense of denoting a mean for the members of an ensemble without reference to the necessity or not for first taking a mean for each member.

III.IV Mean values in terms of the density operator

Since $W_n = a_n^* a_n$ would give the probability of finding an individual system described by Eq. (3.32) in the characteristic state corresponding to the eigenfunction $u_n(q)$ we saw that

$$\begin{aligned} P_n = \rho_{n,n} &= \langle\langle W_n \rangle\rangle \\ &= \langle\langle a_n^* a_n \rangle\rangle \end{aligned} \tag{3.47}$$

is the probability that a system chosen at random from the ensemble would be found in the state *n*, so that summing the individual probabilities

$$\begin{aligned} \sum_k P_k &= \sum_k \rho_{k,k} \\ &= \sum_k \langle\langle W_k \rangle\rangle \\ &= \sum_k \langle\langle a_k^* a_k \rangle\rangle \\ &= 1. \end{aligned} \tag{3.48}$$

The sum of the diagonal elements of the $\rho_{k,l}$ is simply the trace of the matrix $\hat{\rho}$ generated by the $\rho_{k,l}$. Thus the classical normalization given by Eq. (3.39) is replaced by

$$\text{Tr}\ \hat{\rho} = 1 \tag{3.49}$$

We now consider the mean value of an observable. We have

$$\begin{aligned} \langle \hat{F} \rangle &= \int \psi^*(q,t)\, F(q, \frac{\hbar}{i}\frac{\partial}{\partial q}) \psi(q,t) dq \\ &= \sum_{m,n} \int a_m^*(t) u_m^*(q) F a_m(t) u_m(q) dq \end{aligned} \tag{3.50}$$

Let us define

$$\begin{aligned} F_{m,n} &= \int u_m^*(q) F(q, \frac{\hbar}{i}\frac{\partial}{\partial q}) u_n(q) dq \\ &= \langle m | F | n \rangle \end{aligned} \tag{3.51}$$

in other words the *matrix elements* of the operator $\hat{F}$. Moreover the $F_{m,n}$ have the Hermitian property

$$F_{m,n}^* = F_{n,m} \tag{3.52}$$

It now follows that Eq. (3.50) becomes

$$\begin{aligned}\langle\langle F\rangle\rangle &= \sum_{m,n} F_{m,n}\langle\langle a_n^* a_m\rangle\rangle \\ &= \sum_{m,n} F_{m,n}\rho_{n,m} \\ &= \sum_m [F\rho]_{mm} \\ &= \mathrm{Tr}\,\hat{\rho}\hat{F}.\end{aligned} \tag{3.53}$$

Thus Eq. (3.41) which in classical statistical mechanics yields the mean value of the observable for all the systems in the ensemble as an integral of the observable over all phase space is replaced by the trace of the corresponding quantum mechanical matrix as first shown by von Neumann [6] in 1927.

The Dirac notation embodied in Eq. (3.51) may be also used to clarify the notation for the density matrix in Section III.I above. We have by definition for the matrix elements of the density operator

$$\begin{aligned}\rho_{nm} &= \langle u_m|\hat{\rho}|u_n\rangle \\ &\equiv \int u_m^*\,\hat{\rho}\,u_m dq \\ &\equiv \langle m|\hat{\rho}|n\rangle\end{aligned} \tag{3.54}$$

where as is usual in quantum mechanics we suppress the *u*'s. Hence replacing the *m* and *n* associated with the rows and columns of the density operator by *x* and x' we have

$$\begin{aligned}\rho_{nm} &= \langle x|\hat{\rho}|x'\rangle \\ &= \rho_{xx'}\end{aligned} \tag{3.55}$$

which is usually written as

$$\rho_{nm} = \rho(x, x'). \tag{3.56}$$

III.V The von Neumann equation of motion of the density operator

von Neumann has shown [6] that the evolution in time of the density operator is given by the (von Neumann's) equation:

$$\begin{aligned}\frac{\partial\hat{\rho}}{\partial t} + \frac{1}{i\hbar}\left[\hat{\rho}\hat{H} - \hat{H}\hat{\rho}\right] &\equiv \frac{\partial\hat{\rho}}{\partial t} + \frac{1}{i\hbar}\left[\hat{\rho}, \hat{H}\right] \\ &= 0\end{aligned} \tag{3.57}$$

where $\left[\hat{\rho},\hat{H}\right]$ denotes the commutator of the operators $\hat{\rho}$ and $\hat{H}$. Equation (3.57) is the analogue in quantum statistical mechanics of the Liouville equation derived in Chapter I, namely

$$\begin{aligned} \frac{D\rho}{Dt} &\equiv \frac{\partial\rho}{\partial t} + \{\rho, H\} = 0 \\ \{\rho, \mathrm{H}\} &= \sum_{i=1}^{3N}\left(\frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right) \end{aligned} \tag{3.58}$$

where $\{\rho, H\}$ is the Poisson bracket. Moreover Eq. (3.57) follows from Eq. (3.58) if the classical Poisson bracket is replaced by $(i\hbar)^{-1}$ times the commutator of the operators $\hat{\rho}$ and $\hat{H}$.

To derive this equation we consider the rate of change of the matrix elements ρ_{nm}, i.e. the rate of change of

$$\rho_{nm} = \langle u_m | \hat{\rho} | u_n \rangle \tag{3.59}$$

Thus we consider an expansion for the state of a system in the quite general form (i.e. Eq. (3.42))

$$\psi(q,t) = \sum_k a_k(t) u_k(q)\,, \tag{3.60}$$

where the $u_k(q)$ may be any complete set of orthonormalized eigenfunctions for the system, and the $a_k(t)$ are the corresponding probability amplitudes.

For the rate of change of $a_n(t)$ with time we then have the generalized Schrödinger equation (3.26)

$$\frac{\partial a_n}{\partial t} = -\frac{i}{\hbar}\sum_k H_{n,k} a_k\,, \tag{3.61}$$

where the matrix elements of the Hamiltonian operator are given by

$$H_{n,k} = \int u_n^* \hat{H} u_k \, dq \tag{3.62}$$

which has the Hermitian property

$$H_{n,k} = H_{k,n}^*\,. \tag{3.63}$$

Hence the rate of change of ρ_{nm} with time becomes

$$\begin{aligned}\frac{\partial \rho_{n,m}}{\partial t} &= \frac{\partial \left\langle \left\langle a_m^* a_n \right\rangle \right\rangle}{\partial t} \\ &= -\frac{i}{\hbar}\sum_k \left(H_{n,k} \left\langle \left\langle a_m^* a_k \right\rangle \right\rangle - H_{m,k}^* \left\langle \left\langle a_k^* a_n \right\rangle \right\rangle \right)\end{aligned} \tag{3.64}$$

which can be more simply written as

$$\frac{\partial \rho_{n,m}}{\partial t} = -\frac{i}{\hbar}\sum_k \left(H_{n,k}\rho_{k,m} - \rho_{n,k}H_{k,m} \right). \tag{3.65}$$

This equation is a general expression for the quantum analogue of Liouville's theorem. If we rewrite Eq. (3.65) as

$$\frac{\partial \rho_{n,m}}{\partial t} = -\frac{1}{i\hbar}\sum_k \left(\rho_{n,k}H_{k,m} - H_{n,k}\rho_{k,m} \right) \tag{3.66}$$

and recall that for matrices *A* and *B* [7]

$$AB = C \tag{3.67}$$

iff

$$c_{i,j} = \sum_k a_{i,k}b_{k,j} \tag{3.68}$$

we see that in operator notation Eq. (3.66) is

$$\begin{aligned}\frac{\partial \hat{\rho}}{\partial t} + \frac{1}{i\hbar}\left[\hat{\rho}\hat{H} - \hat{H}\hat{\rho} \right] &\equiv \frac{\partial \hat{\rho}}{\partial t} + \frac{1}{i\hbar}\left[\hat{\rho}, \hat{H} \right] \\ &= 0\end{aligned} \tag{3.69}$$

which proves von Neumann's equation.

In the x, x' representation, Eq. (3.66) becomes for a system under the influence of a potential $V(x)$

$$\begin{aligned}\frac{d\left\langle x \middle| \hat{\rho} \middle| x' \right\rangle}{dt} = &\left\{ \frac{i\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x'^2} \right) - \frac{i}{\hbar}\left(V(x) - V(x') \right) \right\} \\ &\times \left\langle x \middle| \hat{\rho} \middle| x' \right\rangle\end{aligned} \tag{3.70}$$

which is a partial differential equation for the evolution of the matrix elements.

III.VI Applications of the equilibrium density matrix

As an example of the application of the equilibrium density matrix [8] we shall calculate the mean energy of an ideal monatomic gas namely

$$E = \frac{3}{2}NkT \tag{3.71}$$

where N is the number of molecules. Next we will calculate the mean energy of a single simple harmonic oscillator of frequency ν in a system composed of many such oscillators, held at temperature T, in quantum statistical mechanics, namely

$$\frac{E}{N} = \frac{h\nu}{2} + \frac{h\nu}{e^{\beta h\nu} - 1} \tag{3.72}$$

where N is the total number of oscillators. We shall also very briefly treat the Brillouin function for spins [9] which occurs in the theory of paramagnetism.

First we recall that the transition from classical statistical mechanics to quantum statistical mechanics is achieved by replacing the classical partition function, i.e.

$$Z = \int e^{-H/k_B T} dk \tag{3.73}$$

with the quantum partition function

$$Z = \mathrm{Tr}\ (e^{-H/k_B T})\,. \tag{3.74}$$

In Eq. (3.73) the volume element in phase space is defined

$$dk = \prod_{s=1}^{N} d\mu_s \tag{3.75}$$

where $d\mu_s$ is the volume element associated with one of the subsystems defined by

$$d\mu_s \equiv dp_{sx} dp_{sy} dp_{sz} dx_s dy_s dz_s\,. \tag{3.76}$$

The subsystem phase space is called the "micro-phase space" or the "μ-space" and the volume elements always factorizes as in (3.75). If we consider an entity such as an ideal gas where the only potential that remains is that between the (identical) particles and the walls of their container the partition function also factorizes by statistical independence so that

$$\begin{aligned} Z &= \int e^{-H/k_B T} d\lambda \\ &= \prod_{s=1}^{N} \left(\int e^{-\beta h_s} d\mu_s \right) \\ &= z^N \end{aligned} \tag{3.77}$$

where the "one-particle partition function" is defined by

$$z \equiv \int e^{-\beta h} d\mu \tag{3.78}$$

and the subscript *s* is dropped since it will be assumed that the subsystems are identical. In the quantum case we shall again suppose that the system is composed of *N independent subsystems,* therefore the Hamiltonian may be expressed as a sum of individual contributions, say

$$H = \sum_{s=1}^{N} h_s \,. \tag{3.79}$$

The energy is similarly a sum of individual contributions

$$E = \sum_{s=1}^{N} \varepsilon_s \,. \tag{3.80}$$

A state for the macroscopic system is now determined by specifying the set of quantum numbers $\{n\} = \{n_1, n_2, ..., n_N\}$, where n_i refers to the i^{th} subsystem. The partition function then takes the form

$$Z = \sum_{\{n_1\}} ... \sum_{\{n_N\}} e^{-\left(\varepsilon_{n_1} + ... + \varepsilon_{n_N}\right)/k_B T} \,. \tag{3.81}$$

We can factor Eq. (3.81) as

$$Z = \left(\sum_{\{n_1\}} e^{-\varepsilon_{n_1}/k_B T} \right) \left(\sum_{\{n_2\}} e^{-\varepsilon_{n_2}/k_B T} \right) ... \left(\sum_{\{n_N\}} e^{-\varepsilon_{n_N}/k_B T} \right). \tag{3.82}$$

Furthermore, if the subsystems are *identical*, the partition function takes the form

$$Z = z^n \tag{3.83}$$

where the one-particle quantum partition function is defined by

$$z = \sum_{\{n\}} e^{-\varepsilon_n/k_B T} \,. \tag{3.84}$$

This expression is the quantum analogue of the classical "*one-particle partition function*" namely Eq. (3.78)

$$z \equiv \int e^{-\beta h} d\mu \,. \tag{3.85}$$

The lable *s* is again dropped since it will be assumed that the subsystems are *identical*.

III.VI.I Mean energy of an ideal monatomic gas

As our first application of quantum statistical mechanics [8,10], consider an ideal monatomic gas composed of *identical* subsystems with mass *m*. The Hamiltonian for a single subsystem is given by

$$
\begin{aligned}
h &= \frac{\hat{p}^2}{2m} \\
&= \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \\
&= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right).
\end{aligned}
\tag{3.86}
$$

We consider a large cubical box of volume $V = L^3$ and apply periodic boundary conditions. In this case, the wave functions are just plane waves

$$
\phi_{n_x,n_y,n_z}(x,y,z) = \frac{1}{\sqrt{L^3}} e^{i\left(p_x x + p_y y + p_z z\right)/\hbar}. \tag{3.87}
$$

Here $\left(p_x, p_y, p_z\right)$ now denote the momentum *eigenvalues*, they are given by

$$
\left(p_x, p_y, p_z\right) = \frac{2\pi\hbar}{L}\left(n_x, n_y, n_z\right) \;\; ; \;\; n_i = 0, \pm 1, \pm 2, \ldots \pm \infty \qquad i = x, y, z \tag{3.88}
$$

This discrete quantization is imposed by the periodic boundary conditions. The energy eigenvalues are given by since the particles are quasi-independent (particle in a 3-D box problem)

$$
\begin{aligned}
\varepsilon_{n_x,n_y,n_z} &= \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \\
&= \frac{1}{8m}\left(\frac{2\pi\hbar}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)
\end{aligned}
\tag{3.89}
$$

where n_x, n_y, n_z are any integers. The one-particle partition function now takes the form

$$
z = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta\left(n_x^2 + n_y^2 + n_z^2\right)h^2/8mL^2} \tag{3.90}
$$

where, as usual, $\beta \equiv 1/kT$. If the number of levels becomes very dense and the box is large we can evaluate z by replacing the summation by integrals. For example

$$\begin{aligned}\sum_{n_x}\exp\left(-\frac{\beta h^2}{8m}\cdot\frac{n_x^2}{L^2}\right) &= \sum_{n_x}\exp\left(-\alpha^2 n_x^2\right)\\ &\simeq \int_{n_x=0}^{\infty}\exp\left(-\alpha^2 n_x^2\right)dn_x\\ &= \frac{\sqrt{\pi}}{2\alpha}\\ &= \frac{L}{h}\sqrt{\frac{2\pi m}{\beta}}\end{aligned} \tag{3.91}$$

where

$$\alpha^2 = \frac{\beta h^2}{8mL^2}, \tag{3.92}$$

i.e.

$$\sum_{n_x}\exp\left(-\frac{\beta h^2}{8m}[\frac{n_x^2}{L^2}]\right)\to\frac{L}{h}\sqrt{\frac{2\pi m}{\beta}}. \tag{3.93}$$

Therefore, Eq. (3.90) is

$$\begin{aligned}z &= \left(\frac{L}{h}\sqrt{\frac{2\pi m}{\beta}}\right)^3\\ &= V\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}.\end{aligned} \tag{3.94}$$

This is the quantum partition function for a single particle of mass *m* in a box of volume L^3 satisfying periodic boundary conditions in the limit where the volume of the box tends to infinity. The corresponding translational energy of a system composed of *N* such subsystems may be found as follows. First we note that the partition function is

$$Z = z^N \tag{3.95}$$

and that by inspection of Eq. (3.77) the mean energy *E* is given by

$$E = -\frac{\partial \ln Z}{\partial \beta}. \tag{3.96}$$

Hence

$$\begin{aligned}\ln Z &= N\ln z\\ &= N\left\{\ln\left[V\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\right]\right\}\end{aligned} \tag{3.97}$$

which on expanding the logarithm and differentiating as in Eq. (3.96) yields

$$E = \frac{3}{2} \cdot \frac{N}{\beta} \tag{3.98}$$

in agreement with the classical kinetic theory result. Notice that assuming that the volume of the box is very large means that the first excited state lies infinitesimally close to the ground state so that the freezing out of the translational motion then takes at a temperature infinitesimally close to T=0; hence in order to explain results like the Nernst heat theorem one must abandon the continuum approximation.

III.VI.II Mean energy of harmonic oscillator

Consider [8] a macroscopic system composed of N identical subsystems which are one-dimensional simple harmonic oscillators, in other words a perfect quantum gas of harmonic oscillators. The Hamiltonian for a single subsystem is given by

$$\begin{aligned} h &= \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2 \\ &= -\frac{\hbar^2}{2m} \frac{d^2}{dq^2} + \frac{1}{2} m\omega^2 q^2 . \end{aligned} \tag{3.99}$$

It is a basic result of quantum mechanics that the energy spectrum of the one-dimensional simple harmonic oscillator is given by

$$\begin{aligned} \varepsilon_n &= \left(n + \frac{1}{2} \right) \hbar\omega \; ; \; n = 0, 1, 2, ..., \infty \\ &\equiv \left(n + \frac{1}{2} \right) h\nu . \end{aligned} \tag{3.100}$$

The quantum partition function for a single subsystem is defined by

$$z = \sum_n e^{-\beta h\nu (n+1/2)} \tag{3.101}$$

where $\beta = 1/k_B T$. The sum appearing in this expression is simply a geometric series

$$z = e^{-\beta h\nu/2} \left[1 + e^{-\beta h\nu} + \left(e^{-\beta h\nu} \right)^2 + ... \right] \tag{3.102}$$

which is immediately summed to give

$$z = e^{-\beta h\nu/2} \frac{1}{1 - e^{-\beta h\nu}} . \tag{3.103}$$

The partition function for the entire system is again given by Eq. (3.83), i.e.

$$Z = z^n \tag{3.104}$$

and hence

$$\ln Z = N \ln z = N\left[-\frac{\beta h\nu}{2} - \ln\left(1 + e^{-\beta h\nu}\right)\right]. \tag{3.105}$$

The mean energy of one oscillator in this system follows from

$$\begin{aligned} \frac{E}{N} &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \frac{h\nu}{2} + \frac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} h\nu \end{aligned} \tag{3.106}$$

which may be rewritten as

$$\frac{N}{E} = \frac{h\nu}{2} + \frac{h\nu}{e^{\beta h\nu} - 1}. \tag{3.107}$$

This is the *Planck distribution*. It is a crucial result. Equation (3.107) provides the correct expression for the mean energy of a single harmonic oscillator of frequency ν in a system composed of many such oscillators, held at temperature *T*, in quantum statistical mechanics. The first term on the right hand side of Eq. (3.107) is a constant independent of the temperature. It arises because of the *zero-point energy* in the spectrum in Eq. (3.100). We denote this contribution by E_0 so that

$$E_0 \equiv N\left(\frac{h\nu}{2}\right) \tag{3.108}$$

hence

$$\frac{1}{N}\left(E - E_0\right) = \frac{h\nu}{e^{h\nu/k_B T} - 1} \tag{3.109}$$

Consider the limiting cases of this equation. Suppose first that one is interested in *high temperature* so that

$$\beta h\nu \ll 1 \quad \text{or} \quad T \gg h\nu/k_B \tag{3.110}$$

In this case the exponential in the denominator can be expanded in a power series

$$e^{h\nu/k_B T} = 1 + \frac{h\nu}{k_B T} + \ldots \tag{3.111}$$

which yields

$$\frac{1}{N}\left(E - E_0\right) = k_B T\,. \tag{3.112}$$

This is the classical result for the energy of a simple harmonic oscillator; it follows from the equipartition theorem essentially due to the fact that the potential energy is quadratic in the displacement. At high temperature we thus recover the classical result.

Consider next the case of *low temperature* where

$$\beta h\nu \gg 1 \quad \text{or} \quad T \ll h\nu/k_B \,. \tag{3.113}$$

The exponent in Eq. (3.109) now becomes very large, the exponent dominates in the denominator, and one has

$$\frac{1}{N}\left(E - E_0\right) = h\nu e^{-h\nu/k_B T} \,. \tag{3.114}$$

The contribution to the energy in Eq. (3.114) falls exponentially to zero under the conditions of Eq. (3.113). We thus explicitly exhibit the "freezing out" of the excitations at low temperatures in quantum statistical mechanics. One of the failures of classical statistical mechanics was the inability to account for this freezing out of the modes at low temperature as evidenced by the experimental data in a wide variety of physical phenomena.

III.VI.III Paramagnetism: The Brillouin function

We consider an ensemble of atoms and assume that each of them has a fixed magnetic moment $\mathbf{m}$ of magnitude $g\mu_B S$ where g is the so called 'Landé factor' or 'spectroscopic splitting factor', and

$$\mu_B = \frac{|e|\hbar}{2m_e c} \tag{3.115}$$

is known as the *Bohr magneton*. e is electron charge, m_e is the electron mass and c is the speed of light. The spin operator $\hat{S}$ has the property that the component S_z can only assume the $2S+1$ discrete values $-S, -S+1, ..., S$, i.e. one of the integer or half integer values between $-S$ and $+S$ in integer steps.

The magnetic moments interact with an applied magnetic field **H** but not with each other. Therefore if **H** is applied along the z-axis we have cf Eq. (3.19) above that

$$\langle m_z \rangle = \frac{\sum m_z \exp m_z \beta H}{\sum \exp m_z \beta H} = \frac{\sum_{n=-S}^{S} g\mu_B n \exp g\mu_B \beta H n}{\sum_{n=-S}^{S} \exp g\mu_B \beta H n}. \quad (3.116)$$

After considerable manipulation this can be written [9] essentially because the partition function is a geometric series in $\exp\left(g\mu_B \beta H\right)$ in the closed form

$$\frac{\langle S_z \rangle}{S} = \frac{\langle m_z \rangle}{g\mu_B S} = B_S\left(g\mu_B SH\beta\right) \quad (3.117)$$

where the function $B_S(x)$

$$B_S(x) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{x}{2S}\right) \quad (3.118)$$

is called the *Brillouin function*. Along with the argument *x* it also depends on the spin number, *S* which is one of the principal differences between it and the Langevin function arising in the classical theory of paramagnetism. In the classical limit defined by high temperature $\beta \to 0$ and a large spin number

$$B_S(x) \to L(x) = \coth(x) - \frac{1}{x}. \quad (3.119)$$

The quantum effects contained in the Brillouin function become important either for *small S* or *very low* temperatures or *very intense* fields. Note that for small *H*, Eq. (3.117) may be written

$$\langle S_z \rangle = \frac{g\mu_B \beta S(S+1)}{3} H. \quad (3.120)$$

Further discussion of the representation of spin dynamics in terms of phase space distributions is given in the next Chapter. Notice that if a mean field potential is included e.g. arising from uniaxial anisotropy with ξ and σ being the external and anisotropy field parameters respectively

$$Z_S = \sum_{m=-S}^{S} e^{\sigma m^2 + \xi m} \quad (3.121)$$

it does not in general appear possible to get a simple closed expression for $\langle S_z \rangle$.

III.VII Irreversibility-quantum collision kernels

In Chapter I we saw that the classical dynamics of a collection of N particles where N is of the order of 10^{23} say, is described by the Liouville equation in the $6N$ phase space (q,p) where $q(t)$ and $p(t)$ denote the collection of $3N$ positions and $3N$ momenta. The Liouville equation describes the time evolution of the phase space density of representative points $\rho(q,p)$ and is

$$\frac{D\rho}{Dt} \equiv \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \tag{3.122}$$

where

$$\{\rho, \mathrm{H}\} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} \right) \tag{3.123}$$

is the Poisson bracket, H is the Hamiltonian and the large D's denote the hydrodynamical derivative. Furthermore we saw that it is a purely dynamical theorem and that Boltzmann's microscopic explanation of the 2nd law of thermodynamics contained in it the idea that one may essentially replace the entire system of 10^{23} degrees of freedom by a single (tagged) system of 3 degrees of freedom interchanging energy with the rest of universe or heat bath, i.e. the effect of the remaining $10^{23} - 3$ degrees of freedom is represented by collisions (this is the *Stosszahlansatz*) so that for the tagged system $\frac{D\rho}{Dt}$ is no longer zero and the (q,p) for the universe is now reduced to (q_s, p_s) for the single system, ρ is then the reduced or single particle distribution function which obeys the famous Boltzmann equation describing the evolution of the single particle distribution function from an initial state. Since the hydrodynamical derivative is no longer zero, i.e. the trajectories of the single system in the (q_s, p_s) phase space exhibit energy diffusion and no longer purely stream.

In like manner in the quantum mechanics von Neumann's equation of motion of the density operator namely

$$\frac{\partial \hat{\rho}}{\partial t} + \frac{1}{i\hbar}\left[\hat{\rho}\hat{H} - \hat{H}\hat{\rho}\right] \equiv \frac{\partial \hat{\rho}}{\partial t} + \frac{1}{i\hbar}\left[\hat{\rho}, \hat{H}\right] = 0 \tag{3.124}$$

where $\left[\hat{\rho},\hat{H}\right]$ denotes the commutator of the operators $\hat{\rho}$ and $\hat{H}$ may be reduced and generalized; reduced by confining the number of degrees of freedom to a small but representative set and generalized by adding a collision operator to account for the bath degrees of freedom and the bath system interaction. Hence the equation of motion of the reduced density operator is analogous to the Boltzmann equation viz.,

$$\frac{\partial\hat{\rho}_s}{\partial t}+\frac{i}{\hbar}\left[\hat{H}(t),\hat{\rho}_s\right]=\frac{D\hat{\rho}_s}{Dt} \tag{3.125}$$

where $\hat{H}(t)$ is now a time dependent Hamiltonian. An example of collision integrals which in the classical mechanics is known as the Van Vleck- Weisskopf model [11] is

$$\frac{D\rho_s}{Dt}=-\frac{\rho}{\tau}+\frac{\rho_{eq}}{\tau} \tag{3.126}$$

with

$$\rho_{eq}=\frac{e^{-\beta H(t)}}{\int e^{-\beta H(t)}dpdq} \tag{3.127}$$

which becomes in the quantum mechanics

$$\frac{D\hat{\rho}_s}{Dt}=-\frac{\hat{\rho}}{\tau}+\frac{\hat{\rho}_{eq}}{\tau} \tag{3.128}$$

where

$$\hat{\rho}_{eq}=\frac{e^{-\beta\hat{H}(t)}}{\mathrm{Tr}\left(e^{-\beta\hat{H}(t)}\right)}. \tag{3.129}$$

This model which is simply exponential relaxation towards an equilibrium distribution has been extensively used by Karplus and Schwinger [12] in order to obtain a theory of microwave line shape. This is an example where the density operator formalism shows clearly the connection between the classical and quantum collision terms called kernels in the exposition of Gross and Lebowitz [13]. According to them [13] the analogy is not usually as transparent as in the Van Vleck-Weisskopf model so that it is easier to see the correspondence by proceeding via Wigner's phase space representation of the density matrix using an collision integral which has the same form as that which occurs in the classical distribution function (e.g. the assumption used extensively by us throughout the

Thesis that the collision term in the quantum Brownian motion master equation for the time evolution of the Wigner function has the form of a Kramers-Moyal term truncated at the second term just as in the classical Brownian motion). The density matrix elements may then be found by inverse Fourier transformation. An illuminating account of the calculation of the density matrix elements directly from Eq. (3.125) may be found in Gross and Lebowitz [13] for a system of fixed axis rotators for the strong collision model where in the classical mechanics a rotator instantaneously assumes the Maxwellian distribution of velocities after a collision. We shall not enter into any further detailed discussion of the nonequilibrium density matrix as in this Thesis we treat nonequilibrium problems by using the Wigner representation.

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CHAPTER IV

Representation distributions and quantum master equations for closed systems

We commence our formulation of quantum master equations in terms of representation distributions by describing Wigner's solution [1,2] for the stationary distribution in phase and configuration spaces for translational motion of particles with separable and additive Hamiltonians. In all that follows it will be helpful to recall [3] that **Wigner's representation of quantum mechanics can be formally defined as a means of associating a *c*-number function in phase space (x, p) with every operator which is a function of position and momentum operators $(\hat{x}, \hat{p})$ and is in effect the inverse of Weyl's rule which is used to calculate quantum mechanical operators from classical quantities.**

IV.I Wigner's stationary distribution for closed systems

Wigner's original objective in introducing his phase space representation of quantum mechanics was to study quantum corrections to thermodynamic equilibrium, i.e., to the Maxwell-Boltzmann distribution of classical statistical mechanics [1,2,4]. We have already emphasised that the Wigner phase space distribution $W(x, p, t)$ allows one to calculate quantum mechanical expectation values using concepts of classical statistical mechanics. In this respect however, the Wigner function is not unique, being one of many such phase space representations [4-6]. However, of all such representations it has the simplest properties [4-6] as noted by Wigner although he knew only that it yields the correct marginal distributions for position and momenta respectively [7]. For a quantum system with a Hamiltonian operator

$$\hat{H} = \hat{p}^2 / 2m + V(\hat{x}) \tag{4.1}$$

the Wigner distribution function $W(x, p, t)$ for a pure state is defined to be [1,2]

$$W(x,p)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\psi^{*}\left(x+\frac{y}{2}\right)\psi\left(x-\frac{y}{2}\right)e^{-ipy/\hbar}dy\,, \tag{4.2}$$

which is real but not everywhere positive so that it is a quasiprobability distribution. Here $\hbar$ is Planck's constant. Equation (4.2) holds if the function ψ evolves according to the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V(x)\psi\,. \tag{4.3}$$

Integration of the joint quasi-probability density $W(x,p,t)$ with respect to the momentum *p* yields the marginal distribution

$$\left|\psi(x)\right|^2=\psi(x)^{*}\psi(x) \tag{4.4}$$

i.e., the correct quantum mechanical probability for the various values of the coordinate *x*. Integration of *W* with respect to the position *x* yields the correct quantum mechanical probability for the momentum *p*, viz., the marginal distribution (see Appendix IV.I)

$$\left|\int_{-\infty}^{\infty}\psi(x)e^{-ipx}dx\right|^2. \tag{4.5}$$

By introducing a density matrix for a pure state

$$\hat{\rho}(x_1,x_2)=\psi(x_1)\psi^{*}(x_2) \tag{4.6}$$

and new coordinates $x=(x_1+x_2)/2$ and $y=x_2-x_1$, one can write Eq. (4.2) as

$$W(x,p,t)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\hat{\rho}\left(x+\frac{1}{2}y,x-\frac{1}{2}y\right)e^{-ipy/\hbar}dy\,. \tag{4.7}$$

Equation (4.7) which is merely a special representation (Weyl-Wigner) of the density matrix is simply the Fourier transform of the density operator expressed in terms of the above variables and is the generating function for all spatial autocorrelation functions of a given quantum mechanical wave function $\psi(x)$.

IV.II Moyal's statistical interpretation of the Wigner function

The Wigner function may also be couched as accomplished by Moyal [8] in familiar probability theory language as the inverse Fourier transform of a characteristic function (moment generating function) whence observables may be calculated by parametric differentiation with respect to μ,ν. Moreover in so

doing he showed that the Wigner function is the correct joint distribution if we make the Weyl correspondence between operators and phase space functions [7]. In order to establish the Weyl correspondence we form the characteristic function operator (it is useful to conceive of the operators $\hat{p}$ and $\hat{x}$ as random "variables" and the *c*-numbers *x* and *p* as their realizations)

$$\begin{aligned}\hat{\chi}_{\hat{x},\hat{p}}(\mu,\nu) &= \exp\{i(\mu\hat{p}+\nu\hat{x})\} \\ &= \sum_{n=0}^{\infty}\frac{i^n}{n!}(\mu\hat{p}+\nu\hat{x})^n\end{aligned}. \tag{4.8}$$

The characteristic function in a state $\psi(x)$ is then given by the scalar product

$$\begin{aligned}\chi_{\hat{x},\hat{p}}(\mu,\nu) &= (\psi,\hat{\chi}_{\hat{x},\hat{p}}(\mu,\nu)\psi) \\ &= (\psi,e^{i(\mu\hat{p}+\nu\hat{x})}\psi) \\ &= \int_{-\infty}^{\infty}\psi^*(x)e^{i(\mu p+\nu x)}\psi(x)\,dx \\ &= \langle e^{i(\mu\hat{p}+\nu\hat{x})}\rangle \\ &= \mathrm{Tr}\,\{\hat{\rho}e^{i(\mu\hat{p}+\nu\hat{x})}\}.\end{aligned} \tag{4.9}$$

The phase space distribution is thus by Fourier inversion

$$W(x,p) = \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-i\mu p-i\nu x}\chi_{\hat{x},\hat{p}}(\mu,\nu)\,d\nu d\mu \tag{4.10}$$

where of course the mixture $\sum c_n\psi_n^*(x)\psi_n(x)$ is now assumed. Furthermore since $\hat{p},\hat{x}$ are canonically conjugate operators we may use the Baker-Campbell-Hausdorff identity (proof in Appendix IV.II)

$$\exp(\hat{\mathrm{A}}+\hat{\mathrm{B}}) = \exp(\hat{\mathrm{A}})\exp(\hat{\mathrm{B}})\exp\left\{\frac{1}{2}([\hat{\mathrm{B}},\hat{\mathrm{A}}])\right\} \tag{4.11}$$

noting that

$$\begin{aligned}[\hat{p},\hat{x}] &= \hat{p}\hat{x}-\hat{x}\hat{p} \\ &= \frac{\hbar}{i}\end{aligned} \tag{4.12}$$

is the commutator of the operators $\hat{x},\hat{p}$, so that the characteristic function operator becomes

$$\begin{aligned}\hat{\chi}_{\hat{x},\hat{p}}(\mu,\nu) &= e^{\frac{1}{2}i\hbar\mu\nu}e^{i\nu\hat{x}}e^{i\mu\hat{p}} \\ &= e^{-\frac{1}{2}i\hbar\mu\nu}e^{i\mu\hat{p}}e^{i\nu\hat{x}}\end{aligned}. \tag{4.13}$$

The Baker-Campbell-Hausdorff identity may now be used to evaluate the characteristic function. We have

$$\chi_{\hat{x},\hat{p}}(\mu,\nu)=\int_{-\infty}^{\infty}\psi*(x)\,e^{i\nu\left(x+\frac{\mu\hbar}{2}\right)}e^{i\mu\hat{p}}\psi(x)dx\,. \tag{4.14}$$

We then have using the shifting property (proof in Appendix IV.III)

$$e^{i\mu\hat{p}}\psi(x)=\psi(x+\mu\hbar) \tag{4.15}$$

so that

$$\chi_{\hat{x},\hat{p}}(\mu,\nu)=\int_{-\infty}^{\infty}\psi*(x)\,e^{i\nu\left(x+\frac{\mu\hbar}{2}\right)}\psi(x+\mu\hbar)dx \tag{4.16}$$

which with the replacement

$$x\to x-\frac{\mu\hbar}{2} \tag{4.17}$$

becomes

$$\chi_{\hat{x},\hat{p}}(\mu,\nu)=\int_{-\infty}^{\infty}\psi^{*}\left(x-\frac{1}{2}\hbar\mu\right)e^{i\nu x}\psi\left(x+\frac{1}{2}\hbar\mu\right)dx\,. \tag{4.18}$$

We have given the details of this derivation as it is somewhat obscure in Moyal's original paper. We remark that Moyal's formulation as expressed by Eq. (4.9) fails however for spins as commented upon by Stratonovich [9]. To see this let us take as non-commuting operators two components of the spin say $\hat{S}_y$ and $\hat{S}_z$ then the characteristic function must be periodic in μ and ν and in general the function

$$\text{Tr}\,\exp\left\{i\left(\mu\hat{S}_y+\nu\hat{S}_z\right)\right\}\hat{\rho} \tag{4.19}$$

is not periodic in these so that Moyal's formulation fails for the canonical variables in the phase space of orientations. Compare for example the differences in the transition probabilities (Green's functions) for the Brownian motion of a fixed axis rotator specified by the angular coordinate ϕ and a particle moving along the *x*-axis as demonstrated in [10].

$$W\left(\phi,t\,|\phi_0,0\right)=\frac{1}{2\pi}\sum_{p=-\infty}^{\infty}e^{ip(\phi-\phi_0)-p^2t/\tau},\ t\geq 0 \tag{4.20}$$

which is periodic in ϕ unlike

$$W(x,t|x_0,0)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\xi(x-x_0)-\xi^2Dt/2}d\xi$$
$$=\frac{1}{\sqrt{4\pi Dt}}e^{-(x-x_0)^2/(4Dt)}. \tag{4.21}$$

Stratonovich has shown how to correctly construct the Wigner function in the phase space of orientations as part of his general discussion of representation distributions for quantum systems which we summarize in Section IV.IV.

Returning to translational motion we have

$$\chi_{\hat{x},\hat{p}}(\mu,\nu)=\int_{-\infty}^{\infty}\psi^*\left(x-\frac{1}{2}\hbar\mu\right)e^{i\nu x}\psi\left(x+\frac{1}{2}\hbar\mu\right)dx. \tag{4.22}$$

Thus by Fourier inversion using the definition of the delta-function

$$\delta(\xi)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{\pm i\xi\eta}d\eta \tag{4.23}$$

we have

$$W(x,p)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\psi^*\left(x-\frac{1}{2}\hbar\mu\right)e^{-i\mu p}\psi^*\left(x+\frac{1}{2}\hbar\mu\right)d\mu \tag{4.24}$$

which by elementary transformations is Eq. (4.7). Hence Moyal's formulation in terms of characteristic functions constitutes a systematic study of expectation values of all Weyl ordered operators *for particles* and identifies the inverse Fourier transform of their moment generating function to the Wigner function [11]. The calculation of expectation values from the characteristic functions is illustrated in Appendix IV.IV.

IV.III Time evolution of the Wigner function

Equation (4.7) may be used to demonstrate that the Wigner function W satisfies the evolution equation [1,2] (for details see Appendix IV.V)

$$\frac{\partial W}{\partial t}+\hat{M}_W W=0, \tag{4.25}$$

where the operator $\hat{M}_W$ is defined as

$$\hat{M}_W W=\frac{p}{m}\frac{\partial W}{\partial x}-\frac{1}{i\hbar}\left[V\left(x+\frac{i\hbar}{2}\frac{\partial}{\partial p}\right)-V\left(x-\frac{i\hbar}{2}\frac{\partial}{\partial p}\right)\right]W$$
$$=\frac{p}{m}\frac{\partial W}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}-\sum_{r=1}^{\infty}\frac{(i\hbar/2)^{2r}}{(2r+1)!}\frac{\partial^{2r+1}V}{\partial x^{2r+1}}\frac{\partial^{2r+1}W}{\partial p^{2r+1}}. \tag{4.26}$$

Equation (4.25) is an analogue of the classical Liouville equation; indeed the leading order term is noneother than that equation. It may be solved exactly for the harmonic oscillator where the Wigner operator is the same as the classical Liouville operator as shown in Chapter V. For other potentials it may be solved by perturbation theory in $\hbar^2$ as we shall also show in Chapters VII and VIII. Yet another method of calculating the Wigner function is by direct Wigner transformation using Eq. (4.7), however this requires a knowledge of the matrix elements of the density matrix. This procedure is illustrated for spins in Section IV.IV below where it is explicitly demonstrated how a knowledge of the matrix elements of the equilibrium spin density matrix leads to a series expression in the representation space of polar angles for the Wigner function of a spin with an axially symmetric Hamiltonian.

Clearly the Wigner function $W(x,p)$ [3] exhibits most of the properties of a classical phase space distribution and in the classical limit $W(x,p)$ changes in time like a classical statistical mechanics distribution would. This is equivalent to saying it reduces to a phase point executing a trajectory in phase space rather than the fuzzy quasi-phase point dictated by the uncertainty principle. Moreover the expectation value of a quantum operator $\hat{Q}$ may be calculated using the Wigner function from the corresponding classical variable $Q(x,p)$ as (Q is the Weyl symbol of the quantum operator $\hat{Q}$)

$$\langle Q\rangle(t) = \mathrm{Tr}\left(\hat{\rho}\hat{Q}\right) = \int W(x,p,t)Q(x,p)dx\,dp\ . \qquad (4.27)$$

This is a key result since it expresses the ensemble average of an operator $\hat{Q}$ as a phase space integral. The Wigner representation contains only such features as are common to both quantum and classical statistical mechanics as is evident from the representation of the Wigner function in terms of the characteristic function and formally represents quantum mechanics as a statistical theory on classical phase space [4]. Therefore it is especially suitable for the development of semiclassical methods of solution, for example, for the purpose of analysis of two interacting systems, where one is treated quantum mechanically while the other is treated by using classical theory. Here the Wigner representation allows one to easily obtain quantum corrections to the classical results [1,2] since in effect the only property it does not share with the classical theory is that $W\left(x,p,t\right)$ is positive everywhere

because in quantum theory it may have negative values for some regions of x and p. That we still have a viable physical theory is ensured by the uncertainty principle that no measurement can be made of momentum and position simultaneously beyond a certain accuracy [12]. This has been put in another way by Baker [7]; we quote "when quantum mechanics predicts an impossible result like a "negative probability" then the interpretation is that there is no physically realizable experiment to measure the joint distribution."

IV.IV Stratonovich's general analysis of representation distributions for quantum systems

The above analysis applies to particles with separable and additive Hamiltonians. We mention that a different analysis is required in order to provide a Wigner function representation for spins (essentially because in rotation the distribution functions are always periodic). In order to accomplish this Stratonovich [9] as part of a general discussion of representation distributions for quantum systems introduced the quasiprobability density function $W(\vartheta,\phi,t)$ for the spin orientations in configuration space. ϑ and ϕ, the polar angles, are now the canonical variables. Stratonovich prompted by the failure of his initial attempt to generalize Moyal's quantization procedure to spins introduced a quasiprobability density function on the sphere which he defined as the trace of the product of the system density matrix and the irreducible tensor operators having matrix elements in the spherical basis representation given by the Clebsch-Gordan coefficients. Hence the average value of a quantum spin operator may be calculated just as the corresponding classical function from the Weyl symbol of the operator. Moreover as shown much later by Klimov [11], for a general Hamiltonian, the evolution equation for the Wigner function of the closed system proposed by Stratonovich may be expanded for large spins ($S \gg 1$) in powers of the small parameter $\eta = S^{-1}$ with the term linear in η being the same as the classical Liouville equation (analogous to the result for particles). Thus the Stratonovich representation for spins [9], just as the Wigner representation for particles, is well suited to the development of semiclassical methods of solution allowing one to obtain quantum corrections to the classical results in the simplest possible way. The c-number representation of the quantum spin dynamics is

especially important in treating magnetic relaxation [13]. In view of the importance of and generality of Stratonovich's study of representation distributions for quantum systems we shall attempt to summarize the general principles underlying such representations as given by him and we shall apply them to derive the Wigner distribution and the representation distribution for systems with symmetries described by the SU(2) rotation group.

Stratonovich [9] defines the "representation distribution" by the following requirements:

1. The space M in which it is defined has as a *classical* interpretation, for example, phase space (which we have just considered) or the space of orientations.
2. The distribution can be expressed *linearly* in terms of the density matrix $\hat{\rho}$. This requirement is directly related to the linearity of the whole apparatus of quantum theory, i.e., it is connected with the statistical interpretation of the theory. The density matrix $\hat{\rho}$ like any other operator $\hat{A}$, has associated with it a (*c*-number) function in the representation space

$$\rho(M) = \mathrm{Tr}\,\hat{\rho}\hat{L}(M); \quad A(M) = \mathrm{Tr}\,\hat{A}\hat{L}(M) \tag{4.28}$$

via the kernel $\hat{L}(M)$, which is an operator depending on the point M as a parameter. For example the point M of the representation space could be a point on the unit sphere, so that $M = (\vartheta, \phi)$.

3. The distribution must be a real function; in general, to a Hermitian operator $\hat{A}$ there must correspond a real function *A(M)* (Weyl symbol). This requirement amounts to the condition of Hermiticity of the operators $\hat{L}(M)$ for all points *M*.
4. Statistical averaging of the classical functions *A(M)* (Weyl symbols) must give the same results as the rule for averaging of operators viz

$$\begin{aligned} \int A(M)\rho(M)dM &= \mathrm{Tr}\,\hat{A}\hat{\rho} \\ &= \left\langle \hat{A} \right\rangle. \end{aligned} \tag{4.29}$$

Hence from Eq. (4.28) and (4.29) we have as a representation of a quantum operator the inverse transformation

$$\hat{A} = \int A(M)\hat{L}(M)dM \tag{4.30}$$

where the *c*-number representation is given by the transformation

$$A(M) = \mathrm{Tr}\,\hat{A}\hat{L}(M)\,. \tag{4.31}$$

These rules tell one how to get the operator relation from the *c*-number representation and vice-versa. Thus condition 4 is equivalent to the requirement that the direct and inverse transformations are accomplished by means of the same kernel i.e. the mapping given by Eq. (4.31) is *bijective*.

By regarding the operators $\hat{A}, \hat{B}, \ldots$ as elements of a complex Euclidean space with a scalar product given by the trace $(\hat{A}, \hat{B}) = \mathrm{Tr}\,\hat{A}\hat{B}^*$ ($\hat{B}^*$ is the Hermitian adjoint to $\hat{B}$) –we introduce an orthonormal basis $\hat{A}_1, \hat{A}_2, \ldots$ such that

$$\mathrm{Tr}\,\hat{A}_i, \hat{A}_j^* = \delta_{i,j}\,. \tag{4.32}$$

Thus the kernel $\hat{L}(M)$ is represented by the expansion

$$\hat{L}(M) = \sum_i \hat{A}_i^* A_i\left(M\right) \tag{4.33}$$

where

$$A_i\left(M\right) = \mathrm{Tr}\,\hat{A}_i\hat{L}(M)\,. \tag{4.34}$$

This requirement is equivalent to the condition

$$\int A_i\left(M\right) A_j^*\left(M\right)dM = \delta_{i,j}\,. \tag{4.35}$$

According to Eq. (4.29) the normalization condition

$$\mathrm{Tr}\,\hat{\rho} = 1 \tag{4.36}$$

becomes

$$\int \rho(M)\lambda(M)dM = 1 \tag{4.37}$$

where

$$\lambda(M) = \mathrm{Tr}\,\hat{L}(M)\,. \tag{4.38}$$

Thus we must take as the normalized distribution a function of the form

$$w(M) = \rho(M)\lambda(M) \tag{4.39}$$

so that from Eq. (4.29) the rule for averaging must be written

$$\left\langle \hat{A} \right\rangle = \int A(M)\lambda^{-1}(M)w(M)dM \tag{4.40}$$

which by definition is

$$\left\langle A(M)\lambda^{-1}(M)\right\rangle. \tag{4.41}$$

Hence in Stratonovich's formulation the definition of a representation distribution amounts to calculating the inverse of the trace of the operator associated with the mapping of the density matrix unto the representation space. Stratonovich's abstract treatment of the representation space density presented above may be used to derive specific distributions. The Wigner distribution is an important specific case. We have

$$W(x,p)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\hat{\rho}\left(x+\frac{1}{2}y,x-\frac{1}{2}y\right)e^{-ipy/\hbar}dy \tag{4.42}$$

and here

$$\begin{aligned}\hat{L}(M)&=\hat{L}_{x',x''}\\&=\pm\frac{1}{2\pi\hbar}e^{i(x'-x'')p/\hbar}\delta(x-\frac{x'+x''}{2})\end{aligned}. \tag{4.43}$$

Thus the translational Wigner function is simply derived [9] by applying the principles of homogeneity and equivalence of directions embodied in the symmetries of the Heisenberg-Weyl group combined with the notion of a classical representation space. This should be compared with the intuitive method of Wigner who appears to have arrived at his distribution by ad hoc reasoning in so far as his distribution yields the correct marginal probabilities for position and momenta.

As far as systems with SU(2) rotational symmetry is concerned phase space methods have been mainly applied in quantum optics and very little attention has been paid to other spin systems. For example explicit equations for the equilibrium quasiprobability density function $W(\vartheta,\varphi)$ have been presented only for the particular simple case of a spin in a uniform magnetic field $\mathbf{H}_0$ [13,14]. In view of the importance of the magnetocrystalline anisotropy in physical applications [15,16] which in general gives rise to a multi-stable potential we shall illustrate the phase space method [9,11,17-23] by summarizing for completeness and as an example of the generality of Wigner's ideas concerning representation of quantum operators by *c*-number quasiprobability distributions the calculation given by Kalmykov et al. [24] of the equilibrium quasiprobability distribution function for a uniaxial paramagnet of arbitrary spin

value S in a *constant* field $\mathbf{H}_0$ superimposed on an anisotropy field so that the Hamiltonian is

$$\beta\hat{H}_S = -\xi\hat{S}_Z - \sigma\hat{S}_Z^2. \tag{4.44}$$

where $\hat{S}_Z$ is the Z-component of the spin operator $\hat{\mathbf{S}}$, σ and ξ are the dimensionless internal and external field parameters respectively. (In the classical limit, taking a single domain ferromagnetic particle as example, $S \to \infty$, $\xi \to 0$, $\sigma \to 0$, they reduce to $\xi S = const = \xi'$, $\sigma S^2 = const = \sigma'$ which are the well known field and anisotropy parameters, $v\dfrac{M_S H}{kT}$ and $\dfrac{Kv}{kT}$ where v is the volume of the particle, M_S is the saturation magnetization and K is the anisotropy energy density). Thus we shall calculate the quasiprobability density W corresponding to the equilibrium spin density matrix $\hat{\rho}_{eq}$ given by

$$\hat{\rho}_{eq} = \frac{e^{-\beta\hat{H}_S}}{Z_S}, \tag{4.45}$$

where

$$Z_S = \mathrm{Tr}\,\{e^{-\beta\hat{H}_S}\} \tag{4.46}$$

is the partition function. A model Hamiltonian of the type of Eq. (3.18) has a variety of physical applications (see, e.g., [25-27]).

In order to proceed using Stratonovich's method we first recall that the density matrix $\hat{\rho}$ of the spin $\hat{\mathbf{S}}$ is represented by a $(2S+1)\times(2S+1)$ square matrix [28]. The Hermitian ($\hat{\rho} = \hat{\rho}^\dagger$) and normalized ($\mathrm{Tr}\hat{\rho} = 1$) density matrix $\hat{\rho}$ may be expanded as a sum of the polarization operators $\hat{T}_{L,M}^{(S)}$ namely [28]

$$\hat{\rho} = \sum_{L=0}^{2S}\sum_{M=-L}^{L} a_{L,M}^{*}\hat{T}_{L,M}^{(S)}, \tag{4.47}$$

where the asterisk denotes the complex conjugate and the expansion coefficients $a_{L,M}$ (statistical moment tensors) are given by [28]

$$\begin{aligned} a_{L,M}^{*} &= (-1)^M a_{L,-M} \\ a_{L,-M} &= \sqrt{\frac{2L+1}{2S+1}}\sum_{m,m'=-S}^{S} C_{S,m,L,M}^{S,m'}\rho_{m,m'} \end{aligned}. \tag{4.48}$$

Here $C_{S,m,L,m}^{S,m'}$ is the Clebsch-Gordan coefficient [28] and $\rho_{m,m'}$ is the matrix element of the density matrix operator $\hat{\rho}$ in the spherical basis representation. The irreducible tensor operators $\hat{T}_{L,M}^{(S)}$ form an orthogonal basis in the space of $(2S+1)\times(2S+1)$ matrices with matrix elements given by [28]

$$\left[\hat{T}_{L,M}^{(S)}\right]_{m',m} = \sqrt{\frac{2L+1}{2S+1}} C_{S,m,L,m}^{S,m'},$$

where $-S \le m, m' \le S$, $-L < M < L$, and $0 \le L \le 2S$.

The Wigner quasiprobability distribution function $W^s(\vartheta,\varphi)$ on the surface of the unit sphere for a spin system given by Stratonovich [9] (see also [11]) is defined by the invertible map [cf. Eq. (4.28) above with representation space $M = (\vartheta,\varphi)$]

$$W^s(\vartheta,\varphi) = \mathrm{Tr}\left\{\hat{\rho}\hat{w}_s(\vartheta,\varphi)\right\}, \tag{4.49}$$

where *s* parameterizes quasiprobability functions of spins belonging to the SU(2) dynamical symmetry group such as considered here, $\hat{w}_s(\vartheta,\varphi)$ is the Wigner-Stratonovich operator or kernel of the (bijective) transformation given by Eq. (4.49) defined as [11] (recall that the spherical harmonics are the appropriate functions for the description of rotations)

$$\hat{w}_s(\vartheta,\varphi) = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{S,S,L,0}^{S,S}\right)^{-s} Y_{L,M}^{*}(\vartheta,\varphi)\hat{T}_{L,M}^{(S)} \tag{4.50}$$

(which corresponds to the operator $\hat{L}(M)$ such that [cf. Eqs. (4.29) and (4.37) above]

$$\mathrm{Tr}\left\{\hat{w}_s(\vartheta,\varphi)\right\} = 1$$

($\lambda(M) = \mathrm{Tr}\,\hat{\mathrm{L}}(M)$ is normalized to unity) and

$$\frac{2S+1}{4\pi} \int_{\theta,\varphi} \hat{w}_s(\vartheta,\varphi)\sin\vartheta d\vartheta d\varphi = \hat{I}\,.$$

Here $\hat{I}$ is the identity matrix. The density matrix operator $\hat{\rho}$ may then be expressed using the kernel Eq. (4.50) via the inverse transformation

$$\hat{\rho} = \frac{2S+1}{4\pi} \int_{\theta,\varphi} \hat{w}_s(\vartheta,\varphi) W^{-s}(\vartheta,\varphi)\sin\vartheta d\vartheta d\varphi, \tag{4.51}$$

i.e., the mapping given by Eq.(4.49) is bijective. The function $W^{-s}(\vartheta,\varphi)$ now allows us to calculate the *average* value of an arbitrary spin operator $\hat{A}$ in the same way as the corresponding function for translational motion because the $W^{-s}(\vartheta,\varphi)$ are covariant under rotations and provide the overlap relation (which essentially follows from Eq. (4.40) above)

$$\begin{aligned}\left\langle \hat{A} \right\rangle &= \mathrm{Tr}\left\{ \hat{\rho}\hat{A} \right\} \\ &= \frac{2S+1}{4\pi} \int\limits_{\theta,\varphi} A^{s}(\vartheta,\varphi) W^{-s}(\vartheta,\varphi,t) \sin\vartheta d\vartheta d\varphi\end{aligned}, \tag{4.52}$$

where

$$A^{s}(\vartheta,\varphi) = \mathrm{Tr}\left\{ \hat{A}\hat{w}_{s}(\vartheta,\varphi) \right\} \tag{4.53}$$

is the Weyl symbol of the operator $\hat{A}$ (see, e.g., [8]). Substituting Eqs. (4.47) and (4.50) into Eq. (4.49), we have after some algebra the representation distribution

$$\begin{aligned}\mathrm{Tr}\,\hat{\rho}\hat{w}_{s} &= W^{s}(\vartheta,\varphi) \\ &= \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \left(C_{S,S,L,0}^{S,S} \right)^{-s} a_{L,M} Y_{L,M}^{*}(\vartheta,\varphi)\end{aligned} \tag{4.54}$$

where the statistical moment tensors $a_{L,M}$ (so called because the operator $\hat{w}_{s}(\vartheta,\varphi)$ is effectively the analogue of Moyal's characteristic function operator $\hat{M}(\tau,\theta) = \exp\left[i\left(\tau\hat{p} + \theta\hat{x} \right) \right]$) are defined by Eq. (4.48) and we have noted that [28]

$$\mathrm{Tr}\left\{ \hat{T}_{L',M'}^{(S)} \hat{T}_{L,M}^{(S)} \right\} = (-1)^{M'} \delta_{L',L} \delta_{M',-M} . \tag{4.55}$$

The parameter values $s = 0$ and $s = \pm 1$ correspond to the Stratonovich [9] and Beresin [19] contravariant and covariant functions, respectively (the latter are directly related to the *P*- and *Q*-symbols which appear naturally in the coherent state representation; see Ref. 11 for a review). In this Chapter [24], we consider $s = 1$ only ($s = -1$ and $s = 0$ can be treated in like manner); thus we omit everywhere the superscript $-s$ in $W^{-s}(\vartheta,\varphi)$ and subscript s in $\hat{w}_{s}(\vartheta,\varphi)$.

Equation (4.54) for the Wigner function $W^{s}(\vartheta,\varphi)$ is very similar to those introduced by Agarwal et al. [20,29,30], however, in the present form it allows one to readily evaluate equilibrium quasiprobability distributions. In particular problems it can be considerably simplified. As an example, we obtain explicit

equations for the Wigner function of a system with Hamiltonian given by Eq. (3.18). Here the matrix elements $\rho_{m,m'}$ of the equilibrium spin density matrix

$$\hat{\rho}_{eq} = \frac{e^{-\beta \hat{H}_S}}{Z_S} \tag{4.56}$$

are given by

$$\rho_{m,m'} = \frac{\delta_{m,m'} e^{\sigma m^2 + \xi m}}{Z_S}. \tag{4.57}$$

where the partition function Z_S is given by the finite sum

$$Z_S = \sum_{m=-S}^{S} e^{\sigma m^2 + \xi m}. \tag{4.58}$$

Due to the symmetry about the z axis, the general Eq. (4.54) can be simplified yielding the quasiprobability density $W_S(\vartheta)$ for axial symmetry in the series form

$$W_S(\vartheta) = \sum_{L=0}^{2S} \sqrt{\frac{2L+1}{2S+1}} C^{S,S}_{S,S,L,0} a_{L,0} P_L(\cos\vartheta), \tag{4.59}$$

where we have noted that

$$Y_{L,0}(\vartheta,\varphi) = \sqrt{\frac{(2L+1)}{4\pi}} P_L(\cos\vartheta) \tag{4.60}$$

and $P_L(z)$ is the Legendre polynomial [31] of order L. Using Eqs. (4.48) and (3.20), and the explicit form for the Clebsch-Gordan coefficient $C^{S,S}_{S,S,L,0}$, viz.

$$C^{S,S}_{S,S,L,0} = (2S)! \sqrt{\frac{2S+1}{(2S-L)!(2S+L+1)!}},$$

we obtain

$$W_S(\vartheta) = \frac{(2S)!}{Z_S} \sum_{L=0}^{2S} \sum_{m=-S}^{S} \frac{(2L+1) C^{S,m}_{S,m;L,0} P_L(\cos\vartheta) e^{\sigma m^2 + \xi m}}{\sqrt{(2S+1)(2S-L)!(2S+L+1)!}}. \tag{4.61}$$

Equation (4.61) can be presented in an equivalent form which emphasises the relationship with Fourier series representation of the associated classical Boltzmann distribution, namely

$$W_S(\vartheta) = \sum_{L=0}^{2S} (L+1/2) \langle P_L \rangle_{eq} P_L(\cos\vartheta). \tag{4.62}$$

Here $\langle P_L \rangle_{eq}$ is the equilibrium value of the Legendre polynomial P_L given by

$$\left\langle P_L \right\rangle_{eq} = \left(S+\tfrac{1}{2}\right)\int_0^{\pi} P_L(\cos\vartheta) W_{eq}(\vartheta)\sin\vartheta d\vartheta$$
$$= \frac{\sqrt{2S+1}(2S)!}{Z_S\sqrt{(2S-L)!(2S+L+1)!}}\sum_{m=-S}^{S} C_{S,m,L,0}^{S,m} e^{\sigma m^2+\xi m},$$

where the explicit equation for the Clebsch-Gordan coefficient $C_{S,m,L,0}^{S,m}$ is

$$C_{S,m,L,0}^{S,m} = (S+m)!(S-m)!(L!)^2\sqrt{\frac{(2S+1)(2S-L)!}{(2S+L+1)!}}$$
$$\times\sum_{n=0}^{L}\frac{(-1)^n}{\left[(L-n)!\right]^2(n!)^2(S-m-n)!(m+S+n-L)!}.$$

For the particular values of S = 1/2, 1, 3/2, 2, 5/2, and 3, Eq. (4.61) yields the closed form results

$$W_{1/2}(\vartheta) = \frac{e^{\sigma/4}}{Z_{1/2}} f_\xi(\vartheta),$$

$$W_1(\vartheta) = \frac{e^{\sigma}}{Z_1} f_\xi^2(\vartheta)\left[1+\frac{1}{2}\left(e^{-\sigma}-1\right)\frac{\sin^2\vartheta}{f_\xi^2(\vartheta)}\right],$$

$$W_{3/2}(\vartheta) = \frac{e^{9\sigma/4}}{Z_{3/2}} f_\xi^3(\vartheta)\left[1+\frac{3}{4}\left(e^{-2\sigma}-1\right)\frac{\sin^2\vartheta}{f_\xi^2(\vartheta)}\right],$$

$$W_2(\vartheta) = \frac{e^{4\sigma}}{Z_2} f_\xi^4(\vartheta)\left[1+\left(e^{-3\sigma}-1\right)\frac{\sin^2\vartheta}{f_\xi^2(\vartheta)}+\frac{1}{8}\left(3e^{-4\sigma}-4e^{-3\sigma}+1\right)\frac{\sin^4\vartheta}{f_\xi^4(\vartheta)}\right],$$

$$W_{5/2}(\vartheta) = \frac{e^{25\sigma/4}}{Z_{5/2}} f_\xi^5(\vartheta)\left[1+\frac{5}{4}\left(e^{-4\sigma}-1\right)\frac{\sin^2\vartheta}{f_\xi^2(\vartheta)}+\frac{5}{16}\left(2e^{-6\sigma}-3e^{-4\sigma}+1\right)\frac{\sin^4\vartheta}{f_\xi^4(\vartheta)}\right],$$

$$W_3(\vartheta) = \frac{e^{9\sigma}}{Z_3} f_\xi^6(\vartheta)\left[1+\left(e^{-5\sigma}-1\right)\frac{\sin^2\vartheta}{f_\xi^2(\vartheta)}+\frac{3}{16}\left(5e^{-8\sigma}-8e^{-5\sigma}+3\right)\frac{\sin^4\vartheta}{f_\xi^4(\vartheta)}\right.$$
$$\left.+\frac{1}{32}\left(10e^{-9\sigma}-15e^{-8\sigma}+6e^{-5\sigma}-1\right)\frac{\sin^6\vartheta}{f_\xi^6(\vartheta)}\right],$$

where

$$f_\xi(\vartheta) = \cosh\frac{\xi}{2}+\sinh\frac{\xi}{2}\cos\vartheta. \qquad (4.63)$$

Furthermore, for arbitrary $S >> 1$, the leading terms of the series in $\sin^2\vartheta / f_\xi^2(\vartheta)$ for the equilibrium distribution $W_S(\vartheta)$ are given by

$$W_S(\vartheta) = \frac{e^{S^2\sigma}}{Z_S} f_\xi^{2S}(\vartheta)\left\{1 + \frac{S}{2}\left[e^{-(2S-1)\sigma} - 1\right]\frac{\sin^2\vartheta}{f_\xi^2(\vartheta)} + \frac{S}{16}\left[(2S-1)e^{-4(S-1)\sigma} - 4(S-1)e^{-(2S-1)\sigma} + 2S - 3\right]\frac{\sin^4\vartheta}{f_\xi^4(\vartheta)} + \ldots\right\}. \tag{4.64}$$

In particular, Eqs. (4.63) and (4.64) allow one to readily evaluate $W_S(\vartheta)$ at its *maxima* which occur at $\vartheta = 0$ and $\vartheta = \pi$ meaning classically that the spins are concentrated at the bottom of the wells where the minima of the potential occur, the saddle point is at $\vartheta = \cos^{-1}(-\xi'/2\sigma')$, we have

$$W_S\begin{pmatrix}0\\ \pi\end{pmatrix} = \frac{1}{Z_S} e^{\pm S\xi + S^2\sigma}. \tag{4.65}$$

so that the maxima are unequal in height due to the biasing effect of the external field. In the classical limit ($S \to \infty$, $\xi \to 0$, $\sigma \to 0$, $\xi S = const = \xi'$, $\sigma S^2 = const = \sigma'$), the equilibrium distribution $W_S(\vartheta)$ tends to the Boltzmann distribution

$$\left(S + \tfrac{1}{2}\right) W_S(\vartheta) \to \frac{e^{\xi'\cos\vartheta + \sigma'\cos^2\vartheta}}{Z_{cl}},$$

where

$$Z_{cl} = \frac{1}{2}\sqrt{\frac{\pi}{\sigma'}} e^{-h^2\sigma'}\left\{\mathrm{erf}i[(1+h)\sqrt{\sigma'}] + \mathrm{erf}i[(1-h)\sqrt{\sigma'}]\right\}$$

is the classical partition function, $h = \xi'/2\sigma'$, and

$$\mathrm{erf}i(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{t^2} dt \tag{4.66}$$

is the error function of imaginary argument [31]. The distribution $\left(S + \tfrac{1}{2}\right) W_S(\vartheta)$ is shown in Figure IV.I. below.

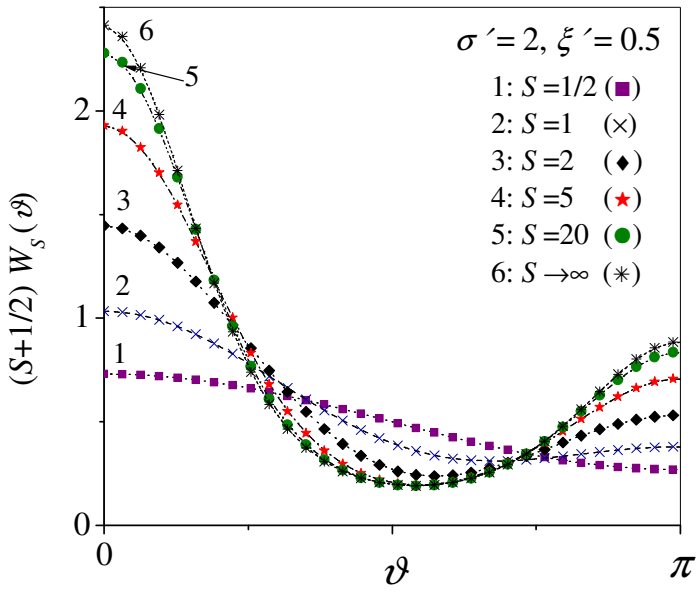

Figure IV.I The distribution $\left(S+\frac{1}{2}\right)W_S(\vartheta)$ for $\sigma'=2$, $\xi'=0.5$, and various values of *S*.

For $\sigma=0$, when the Hamiltonian becomes $\beta\hat{H}_S=-\xi\hat{S}_Z$, Eq. (4.61) reduces to the known results for a spin in a uniform external magnetic field [13,14]

$$W_S(\vartheta)=\frac{\sinh(\xi/2)f_\xi^{2S}(\vartheta)}{\sinh\left[(S+1/2)\xi\right]}. \tag{4.67}$$

The distribution $W_S(\vartheta)$ given by Eq. (4.67) is the *spin analogue* of the Wigner quasiprobability distribution function $W(x,p)$ for a *quantum Brownian oscillator* [32] (see Chapter V) namely

$$W(x,p)=\frac{e^{-\frac{m}{\hbar\omega_0}\tanh\frac{\beta\hbar\omega_0}{2}\left(\omega_0^2x^2+p^2/m^2\right)}}{Z'},$$

where

$$Z'=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-\frac{m}{\hbar\omega_0}\tanh\frac{\beta\hbar\omega_0}{2}\left(\omega_0^2x^2+p^2/m^2\right)}dpdx$$

$$=\pi\hbar\coth\frac{\beta\hbar\omega_0}{2}.$$

In the low temperature limit ($\xi' + 2\sigma' >> 1$), the series expression for $W_S(\vartheta)$ in Eq. (4.61) can be approximated to a very high degree of accuracy in the vicinity of the maxima at $\vartheta = 0$ and $\vartheta = \pi$ as

$$W_S(\vartheta) \approx \frac{e^{-\sigma S(S+1)}}{Z_S} f^{2S}_{\xi+(2S+1)\sigma}(\vartheta), \quad (\vartheta \le 1), \tag{4.68}$$

and

$$W_S(\vartheta) \approx \frac{e^{-\sigma S(S+1)}}{Z_S} f^{2S}_{\xi-(2S+1)\sigma}(\vartheta), \quad (\pi - \vartheta \le 1), \tag{4.69}$$

respectively (see Figure IV.II below). (This is analogous to replacing the potential $V(x)$ in the vicinity of a minimum by a parabola in the case of translational motion). The interpretation of Eqs. (4.68) and (4.69) is that in the vicinity of the maxima at $\vartheta = 0$ and $\vartheta = \pi$, the dynamics of the spin at low temperatures constitutes precession in the effective magnetic field $H^{\pm} = (\beta\gamma\hbar)^{-1}\left[\pm\xi + (2S+1)\sigma\right]$.

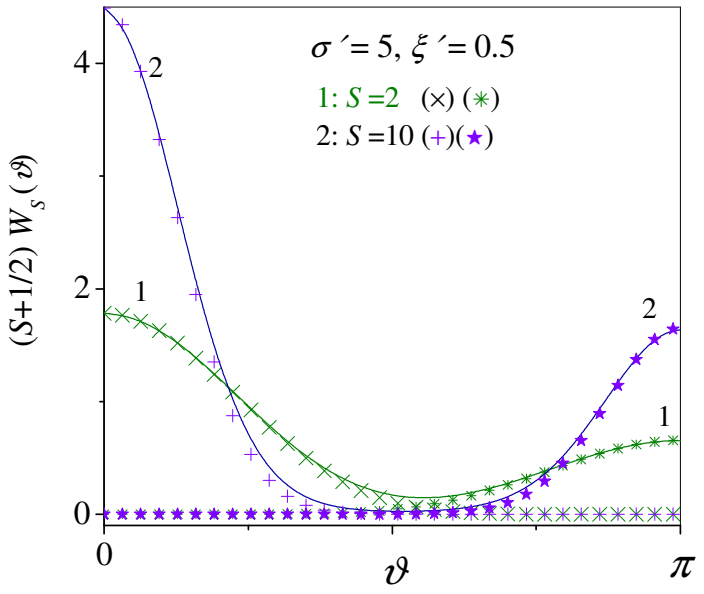

Figure IV.II The distribution $\left(S + \frac{1}{2}\right) W_S(\vartheta)$ (solid lines) for $\sigma' = 5$, $\xi' = 0.5$, and S = 2 and 10. Crosses (× and +): Eq. (4.68). Stars (✳ and ★): Eq. (4.69).

Thus as an illustration of the power and generality of Wigner's method we have summarized how [24] the representation space method which formally represents the quantum mechanics of spins as a statistical theory on the classical configuration space of polar angles (ϑ,φ) (which are now the canonical variables) may be used to construct equilibrium quasiprobability density functions for model spin Hamiltonians. These quasiprobability equilibrium densities are important in quantum tunnelling phenomena in ferromagnetic nanoparticles [33] and molecular magnets [34] and also in the crossover region between reversal of the magnetization of these particles by thermal agitation and reversal by macroscopic quantum tunnelling which is of current topical interest [35]. For example by analogy with the original classical calculation of Néel [36] the simplest description of quantum effects in the magnetization reversal time of a nanoparticle would be provided by the inverse escape rate from the wells of the magnetocrystalline and external field potential as calculated by quantum transition state theory (TST) [37] (which will be summarized for point particles in Chapter V). TST ignores the disturbance to the equilibrium distribution in the wells created by the loss of the magnetization due to escape over the barrier and so involves the equilibrium distribution only as that is assumed to prevail everywhere. However the equilibrium quantum distribution is also essential in the inclusion of *nonequilibrium* effects in the quantum escape rate. In this situation a quantum master equation describing the time evolution of the quasiprobability density in the representation space is required in order to generalize the escape rate calculations pioneered by Kramers [38] for point particles and by Brown [39,40] for single domain ferromagnetic particles in the classical case using the Fokker-Planck equation. Here the diffusion coefficients are calculated (see Chapter II) using Einstein's imposition [40] of the Maxwell-Boltzmann distribution as the equilibrium solution of that equation. In like manner by postulating [41-44] a Kramers–Moyal like expansion truncated at the second term (as in the Fokker-Planck equation) for the collision term in the quantum master equation, the diffusion coefficients in the expansion may be calculated (see Chapter VI) by requiring that the equilibrium quasiprobability distribution in the representation space renders the collision term zero. In the present context this has been illustrated for the particular case of a spin in a uniform field in Ref. [45] and

indicates clearly how all the solution methods developed for the classical Fokker-Planck equation carry over seamlessly to the quantum case just as the corresponding solutions for particles [41-44] (which are summarized in Chapter VII).

This concludes our survey of the early fundamental contributions to phase space quantum mechanics.

APPENDIX IV

Appendix IV.I: Calculation of the marginal distributions

The details of the calculation of the marginal distribution for the quantum mechanical probability for the various values of x and p are as follows. We have with an obvious change of variable, i.e.

$$y_1 = \frac{2}{\hbar} y$$

so

$$dy_1 = \frac{2}{\hbar} dy \, .$$

Hence

$$W(x,p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi^* \left(x + \frac{\hbar}{2} y \right) \psi \left(x - \frac{\hbar}{2} y \right) e^{ipy} dy \, . \quad (4.70)$$

The marginal distribution [46] of the displacement X is then got in the usual way by integrating out the momentum or P dependence. The capital letters are used to denote random variables. We have

$$\int_{-\infty}^{\infty} W(x,p)\, dp = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* \left(x + \frac{\hbar}{2} y \right) \psi \left(x - \frac{\hbar}{2} y \right) e^{ipy} dy dp \quad (4.71)$$

Now using the definition of the delta function

$$\delta(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ipy} dp \quad (4.72)$$

and its sifting property

$$\int_{-\infty}^{\infty} f(y)\, \delta(y-a)\, dy = f(a) \quad (4.73)$$

we get

$$\begin{aligned}\int_{-\infty}^{\infty} W(x,p)\,dp &= \int_{-\infty}^{\infty} \psi^*\left(x+\frac{\hbar}{2}y\right)\psi\left(x-\frac{\hbar}{2}y\right)\delta(y)\,dy \\ &= \psi^*(x)\psi(x) \\ &= \left|\psi(x)\right|^2 .\end{aligned} \tag{4.74}$$

Note that this Eq. (4.74) is the true probability distribution rather than a quasi-probability.

The quantum mechanical probability for the momentum may be found by integrating *W(x,p)* with respect to *x*. We have

$$\int_{-\infty}^{\infty} W(x,p)dx = \int_{-\infty}^{\infty}\frac{dx}{2\pi}\int_{-\infty}^{\infty}\psi^*\left(x+\frac{\hbar}{2}y\right)\psi\left(x-\frac{\hbar}{2}y\right)e^{ipy}dy \tag{4.75}$$

We introduce the variables *u* and *v* in the double integral such that

$$u = x+\frac{\hbar}{2}y$$

$$v = x-\frac{\hbar}{2}y$$

which implies that

$$x = \frac{1}{2}(u+v)$$

$$y = \frac{1}{\hbar}(u-v)$$

and use the following formula for the change of variables in the double integral [47]

$$\iint_R f(x,y)\,dx\,dy = \iint_{R^*} f\left(x(u,v),y(u,v)\right)\left|J\right|du\,dv \tag{4.76}$$

where *J* is the Jacobian and is defined as

$$J = \frac{\partial(x,y)}{\partial(u,v)} = \begin{vmatrix}\dfrac{\partial x}{\partial u} & \dfrac{\partial x}{\partial v}\\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v}\end{vmatrix}.$$

On substituting the values of the derivatives into the determinant, the modulus of the Jacobian has the value of $1/\hbar$ and hence we get

$$\int_{-\infty}^{\infty} W(x,p)dx = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\psi^*(u)\psi(v)}{2\pi\hbar}e^{i\frac{p}{\hbar}(u-v)}du\,dv \tag{4.77}$$

The double integral on the right hand side of Eq. (4.77) can be written as

$$\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi^{*}(u)e^{i\frac{p}{\hbar}u}du\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(v)e^{-i\frac{p}{\hbar}v}dv$$

and since v is a dummy variable it is clearly equal to

$$\frac{1}{2\pi\hbar}\left|\int_{-\infty}^{\infty}\psi(u)e^{i\frac{p}{\hbar}u}du\right|^{2}.$$

This may also be written as the product of the Fourier transform of the wave function $\psi(x)$ viz.

$$\int_{-\infty}^{\infty}W(x,p)dx=\tilde{\psi}^{*}(p)\tilde{\psi}(p).$$

See for example Mandel and Wolf [48], p.542. Hence we have the symmetrical relations

$$\int_{-\infty}^{\infty}W(x,p)dp=\psi^{*}(x)\psi(x)$$

and

$$\int_{-\infty}^{\infty}W(x,p)dx=\tilde{\psi}^{*}(p)\tilde{\psi}(p)$$

where the Fourier transform pair of the wave function are

$$\psi(x)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\tilde{\psi}(p)e^{-i\frac{p}{\hbar}x}dp$$
$$\tilde{\psi}(p)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x)e^{-i\frac{x}{\hbar}p}dx$$

.

Appendix IV.II: Proof of the Baker-Campbell-Hausdorff identity

The Baker-Campbell-Hausdorff identity arises from the fact that in quantum mechanics it is not true to say that $e^{\hat{A}+\hat{B}}=e^{\hat{A}}e^{\hat{B}}$, where $\hat{A}$ and $\hat{B}$ are operators. However suppose that the operators $\hat{A}$ and $\hat{B}$ commute with their commutator, i.e.,

$$\left[\hat{B},\left[\hat{A},\hat{B}\right]\right]=\left[\hat{A},\left[\hat{A},\hat{B}\right]\right]=0 \qquad (4.78)$$

which is the case for the position and momentum operators $\hat{q}$ and $\hat{p}$.

To prove the Baker-Campbell-Hausdorff identity namely

$$\exp\left(\hat{\mathrm{A}}+\hat{\mathrm{B}}\right)=\exp\left(\hat{\mathrm{A}}\right)\exp\left(\hat{\mathrm{B}}\right)\exp\left\{\frac{1}{2}\left(\left[\hat{\mathrm{B}},\hat{\mathrm{A}}\right]\right)\right\}, \qquad (4.79)$$

we [49] consider an operator $\hat{F}(s)$ depending on the real parameter *s*:

$$\hat{F}(s) = e^{\hat{A}s} e^{\hat{B}s}. \tag{4.80}$$

The derivative of $\hat{F}$ with respect to *s* is

$$\begin{aligned} \frac{d\hat{F}}{ds} &= \left(\frac{de^{\hat{A}s}}{ds}\right) e^{\hat{B}s} + e^{\hat{A}s}\left(\frac{de^{\hat{B}s}}{ds}\right) \\ &= \hat{A}e^{\hat{A}s}e^{\hat{B}s} + e^{\hat{A}s}Be^{\hat{B}s} \\ &= \hat{A}e^{\hat{A}s}e^{\hat{B}s} + e^{\hat{A}s}\hat{B}e^{-\hat{A}s}e^{\hat{A}s}e^{\hat{B}s} \\ &= \left(\hat{A} + e^{\hat{A}s}\hat{B}e^{-\hat{A}s}\right)\hat{F}(s) \end{aligned} \tag{4.81}$$

Next we use the property that for every analytic function $F(x)$

$$\left[\hat{A}, F(\hat{B})\right] = \left[\hat{A}, \hat{B}\right] F'(\hat{B}) \tag{4.82}$$

where $F'(x)$ denotes the derivative of $F(x)$ (where the property of the operators is as above i.e. Eq. (4.78)). We can write

$$\begin{aligned} \left[e^{\hat{A}s}, \hat{B}\right] &= -\left[\hat{B}, e^{\hat{A}s}\right] \\ &= -s\left[\hat{B}, \hat{A}\right] e^{\hat{A}s} \\ &= s\left[\hat{A}, \hat{B}\right] e^{\hat{A}s}. \end{aligned} \tag{4.83}$$

Therefore,

$$e^{\hat{A}s}\hat{B} = \hat{B}e^{\hat{A}s} + s\left[\hat{A}, \hat{B}\right] e^{\hat{A}s} \tag{4.84}$$

and

$$e^{\hat{A}s}\hat{B}e^{-\hat{A}s} = \hat{B} + s\left[\hat{A}, \hat{B}\right]. \tag{4.85}$$

On substitution of Eqs. (4.84) and (4.85) into Eq. (4.81) we obtain

$$\frac{d\hat{F}}{ds} = \left(\hat{A} + \hat{B} + s\left[\hat{A}, \hat{B}\right]\right)\hat{F}(s). \tag{4.86}$$

Since $\hat{A} + \hat{B}$ and $\left[\hat{A}, \hat{B}\right]$ commute, we can integrate this differential equation. This yields

$$\hat{F}(s) = \hat{F}(0) e^{\left(\hat{A}+\hat{B}\right)s + \left[\hat{A},\hat{B}\right]s^2/2}. \tag{4.87}$$

Setting $s = 0$ (in Eq. (4.80)) we obtain

$$\begin{aligned} \hat{F}(0) &= e^{\hat{A}.0} e^{\hat{B}.0} \\ &= 1 \end{aligned} \tag{4.88}$$

so that Eq. (4.87) becomes

$$\hat{F}(s) = e^{\left(\hat{A}+\hat{B}\right)s+\left[\hat{A},\hat{B}\right]s^2/2}. \tag{4.89}$$

Now set $s=1$ in Eqs. (4.80) and (4.89) gives

$$e^{\hat{A}}e^{\hat{B}} = e^{\left(\hat{A}+\hat{B}\right)+\left[\hat{A},\hat{B}\right]1/2}. \tag{4.90}$$

This is the Baker-Campbell-Hausdorff identity and is entirely equivalent to that given above in Eq. (4.79) because $\left[\hat{\mathrm{A}},\hat{\mathrm{B}}\right] = -\left[\hat{\mathrm{B}},\hat{\mathrm{A}}\right]$ and the fact that the commutator is a number.

Appendix IV.III: Proof of how the operator exp(-*ilp*$_x$/*ħ*) describes a displacement of a distance *l* along the *x*-direction

Here we show the proof of

$$e^{i\mu\hat{p}}\psi(x) = \psi(x+\mu\hbar). \tag{4.91}$$

We do so [49] by searching for an operator $\hat{A}$ acting on a wave function $\psi(x)$, with

$$\hat{A}\psi(x) = \psi(x-l). \tag{4.92}$$

Using the Taylor expansion, we can write

$$\psi(x-l) = \psi(x) - l\psi'(x) + \frac{l^2}{2!}\psi''(x) + \cdots + \frac{(-l)^n}{n!}\psi^{(n)}(x) + \cdots \tag{4.93}$$

In the *x*-representation the momentum operator acts as

$$\hat{p}_x\psi(x) = -i\hbar\frac{\partial\psi(x)}{\partial x}.$$

Therefore

$$\begin{aligned}\psi(x-l) &= \psi(x) - \frac{il}{\hbar}\hat{p}_x\psi(x) + \frac{1}{2!}\left(\frac{il}{\hbar}\right)^2\hat{p}_x^2\psi(x) + \cdots + \frac{1}{n!}\left(\frac{-il}{\hbar}\right)^n\hat{p}_x^n\psi(x) + \cdots \\ &= e^{-\frac{il\hat{p}_x}{\hbar}}\psi(x)\end{aligned} \tag{4.94}$$

which is equivalent to Eq. (4.91) with $l = -\mu\hbar$.

Appendix IV.IV: Calculation of the moments i.e. observables via the derivatives of the characteristic function

Here we simply treat *x* and *p* as *c*-numbers and regard $W(x,p)$ as a joint probability distribution in the random variable *X,P.* Hence we have from the usual

definition of the characteristic function as the Fourier transform over the probability density function $W(x,p)$.

At this stage it is also useful to introduce the characteristic function of the Wigner distribution function. The characteristic function is the (in this case) the two dimensional Fourier transform of *W* and it is

$$\chi_{\hat{x},\hat{p}}(\mu,\nu) = \left\langle e^{i(\nu\hat{x}+\mu\hat{p})} \right\rangle$$
$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\psi^*\left(x+\frac{y}{2}\right)\psi\left(x-\frac{y}{2}\right)e^{-i\frac{y}{\hbar}p}dy\right)e^{i(\nu x+\mu p)}dx\,dp. \tag{4.95}$$

Now considering the integration with respect to *p*

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}e^{-i\frac{y}{\hbar}p}e^{i\tau p}dp = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}e^{i\left(\mu-\frac{y}{\hbar}\right)p}dp$$
$$= \frac{1}{\hbar}\delta\left(\mu-\frac{y}{\hbar}\right) \tag{4.96}$$

yielding

$$\chi_{\hat{x},\hat{p}}(\mu,\nu) = \frac{1}{\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*\left(x+\frac{y}{2}\right)\psi\left(x-\frac{y}{2}\right)\delta\left(\mu-\frac{y}{\hbar}\right)e^{i\nu x}dx\,dy. \tag{4.97}$$

Clearly this is going to reduce to an integral involving *x* only. In order to avoid difficulties with delta functions, we should change the variable in the delta function integral above, namely

$$\mu-\frac{y}{\hbar} = y_1$$
$$\Rightarrow dy = -\hbar\,dy_1 \quad .$$

Therefore

$$\chi_{\hat{x},\hat{p}}(\mu,\nu) = \int_{-\infty}^{\infty}\psi^*\left(x+\frac{\hbar\mu}{2}\right)\psi\left(x-\frac{\hbar\mu}{2}\right)e^{i\nu x}dx \tag{4.98}$$

This is the characteristic function of the Wigner distribution. We can use this to evaluate observables.

Consider

$$\frac{\partial\chi_{\hat{x},\hat{p}}(\mu,\nu)}{\partial\nu} = \int_{-\infty}^{\infty}\psi^*\left(x+\frac{\hbar\mu}{2}\right)\psi\left(x-\frac{\hbar\mu}{2}\right)i\,x\,e^{i\nu x}dx\,. \tag{4.99}$$

Clearly

$$\left(\frac{\partial \chi_{\hat{x},\hat{p}}}{\partial \nu}\right)_{\mu=0,\nu=0} = i\int_{-\infty}^{\infty} x\psi^*(x)\psi(x)dx = i\langle x\rangle \tag{4.100}$$

which is the correct quantum mechanical average. In like manner

$$\frac{\partial \chi_{\hat{x},\hat{p}}}{\partial \mu} = \int_{-\infty}^{\infty}\left(\psi^*\frac{\partial \psi}{\partial t} + \psi\frac{\partial \psi^*}{\partial t}\right)e^{i\nu x}dx \tag{4.101}$$

or on introducing

$$u = x \pm \frac{\hbar\mu}{2}$$

we have

$$\frac{\partial \chi_{\hat{x},\hat{p}}}{\partial \mu} = \int_{-\infty}^{\infty}\left(\psi^*\frac{\hbar}{2}\frac{\partial \psi}{\partial u} + \psi\left(-\frac{\hbar}{2}\right)\frac{\partial \psi^*}{\partial u}\right)e^{i\nu x}dx$$

and if $\mu = 0$, $u = x$ and also set $\nu = 0$ we get

$$\left(\frac{\partial \chi_{\hat{x},\hat{p}}}{\partial \mu}\right)_{\mu=0,\nu=0} = \frac{\hbar}{2}\int_{-\infty}^{\infty}\left(\psi^*\frac{\partial \psi}{\partial x} - \psi\frac{\partial \psi^*}{\partial x}\right)dx. \tag{4.102}$$

Now, recalling that

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* p \psi \, dx$$

$$p = -i\hbar\frac{\partial}{\partial x}$$

we have

$$\langle p\rangle = -i\hbar\int_{-\infty}^{\infty}\psi^*\frac{\partial \psi}{\partial x}dx$$

$$\langle p^*\rangle = i\hbar\int_{-\infty}^{\infty}\psi\frac{\partial \psi^*}{\partial x}dx$$

$$\langle p\rangle = \langle p^*\rangle = \langle p\rangle^*$$

because p is observable and therefore real.

We have

$$\left(\frac{\partial \chi_{\hat{x},\hat{p}}}{\partial \mu}\right)_{\mu=0,\nu=0} = \frac{i}{2}\langle p\rangle + \frac{i}{2}\langle p^*\rangle = i\langle p\rangle. \tag{4.103}$$

Hence it follows that just as in conventional statistics we can evaluate any desired quantum mechanical average from the characteristic function of the Wigner distribution.

Appendix IV.V: Derivation of the evolution equation for Wigner's distribution function

The calculation of the time evolution equation for Wigner's distribution function, i.e. Eq. (4.2) that is (for a pure state)

$$W(x,p)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\psi^{*}\left(x+\frac{y}{2}\right)\psi\left(x-\frac{y}{2}\right)e^{-ipy/\hbar}dy \tag{4.104}$$

which is an equivalent definition to that given by Hillery et al. [46] (their equation (2.2a)) as

$$P_W(x,p)=\frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\psi^{*}(x+y)\psi(x-y)e^{2ipy/\hbar}dy\,. \tag{4.105}$$

This equivalence can be demonstrated through the substitution of the variable y with

$$y=\frac{y_1}{2}\ \text{and hence}\ dy=\frac{dy_1}{2}$$

yielding

$$P_W(x,p)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\psi^{*}\left(x+\frac{y_1}{2}\right)\psi\left(x-\frac{y_1}{2}\right)e^{-ipy_1/\hbar}dy_1 \tag{4.106}$$

which is the same as the Wigner distribution $W(x,p,t)$ defined above. In deriving the time dependence of the Wigner function we follow Hillery et al. [46] and proceed using the notation of Eq. (4.105).

Taking the derivative of w.r.t. t we must remember that $\psi(x+y)$ is also a function of t, since we are using $\psi(x+y)$ as short notation for $\psi(x+y,t)$ and similarly for $\psi(x-y,t)$. Hence using the product rule of differentiation we get

$$\frac{\partial P_W(x,p)}{\partial t}=\frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\left[\psi^{*}(x+y)\frac{\partial\psi(x-y)}{\partial t}+\frac{\partial\psi^{*}(x+y)}{\partial t}\psi(x-y)\right]e^{2ipy/\hbar}dy. \tag{4.107}$$

Since the function ψ must evolve according to the Schrödinger equation (Eq. (4.3)) we can make the following substitutions:

$$-i\hbar\frac{\partial\psi^*(x,t)}{\partial t}=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi^*(x,t) \qquad (4.108)$$

and correspondingly

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi(x,t) \qquad (4.109)$$

where the variable x is replaced by the variable $x+y$ and $x-y$ respectively. Thus we obtain

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

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

(4.110)

The time evolution of $P_W(x,p)$ may be decomposed into two parts because the Schrödinger equation is linear. Thus we can consider the free kinetic energy and potential energy terms separately. In the first part we consider the contribution from the free kinetic energy term and let the potential energy term $V(x)=0$ obtaining

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

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

(4.111)

The integral is with respect to y so

$$\frac{\partial^2\psi(x-y)}{\partial(x-y)^2} \Rightarrow \frac{\partial^2\psi(x-y)}{\partial y^2} \tag{4.112}$$

and similarly for $x+y$, i.e.

$$\frac{\partial P_W(x,p)}{\partial t} = -\frac{i}{2m\pi}\int_{-\infty}^{\infty}\left[\psi(x-y)\frac{\partial^2\psi^*(x+y)}{\partial y^2} - \psi^*(x+y)\frac{\partial^2\psi(x-y)}{\partial y^2}\right]e^{2ipy/\hbar}dy. \tag{4.113}$$

Equation (4.113) is in exact accordance with Hillery et al. [46], (their equation (2.48)). We now use the following two operators

$$y = \frac{\hbar}{2i}\frac{\partial}{\partial p}, \quad p = -\frac{\hbar}{2i}\frac{\partial}{\partial y} \tag{4.114}$$

so that we may rewrite Eq. (4.113) in accordance with Hillery et al., equation (2.49)

$$\begin{aligned}\frac{\partial P_W(x,p)}{\partial t} &= -\frac{i}{2m\pi}\int_{-\infty}^{\infty}\left[-\psi(x-y)\frac{\hbar}{2i}\frac{\partial^2\psi^*(x+y)}{\partial y^2} + \psi^*(x+y)\frac{\hbar}{2i}\frac{\partial^2\psi(x-y)}{\partial y^2}\right]\left(-\frac{2i}{\hbar}\right)e^{2ipy/\hbar}dy \\ &= -\frac{i}{2m\pi}\left(-\frac{2i}{\hbar}\right)\int_{-\infty}^{\infty}\left[\psi(x-y)\,p\frac{\partial\psi^*(x+y)}{\partial y} - \psi^*(x+y)\,p\frac{\partial\psi(x-y)}{\partial y}\right]e^{2ipy/\hbar}dy \\ &= -\frac{p}{m\pi\hbar}\int_{-\infty}^{\infty}\left[\psi(x-y)\frac{\partial\psi^*(x+y)}{\partial y} - \psi^*(x+y)\frac{\partial\psi(x-y)}{\partial y}\right]e^{2ipy/\hbar}dy.\end{aligned} \tag{4.115}$$

Next we notice that

$$\begin{aligned}\frac{\partial P_W(x,p)}{\partial t} &= \frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\frac{\partial}{\partial y}\left(\psi^*(x+y)\psi(x-y)\right)e^{2ipy/\hbar}dy \\ &= \frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\left[\psi(x-y)\frac{\partial\psi^*(x+y)}{\partial y} - \psi^*(x+y)\frac{\partial\psi(x-y)}{\partial y}\right]e^{2ipy/\hbar}dy.\end{aligned} \tag{4.116}$$

Thus we can write Eq. (4.115) as

$$\frac{\partial P_W}{\partial t} = -\frac{p}{m}\frac{\partial P_W}{\partial t}. \tag{4.117}$$

Taking advantage of the functional dependence of $\psi(x,t)$ we can change dy to dx and switching back to our equivalent notation, $W(x,p,t)$ as per Eq. (4.106), we have

$$\frac{\partial W}{\partial t} = -\frac{p}{m}\frac{\partial W}{\partial x}. \tag{4.118}$$

This equation is identical to the classical Liouville equation in the force-free case and is in accordance with Hillery et al.

Next we calculate the contribution due to the potential energy term. In general we have

$$\frac{\partial P_W(x,p)}{\partial t} = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\left\{\psi^*(x+y)\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial(x-y)^2}+V(x-y)\psi\right](-i/\hbar)e^{2ipy/\hbar}\right.$$
$$\left.+\psi(x-y)\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial(x+y)^2}+V(x+y)\psi^*\right](i/\hbar)e^{2ipy/\hbar}\right\}dy. \tag{4.119}$$

This time we consider only the contribution of the potential energy term $V(x)$ while temporarily letting the

$$\frac{\partial^2\psi}{\partial(x-y)^2} = 0$$

yielding

$$\frac{\partial P_W(x,p)}{\partial t} = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\left[-\frac{i}{\hbar}\psi^*(x+y)V(x-y)\psi(x-y)+\frac{i}{\hbar}\psi(x-y)V(x+y)\psi^*(x+y)\right]e^{2ipy/\hbar}dy$$
$$= -\frac{i}{\pi\hbar^2}\int_{-\infty}^{\infty}\left[\psi^*(x+y)V(x-y)\psi(x-y)-\psi(x-y)V(x+y)\psi^*(x+y)\right]e^{2ipy/\hbar}dy$$
$$= \frac{i}{\pi\hbar^2}\int_{-\infty}^{\infty}\left[\psi^*(x+y)\psi(x-y)\right]\left[V(x+y)-V(x-y)\right]e^{2ipy/\hbar}dy. \tag{4.120}$$

We now expand the potential $V(x,y)$ in a Taylor series about the point *x,*

$$V(x+y) = \sum_{\lambda=0}^{\infty}V^{(\lambda)}(x)\frac{y^\lambda}{\lambda!} \tag{4.121}$$

where $V^{(\lambda)}(x)$ is the λ^{th} derivative of $V(x)$. Expanding out this sum for $V(x+y)$ and $V(x-y)$ respectively we have

$$V(x+y) = V(x)+yV'(x)+\frac{y^2}{2!}V''(x)+\frac{y^3}{3!}V'''(x)+\ldots \tag{4.122}$$

and

$$V(x-y)=V(x)-yV'(x)+\frac{y^2}{2!}V''(x)-\frac{y^3}{3!}V'''(x)+\ldots \quad (4.123)$$

We then take the sum

$$V(x+y)-V(x-y)$$

noticing how all even terms will cancel each other. Thus

$$\begin{aligned} V(x+y)-V(x-y) &= 2yV'(x)+2\frac{y^3}{3!}V'''(x)+2\frac{y^5}{5!}V^{(5)}(x)+\ldots \\ &= 2\sum_{\lambda=1}^{\infty}\frac{y^{2\lambda-1}}{(2\lambda-1)!}V^{(2\lambda-1)}(x). \end{aligned} \quad (4.124)$$

Substituting Eq. (4.124) into Eq. (4.120) we obtain the contribution due to the potential energy term

$$\begin{aligned} \frac{\partial P_W}{\partial t} = \frac{2i}{\pi\hbar}\int_{-\infty}^{\infty}\sum_{\lambda=1}^{\infty}\frac{y^{2\lambda-1}}{(2\lambda-1)!}V^{(2\lambda-1)}(x) \\ \times\left[\psi^*(x+y)\psi(x-y)\right]e^{2ipy/\hbar}dy. \end{aligned} \quad (4.125)$$

We wish to substitute out $y^{2\lambda-1}$. We begin by taking the derivative of $e^{2ipy/\hbar}$ w.r.t. *p*.

$$\frac{\partial e^{2ipy/\hbar}}{\partial p}=\frac{2iy}{\hbar}e^{2ipy/\hbar} \quad (4.126)$$

and then the $2\lambda-1$ derivative,

$$\begin{aligned} \frac{\partial^{2\lambda-1}e^{2ipy/\hbar}}{\partial p^{2\lambda-1}} &= \left(\frac{2iy}{\hbar}\right)^{2\lambda-1}e^{2ipy/\hbar} \\ &= \left(\frac{2i}{\hbar}\right)^{2\lambda-1}y^{2\lambda-1}e^{2ipy/\hbar} \end{aligned} \quad (4.127)$$

and therefore

$$y^{2\lambda-1}e^{2ipy/\hbar}=\left(\frac{\hbar}{2i}\right)^{2\lambda-1}\frac{\partial^{2\lambda-1}e^{2ipy/\hbar}}{\partial p^{2\lambda-1}} \quad (4.128)$$

and

$$y^{2\lambda-1}=\left(\frac{\hbar}{2i}\right)^{2\lambda-1}\frac{\partial^{2\lambda-1}}{\partial p^{2\lambda-1}}. \quad (4.129)$$

Notice that Eq. (4.129) follows simply from the operators as per Eq. (4.114) above. Substituting Eq. (4.129) into Eq. (4.125) we get

$$\frac{\partial P_W}{\partial t} = \frac{2i}{\pi\hbar^2}\sum_{\lambda=1}^{\infty}\frac{V^{(2\lambda-1)}(x)}{(2\lambda-1)!}\left(\frac{\hbar}{2i}\right)^{2\lambda-1}\frac{\partial^{2\lambda-1}}{\partial p^{2\lambda-1}}\int_{-\infty}^{\infty}\left[\psi^*(x+y)\psi(x-y)\right]e^{2ipy/\hbar}dy\,.$$

(4.130)

We can now substitute in Eq. (4.106) to get the contribution of the potential energy term

$$\frac{\partial P_W}{\partial t} = \frac{2i}{\hbar}\sum_{\lambda=1}^{\infty}\frac{V^{(2\lambda-1)}(x)}{(2\lambda-1)!}\left(\frac{\hbar}{2i}\right)^{2\lambda-1}\frac{\partial^{2\lambda-1}P_W}{\partial p^{2\lambda-1}}. \qquad (4.131)$$

Expanding out the sum we obtain the end result for the potential energy term

$$\begin{aligned}\frac{\partial P_W}{\partial t} &= \frac{2i}{\hbar}\left(V'\frac{\hbar}{2i}\frac{\partial P_W}{\partial p}+\frac{V'''}{3!}\left(\frac{\hbar}{2i}\right)^3\frac{\partial^3 P_W}{\partial p^3}+\ldots\right)\\ &= V'\frac{\partial P_W}{\partial p}+\frac{V'''}{3!}\left(\frac{\hbar}{2i}\right)^2\frac{\partial^3 P_W}{\partial p^3}+\ldots\\ &= V'\frac{\partial P_W}{\partial p}-V'''\frac{\hbar^{\,2}}{24}\frac{\partial^3 P_W}{\partial p^3}+\ldots\\ &= \frac{\partial V}{\partial x}\frac{\partial P_W}{\partial p}+\sum_{r=1}^{\infty}\frac{(i\hbar/2)^{2r}}{(2r+1)!}\frac{\partial^{2r+1}V}{\partial x^{2r+1}}\frac{\partial^{2r+1}P_W}{\partial p^{2r+1}}.\end{aligned} \qquad (4.132)$$

Combining the contributions from the free kinetic energy and the potential energy we have the equation for the time evolution of the Wigner distribution function

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

(4.133)

which is precisely as given in Eq. (4.25). This equation excluding dissipation, that is, for a *closed system* may be solved [1] by perturbation theory to any order in $\hbar^{2r}$ to yield quantum corrections to the classical Maxwell-Boltzmann distribution.

Appendix IV.VI: Fourier transforms and Wigner distributions

Take the Fourier transform pair:

$$F(\xi) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(\eta)e^{-i\eta\xi}d\eta, \qquad (4.134)$$

$$f(\eta) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} F(\xi)e^{i\eta\xi}d\xi\,. \qquad (4.135)$$

Consider the definition of the Wigner distribution i.e.

$$W(x,p) = \frac{1}{\hbar\pi}\int_{-\infty}^{\infty}\psi^*(x+y)\psi(x-y)e^{2ipy/\hbar}dy\,. \qquad (4.136)$$

We want to write down $\psi^*(x+y)\psi(x-y)$ in terms of a Fourier integral. First we write (in the symmetrical form of the Fourier integral)

$$W(x,p)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{2\psi^*(x+y)\psi(x-y)}{\hbar\sqrt{2\pi}}e^{2ipy/\hbar}dy \quad (4.137)$$

then we will have by Fourier's integral theorem

$$\frac{2\psi^*(x+y)\psi(x-y)}{\hbar\sqrt{2\pi}}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}W(x,p)\,e^{-2ipy/\hbar}d\left(\frac{2p}{\hbar}\right)$$

or

$$\psi^*(x+y)\psi(x-y)=\int_{-\infty}^{\infty}W(x,p)\,e^{-2ipy/\hbar}dp\,. \quad (4.138)$$

If we set $y=0$, we have

$$\psi^*(x)\psi(x)=|\psi(x)|^2=\int_{-\infty}^{\infty}W(x,p)dp\,. \quad (4.139)$$

To continue we will define the *quantum* Fourier transform pair

$$\phi(p)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x)e^{i\frac{p}{\hbar}x}dx\,, \quad (4.140)$$

$$\psi(x)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\phi(p)e^{-i\frac{x}{\hbar}p}dp\,. \quad (4.141)$$

We already found by evaluating the double integrals (see above) in Eqs. (4.71) and (4.75) that

$$\int_{-\infty}^{\infty}W(x,p)dx=\frac{1}{2\pi\hbar}\left|\int_{-\infty}^{\infty}\psi(u)e^{i\frac{p}{\hbar}u}du\right|^2$$

which is clearly

$$\phi^*(p)\phi(p)$$

by using Eq. (4.140). We now clearly have

$$\begin{aligned}\int_{-\infty}^{\infty}W(x,p)dp&=\psi(x)\psi^*(x),\\ \int_{-\infty}^{\infty}W(x,p)dx&=\phi(p)\phi^*(p).\end{aligned} \quad (4.142)$$

Wigner also defines

$$P(x,p) = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty} \phi^*(p+p')\phi(p-p')e^{-2i\frac{x}{\hbar}p'}dp' \\ = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \frac{2\phi^*(p+p')\phi(p-p')}{\hbar\sqrt{2\pi}} e^{-2i\frac{x}{\hbar}p'}dp'. \tag{4.143}$$

Now we apply Fourier integral theorem and so we have

$$\frac{\phi^*(p+p')\phi(p-p')}{\sqrt{2\pi}} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} P(x,p')e^{2i\frac{p'}{\hbar}x}dx \tag{4.144}$$

or

$$\phi^*(p+p')\phi(p-p') = \int_{-\infty}^{\infty} P(x,p')e^{2i\frac{p'}{\hbar}x}dx \tag{4.145}$$

which on letting $p' = 0$

$$\phi^*(p)\phi(p) = \int_{-\infty}^{\infty} P(x,0)dx\,. \tag{4.146}$$

Note that *P* is not the same as *W*. See also p277 of [50].

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CHAPTER V

Stationary solution of the evolution equation for the Wigner distribution: Application to transition state theory

V.I Perturbation solution of Wigner's stationary equation

This chapter is mainly concerned with the calculation of stationary Wigner functions for particles using Eq. (4.25) for the evolution of the Wigner distribution in phase space and how it may be used to calculate reaction rates assuming that thermal equilibrium prevails everywhere. We remark that since in general the matrix elements of the density matrix are not known exactly for all but the simplest particle Hamiltonians, e.g. the harmonic oscillator, direct transformation of these using the Stratonovich bijective mapping in the manner outlined for spins in Section IV.IV is not usually feasible. Equation (4.25) in the general time dependent case reads

$$\frac{\partial W}{\partial t}+\hat{M}_W W=0 \tag{5.1}$$

where the Wigner-Liouville operator $\hat{M}_W$ is defined as

$$\begin{aligned}\hat{M}_W W &= \frac{p}{m}\frac{\partial W}{\partial x}-\frac{1}{i\hbar}\left[V\left(x+\frac{i\hbar}{2}\frac{\partial}{\partial p}\right)-V\left(x-\frac{i\hbar}{2}\frac{\partial}{\partial p}\right)\right]W \\ &= \frac{p}{m}\frac{\partial W}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}-\sum_{r=1}^{\infty}\frac{(i\hbar/2)^{2r}}{(2r+1)!}\frac{\partial^{2r+1}V}{\partial x^{2r+1}}\frac{\partial^{2r+1}W}{\partial p^{2r+1}}.\end{aligned} \tag{5.2}$$

The stationary solution is then obtained by setting the time derivative equal to zero. We remark that Wigner [1] originally calculated quantum correction terms to the classical stationary distribution functions for a system with *n* degrees of freedom. For illustrative purposes, we consider a system with *n* = 1, i.e., a canonical ensemble of particles each of mass *m* moving in a potential $V(x)$ at temperature *T*. Each particle is characterized by the energy

$$\varepsilon(x,p)=\frac{p^2}{2m}+V(x) \tag{5.3}$$

Following Wigner [1] we develop the stationary probability function $W_{st}(x,p)$ in the power series in Planck's constant

$$W_{st}(x,p)=W_0(x,p)+\hbar^2W_2(x,p)+\hbar^4W_4(x,p)+... \tag{5.4}$$

where

$$W_0(x,p)=e^{-\beta\varepsilon(x,p)} \tag{5.5}$$

is the classical stationary distribution i.e. the Maxwell-Boltzmann distribution. As shown in Appendix V.I, the functions $W_2(x,p)$ and $W_4(x,p)$ representing the second and fourth order of perturbation theory can be readily evaluated. (Wigner showed that the odd order terms in Planck's constant are all zero). Thus we have

$$\begin{aligned}W_{st}(x,p)=e^{-\beta\varepsilon(x,p)}\Bigg\{1+\Lambda\left(\frac{\beta p^2}{m}V''-3V''+\beta V'^2\right)\\ +3\Lambda^2\Bigg[\frac{p^4}{m^2}\left(\frac{(\beta V'')^2}{6}-\frac{\beta V^{(4)}}{10}\right)\\ +\frac{p^2}{m}\left(V^{(4)}-\frac{2\beta V'''V'}{5}+\frac{V''(\beta V')^2}{3}-\frac{9\beta V''^2}{5}\right)\\ +\frac{\beta^2V'^4}{6}+\frac{5V''^2}{2}-\frac{9\beta V''V'^2}{5}+2V'''V'-\frac{3V^{(4)}}{2\beta}\Bigg]+...\Bigg\}\end{aligned} \tag{5.6}$$

where

$$\Lambda=\frac{\hbar^2\beta^2}{24m} \tag{5.7}$$

is the characteristic quantum parameter. One may infer from the form of the first and second order perturbation solutions for $W_2(x,p)$ and $W_4(x,p)$ that in general in the $2n^{th}$ order of perturbation theory, correction terms to the classical Gaussian momentum distribution and spatial derivatives of the potential will occur. 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 $o\left(\hbar^4\right)$. 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 $\hbar^{2r}$. Methods for the calculation of Wigner functions are described in Appendix V.II.

V.II Configuration space distribution

The phase space distribution is a joint distribution so that the corresponding equilibrium distribution function in configuration space namely the quantum mechanical probability of the displacements for a system with density matrix $\hat{\rho}$

$$P_{st}(x) = \frac{\int_{-\infty}^{\infty} W_{st}(x,p)dp}{\int_{-\infty}^{\infty} e^{-\beta p^2/(2m)}\,dp} = \sqrt{\frac{\beta}{2\pi m}}\int_{-\infty}^{\infty} W_{st}(x,p)dp \tag{5.8}$$

can be readily evaluated from Eq.(5.6). We have

$$P_{st}(x) = e^{-\beta V}\left\{1+\Lambda\left[\beta\left(V'\right)^2 - 2V''\right] + \frac{\Lambda^2}{10}\left[36V''^2 + 48V'''V' - 44\beta V''V'^2 + 5\beta^2 V'^4 - 24V^{(4)}/\beta\right] + \ldots\right\}. \tag{5.9}$$

Equation (5.9) demonstrates how the probability of a configuration given by the Boltzmann factor $e^{-\beta V(x)}$ in classical theory (and holding in quantum theory for high temperatures) is modified for lower temperatures.

V.III Calculation of equilibrium averages

The equilibrium distribution function in configuration space $P_{st}(x)$ can be used to evaluate the equilibrium average of any function *F*(*x*) in semiclassical fashion as alluded to in Chapters I and IV. We demonstrate this retaining terms to $o(\hbar^4)$. We have for the semiclassical equilibrium average

$$\langle F\rangle = \frac{\int F P_{st}(x)dx}{\int P_{st}(x)dx}$$

$$= \left(\int Fe^{-\beta V}dx - 2\Lambda\int FV''e^{-\beta V}dx + \Lambda\beta\int FV'^2e^{-\beta V}dx\right) \quad (5.10)$$

$$\times\left(Z_{cl} - 2\Lambda\int V''e^{-\beta V}dx + \Lambda\beta\int V'^2e^{-\beta V}dx\right)^{-1} + ...,$$

where

$$Z_{cl} = \int e^{-\beta V}dx \quad (5.11)$$

is the classical partition function. Retaining terms linear in the quantum parameter Λ we have

$$\langle F\rangle = \langle F\rangle_{cl} + \Lambda Z_{cl}^{-1}\left(\beta\int FV'^2e^{-\beta V}dx - 2\int FV''e^{-\beta V}dx + \right.$$

$$\left. + 2Z_{cl}^{-1}\int V''e^{-\beta V}dx\int Fe^{-\beta V}dx - Z_{cl}^{-1}\beta\int V'^2e^{-\beta V}dx\int Fe^{-\beta V}dx\right) + ...,$$

(5.12)

where the classical equilibrium average is defined as

$$\langle F\rangle_{cl} = \frac{\int F(x)e^{-\beta V(x)}dx}{Z_{cl}}. \quad (5.13)$$

Noting that

$$\beta\int V'^2e^{-\beta V}dx = -V'e^{-\beta V}\Big|_{-\infty}^{\infty} + \int V''e^{-\beta V}dx$$

$$= \int V''e^{-\beta V}dx$$

and

$$\beta\int FV'^2e^{-\beta V}dx = -FV'e^{-\beta V}\Big|_{-\infty}^{\infty} + \int\left(FV'' + F'V'\right)e^{-\beta V}dx$$

$$= \int\left(FV'' + F'V'\right)e^{-\beta V}dx,$$

we have finally

$$\langle F\rangle = \langle F\rangle_{cl} + \Lambda\left(\langle F\rangle_{cl}\langle V''\rangle_{cl} + \langle F'V'\rangle_{cl} - \langle FV''\rangle_{cl}\right) + \ldots \quad (5.14)$$

Equation (5.14) clearly demonstrates how quantum mechanical equilibrium averages may be expressed via perturbation theory in terms of classical equilibrium averages.

V.IV Wigner's stationary solution for a harmonic oscillator

Obviously, the calculation of the Wigner distribution $W_{st}(x,p)$ is a tedious task for an arbitrary potential $V(x)$ (see the Appendices V.I and V.II). However, in some cases the stationary Wigner distribution $W_{st}(x,p)$ can be found in closed form. A famous example is the quantum harmonic oscillator, where the potential

$$V(x) = \frac{m\omega_0^2 x^2}{2} \quad (5.15)$$

and the equilibrium Wigner function can be presented in the simple exact form [2,3,4] (see Appendix V.II)

$$W_{st}(x,p) = \frac{\exp\left\{-\frac{1}{2}\left(\frac{x^2}{\langle x^2\rangle} + \frac{p^2}{\langle p^2\rangle}\right)\right\}}{Z'} \quad (5.16)$$

where

$$\begin{aligned}\langle x^2\rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^2 W_{st}(x,p)\,dpdx \\ &= \frac{1}{m\beta\omega_0^2}\left(1 + 2m\omega_0^2\Lambda - \frac{4}{5}m^2\omega_0^4\Lambda^2 + \ldots.\right) \\ &= \frac{\hbar}{2m\omega_0}\coth\frac{\beta\hbar\omega_0}{2},\end{aligned} \quad (5.17)$$

$$\begin{aligned}\langle p^2\rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p^2 W_{st}(x,p)\,dpdx \\ &= \frac{m}{\beta}\left(1 + 2m\omega_0^2\Lambda - \frac{4}{5}m^2\omega_0^4\Lambda^2 + \ldots.\right) \\ &= \frac{m\hbar\omega_0}{2}\coth\frac{\beta\hbar\omega_0}{2},\end{aligned} \quad (5.18)$$

and

$$Z' = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left\{-\frac{1}{2}\left(\frac{x^2}{\langle x^2\rangle}+\frac{p^2}{\langle p^2\rangle}\right)\right\} dpdx$$
$$= \pi\hbar \coth\frac{\beta\hbar\omega_0}{2}. \tag{5.19}$$

Here we have used the series expansion of $\coth z$ see Eq. (4.5.67) of [5], viz.,

$$\coth z = \frac{1}{z}+\frac{z}{3}-\frac{z^3}{45}+\frac{2}{945}z^5-.... \tag{5.20}$$

We shall demonstrate in Chapter VI how the Wigner stationary distribution can be used in the establishment of semiclassical Fokker-Planck equations and so in the quantum-classical correspondence which is the main objective of this review. However, many other applications exist and one of the most important of these in the present context is how Eq. (5.6) can be used to correct the classical transition state theory equation for the escape rate from a potential well which was first accomplished by Wigner [6,7].

V.V Application of the Wigner stationary distribution to transition state theory

The simplest description of thermally activated decay which involves escape of particles over a potential barrier due to thermal agitation, is in terms of classical transition state theory (TST). In the simplest form of TST we consider a system with one degree of freedom in the absence of a reservoir where two assumptions are made [8]. First thermal equilibrium prevails in the well (for example, through the action of Maxwell's demon who keeps replenishing the particles at the source) so that the metastable state is represented by a canonical equilibrium distribution (unlike in the Kramers [9] treatment of the escape rate where nonequilibrium effects due to the loss of particles from the well are taken account of by means of the theory of Brownian motion leading to friction dependence of the transmission coefficient). Secondly a particle is supposed never to return once it has crossed the potential barrier. The first assumption means that friction, i.e., dissipation to the bath does not affect the escape rate. Thus the system in effect is a closed classical system. However, according to Mel'nikov [10] the results of classical TST should also be applicable in a *wide range of dissipation* for which thermal noise is sufficiently strong to thermalize the escaping particles yet not so strong as to affect particle motion across the top of

the potential barrier, i.e., a Maxwell-Boltzmann distribution still holds at the top of the barrier. In the context of the Kramers model this is the so called *intermediate damping* case (cf. Fig. 1.13.2 of [11]). In the treatment of Kramers, however, which explicitly involves an *open* classical system with dissipation to the bath described by the Brownian motion *stosszahlansatz*, he shows that for sufficiently weak friction the escape rate is suppressed because of the depletion of the well population while for strong friction the escape rate is suppressed due to the slowing down of the particle motion at the top of the barrier. This behaviour is contained in the transmission coefficient. The IHD escape rate and Melnikov's extension of it to provide a solution for all values of the dissipation is treated in Chapter VI.

The suggestion that quantum mechanical tunnelling might play a significant role in some chemical reactions, was first made in 1927 by Hund [12] almost at the inception of quantum mechanics. The first guess at a quantum transition state theory appears to have been made by Wigner who proposed a quantum generalization of the classical TST [8,12,13], where the reaction rate Γ is given by

$$\begin{aligned}\Gamma &\sim Z_a^{-1}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{p}{m}\theta(p)\delta(x-x_c)W_{st}(x,p)dpdx \\ &= Z_a^{-1}\int_{-\infty}^{\infty}\frac{p}{m}\theta(p)W_{st}(x_c,p)dp \\ &= Z_a^{-1}\int_{-\infty}^{\infty}J(x_c,p)dp.\end{aligned} \tag{5.21}$$

In the above equation the delta function means that all the particles cross at $x = x_c$ while the step function means that only particles with positive momentum can escape. The probability current or flow of phase points in phase space is defined as

$$J(x,p) = \theta(p)\frac{p}{m}W_{st}(x,p)\,, \tag{5.22}$$

where we note that physically $W_{st}(x,p)$ corresponds to a *concentration in phase space*, and of course the concentration as commonly conceived which in this instance is the Wigner configuration space distribution is got by integrating out the p dependence. In like manner the flow of points in configuration space is got

by integrating the phase space current with respect to *p*. In all calculations of the current densities the bottleneck at x_c has unit cross-sectional area and the current density is uniform across this section. The constant current is maintained by the Maxwell demon. Here θ is the unit step function, point *c* is the top of the barrier, point *a* is the bottom of the well and Z_a is the partition function of the well region which is the population of particles inside the well

$$Z_a = \int\int_{well} W_{st}(x,p)dpdx\,. \tag{5.23}$$

It is clear that the escape rate is then simply the constant current in configuration space divided by the population inside the well. The above considerations show clearly the connection between Wigner's definition (Eq. (5.21)) of the escape rate and the flux over barrier definition used by Farkas [14] and later by Kramers.

Proceeding (see Figure V.I) we remark that near the summit (point *c*) and near the bottom (point *a*) of the well the potential may be described by an inverted harmonic oscillator and harmonic oscillator potentials, namely,

$$V(x) \approx \begin{cases} V(x_c) - \dfrac{m\omega_c^2 x'^2}{2} \\ V(x_a) + \dfrac{m\omega_a^2 x''^2}{2} \end{cases} \tag{5.24}$$

where $\omega_c = \sqrt{|V''(x_c)|/m}$, $\omega_a = \sqrt{V''(x_a)/m}$, $x' = x - x_c$, and $x'' = x - x_a$. Thus near the bottom of the well, the partition function Z_a is approximated by that of a harmonic oscillator (see Eq. (5.63) Appendix V.II below) with $\omega_0 = \omega_a$ and is given by

$$\begin{aligned} Z_a &\approx \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_a(x,p)dxdp \\ &= \frac{\pi\hbar e^{-\beta V(x_a)}}{\sinh\left(\hbar\omega_a\beta/2\right)}. \end{aligned} \tag{5.25}$$

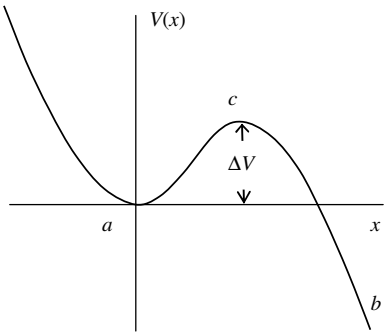

Figure V.I Single well potential function as the simplest example of escape over a barrier. Particles are initially trapped in the well near the point a by a high potential barrier at the point c. They very rapidly thermalise in the well. Due to thermal agitation however very few may attain enough energy to escape over the barrier into region b whence they never return. The escape rate is defined as the flux or current of particles at the barrier divided by the well population which is sensibly approximated by the number of particles near the bottom of the well.

Near the top of the barrier, the Wigner function $W_{st}(x,p)$ is approximated by that of an inverted harmonic oscillator [see Eq. (5.61) below] so that $\omega_0 = i\omega_c$ and is given by

$$W_{st}(x_c,p) \approx e^{-\beta V(x_c)} \sec\left(\hbar\omega_c\beta/2\right) e^{-p^2\tan(\hbar\omega_c\beta/2)/(m\hbar\omega_c)}. \quad (5.26)$$

Substituting Eqs. (5.25) and (5.26) into Eq. (5.21), we obtain

$$\Gamma \approx \frac{\omega_a}{2\pi}\Xi e^{-\beta\Delta V} \quad (5.27)$$

where $\Delta V = V(x_c) - V(x_a)$ is the barrier height and

$$\begin{aligned}\Xi &= \frac{\omega_c}{\omega_a}\frac{\sinh(\hbar\beta\omega_a/2)}{\sin(\hbar\beta\omega_c/2)} \\ &= \frac{1+\left(\hbar\beta\omega_c\right)^2/24+7\left(\hbar\beta\omega_c\right)^4/5760+\ldots}{1-\left(\hbar\beta\omega_a\right)^2/24+7\left(\hbar\beta\omega_a\right)^4/5760+\ldots} \\ &= 1+\frac{\beta^2\hbar^2\left(\omega_c^2+\omega_a^2\right)}{24}+o(\hbar^4)\end{aligned} \quad (5.28)$$

is the quantum correction to the classical TST result. The lowest order quantum correction to this pre-exponential factor was first obtained by Wigner [6] (see also [7]). He emphasized that the quantum factor Ξ represents an effective lowering of the potential barrier so enhancing the escape rate. According to Wigner [6], Eq. (5.27) constitutes the quantum corrections to classical TST at high temperatures.

In the context of quantum dissipation, one may infer that Eq. (5.27) also represents the extension of the intermediate damping Kramers escape rate (for which classical TST provides a reasonably accurate approximation [10,15]) to include quantum effects. An important feature of Eq. (5.27) which does not manifest itself in the first order in $\hbar^2$ approximation is that the prefactor Ξ diverges at a crossover temperature T_c given by $T_c = \hbar\omega_c/(2\pi k)$. The divergence occurs because the parabolic (or inverted oscillator) approximation for the potential is only valid near the top of the barrier. However, at very low temperatures $T \ll T_c$, where the particle is near the bottom of the well, the parabolic approximation to the barrier shape is not sufficient [16] (see also Weiss [8], Chapter 12). On the other hand at $T > T_c$, transitions near the barrier top dominate so that the parabolic approximation is accurate [17]. Moreover the simple approximation appearing on the right hand side of Eq. (5.28) should hold with a reasonable degree of accuracy. This approximation also appears to be in substantial agreement with the experimental results of Bouchaud et al.[18].

We have demonstrated how the quantum escape rate in the absence of dissipation, namely Eq. (5.27), may be obtained by Wigner's perturbation method. The result was originally obtained in a more succinct fashion without using perturbation theory by recalling that the rate constant may be written [12,16]

$$\Gamma = Z_a^{-1} \int_{-\infty}^{\infty} w(\varepsilon) e^{-\beta\varepsilon} d\varepsilon \,. \tag{5.29}$$

Here

$$w(\varepsilon) = \frac{1}{1 + e^{-2\pi(\varepsilon - V_c)/(\hbar\omega_c)}} \tag{5.30}$$

which is the exact quantum transmission coefficient (ignoring dissipation) of a parabolic barrier [19]. We again approximate the potential by that of an inverted harmonic oscillator at the top of the barrier which holds good at the barrier as well as at a small distance below it. This is the reason for regarding the integral in Eq. (5.29) as having infinite limits. Thus one finds on evaluating the integral in Eq. (5.29) with these limits that the escape rate is given by

$$\Gamma = \frac{\hbar\omega_c}{2Z_a \sin(\hbar\beta\omega_c/2)} e^{-\beta V_c} \,. \tag{5.31}$$

Noting Eq. (5.25), one can readily obtain Eq. (5.27) from Eq. (5.31).

Quantum TST as formulated for particles with separable and additive Hamiltonians in the manner just described has also been applied [20] in the context of magnetization reversal to the escape rate of the large spin model of single domain ferromagnetic particles. This model describes a ferromagnetic particle with uniaxial anisotropy with external fields applied parallel and perpendicular to the anisotropy axis. Tunnelling in such a model will be caused by the transverse field [20]. Now, the Hamiltonian of the model (which is not separable and additive as the canonical variables are now the polar angles θ and φ specifying the orientation of the magnetization vector) may be mapped [20] onto that of a mechanical particle moving in a double well potential. Hence the quantum TST rate described above which is a close approximation to the exact escape rate in the intermediate damping region may also be used to study thermally assisted tunnelling of the magnetization of a single domain ferromagnetic particle. The complete solution of the foregoing problem, however, essentially involves the extension of Wigner's formalism to the phase-space description of spin systems as initiated by Stratonovich [21] and recently extended and reviewed by Klimov [22] who gave exact evolution equations for SU(2) dynamical group quasidistribution functions. Applications of the formalism include quantum decoherence in the rotation of small molecules [23], spin squeezing and spin entanglement in the semiclassical limit [24]. In the context of TST for spins described by the SU(2) rotation dynamical group we should remark that the results of the calculation of the Wigner distribution given in Section IV.IV, Eqns. (4.59) et seq., are very important. Essentially these results (ignoring dissipation to the bath) allow one to calculate the escape rate and so the quantum corrections to the magnetization relaxation time for axially symmetric potentials of the magnetocrystalline anisotropy. The foregoing results are also important in the inclusion of dissipation in the calculation of the relaxation time because due to the axial symmetry all that is required to write down such an equation is a knowledge of the stationary distribution as that entirely determines the diffusion coefficients since the precession term drops out of the Liouville operator.

In the next Chapter we shall demonstrate how the Wigner stationary distribution may be used to construct quantum master equations including dissipation.

APPENDIX V

Appendix V.I: Wigner's method of calculation of stationary functions

By substituting Eq. (5.4) into Eq. (5.1) and equating the coefficients of the different powers of $\hbar$, we have [25]

$$-\frac{p}{m}\frac{\partial W_2}{\partial x}+\frac{\partial V}{\partial x}\frac{\partial W_2}{\partial p}-\frac{1}{24}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W_0}{\partial p^3}=0, \tag{5.32}$$

$$-\frac{p}{m}\frac{\partial W_4}{\partial x}+\frac{\partial V}{\partial x}\frac{\partial W_4}{\partial p}-\frac{1}{24}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W_2}{\partial p^3}+\frac{1}{1920}\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W_0}{\partial p^5}=0 \tag{5.33}$$

etc. Following Wigner [1] we seek W_2 as

$$W_2 = e^{-\beta\varepsilon(x,p)}\left[\, p^2(A_2V''+B_2V'^2)+A_0V''+B_0V'^2\,\right]. \tag{5.34}$$

By noting that $W_0 = e^{-\beta\varepsilon(x,p)}$ and substituting Eq. (5.34) into Eq. (5.32), we obtain

$$A_2=\frac{\beta^3}{24m^2},\quad B_2=0,\quad A_0=-\frac{\beta^2}{8m},\quad B_0=\frac{\beta^3}{24m},$$

so that

$$W_2=\frac{\beta^2}{24m}\left[\frac{\beta}{m}p^2V''(x)-3V''(x)+\beta V'(x)^2\right]e^{-\beta\varepsilon(x,p)}. \tag{5.35}$$

In like manner, we seek W_4 as

$$\begin{aligned} W_4 = e^{-\beta\varepsilon(x,p)}[\,& p^4(A_4V''''+B_4V'''V'+C_4V''V'^2+D_4V''^2+E_4V'^4)\\ &+p^2(A_2V''''+B_2V'''V'+C_2V''V'^2+D_2V''^2+E_2V'^4)\\ &+A_0V''''+B_0V'''V'+C_0V''V'^2+D_0V''^2+E_0V'^4\,]. \end{aligned} \tag{5.36}$$

By substituting Eqs. (5.35) and (5.36) into Eq. (5.33), we have

$$A_4=-\frac{\beta}{1920}\left(\frac{\beta}{m}\right)^4,\quad B_4=C_4=E_4=0,\quad D_4=\frac{\beta^2}{1152}\left(\frac{\beta}{m}\right)^4,$$

$$A_2=\frac{\beta}{192}\left(\frac{\beta}{m}\right)^3,\quad B_2=-\frac{\beta^2}{480}\left(\frac{\beta}{m}\right)^3,\quad C_2=\frac{\beta^3}{576}\left(\frac{\beta}{m}\right)^3,\quad D_2=-\frac{3\beta^2}{320}\left(\frac{\beta}{m}\right)^3,$$

$$E_2=0,\quad A_0=-\frac{\beta}{128}\left(\frac{\beta}{m}\right)^2,\quad B_0=\frac{\beta^2}{96}\left(\frac{\beta}{m}\right)^2,\quad C_0=-\frac{3\beta^3}{320}\left(\frac{\beta}{m}\right)^2,$$

$$D_0 = \frac{5\beta^2}{384}\left(\frac{\beta}{m}\right)^2, \quad E_0 = \frac{\beta^4}{1152}\left(\frac{\beta}{m}\right)^2,$$

so that

$$W_4 = e^{-\beta\varepsilon(x,p)}\left(\frac{\beta}{m}\right)^2\left\{\left(\frac{\beta p^2}{4m}\right)^2\left[\frac{(\beta V'')^2}{72} - \frac{\beta V^{(4)}}{120}\right]\right.$$
$$+\frac{\beta p^2}{4m}\left[\frac{\beta V^{(4)}}{48} - \frac{\beta^2 V''' V'}{120} + \frac{\beta V''(\beta V')^2}{144} - \frac{3(\beta V'')^2}{80}\right]$$
$$\left.-\frac{\beta V^{(4)}}{128} + \frac{\beta^2 V''' V'}{96} - \frac{3\beta V''(\beta V')^2}{320} + \frac{5(\beta V'')^2}{384} + \frac{(\beta V')^4}{1152}\right\}.$$

(5.37)

On taking into account Eqs. (5.35) and (5.37) we obtain Eq. (5.6). The function W_4 can be rewritten in terms of the Hermite polynomials $H_2(z)$ and $H_4(z)$ as

$$W_4 = \left(\frac{\beta}{8m}\right)^2 e^{-\beta\varepsilon(x,p)}\left\{H_4(q)\left[\frac{(\beta V'')^2}{72} - \frac{\beta V^{(4)}}{120}\right]\right.$$
$$+H_2(q)\left[\frac{\beta V^{(4)}}{15} - \frac{\beta^2 V''' V'}{15} + \frac{\beta V''(\beta V')^2}{18} - \frac{2(\beta V'')^2}{15}\right]$$
$$\left.-\frac{4\beta V^{(4)}}{15} + \frac{8\beta^2 V''' V'}{15} - \frac{22\beta V''(\beta V')^2}{45} + \frac{2(\beta V'')^2}{5} + \frac{(\beta V')^4}{18}\right\},$$

(5.38)

where

$$q = p\sqrt{\frac{\beta}{2m}} \tag{5.39}$$

and the $H_n(z)$ are defined by the generating function [26]

$$H_n(z) = (-1)^n \mathrm{e}^{z^2}\frac{d^n}{dz^n}\mathrm{e}^{-z^2}, \quad n = 0,1,2,3... \tag{5.40}$$

This result was originally obtained by Wigner (see Eq. (26) of [1]).

Appendix V.II: Calculation of stationary Wigner functions

The purpose of this Appendix [25] is to present a method of obtaining a complete solution of Eq. (5.1) which governs the behaviour of the Wigner function. Equation (5.1) reduces to the classical Liouville equation if $\hbar$ is set equal

to zero. The $\hbar^{2r}$ terms give the quantum correction if this is very small. From Eq. (5.1) it is clear that the quantum equation of motion is the same as the classical equation of motion when the potential $V(x)$ has no third and higher derivatives, e.g. for a uniform electric field or for a system of oscillators. However, a subtle difference exists in so far as the possible initial conditions are restricted because not all $W(x,p,t)$ are now permissible. Equation (5.1) can be presented in the equivalent form [2]

$$\hbar\frac{\partial W(x,p)}{\partial t} = -2\varepsilon(x,p)\sin(\hbar\Theta/2)W(x,p) \tag{5.41}$$

where

$$\varepsilon(x,p) = \frac{p^2}{2m} + V(x) \tag{5.42}$$

is the energy corresponding to the Hamiltonian operator $\hat{H}$ of the system, Θ is an operator defined as

$$\Theta = \frac{\overleftarrow{\partial}}{\partial p}\frac{\vec{\partial}}{\partial x} - \frac{\overleftarrow{\partial}}{\partial x}\frac{\vec{\partial}}{\partial p} \tag{5.43}$$

with the arrows indicating in which direction the derivatives act. In reality, this is merely an abbreviated form of Eq. (5.1) which may be verified by expanding the sine in a power series and using the fact that

$$\frac{\partial}{\partial p}\frac{\partial}{\partial x}\varepsilon(x,p) = 0\,. \tag{5.44}$$

In order to proceed we first recall that at equilibrium the density matrix $\hat{\rho}_{st}$ of a canonical ensemble is given by

$$\hat{\rho}_{st} = \frac{\hat{\rho}}{Z(\beta)}, \tag{5.45}$$

where

$$Z(\beta) = \mathrm{Tr}\left\{e^{-\beta\hat{H}}\right\} \tag{5.46}$$

and

$$\hat{\rho} = e^{-\beta\hat{H}}\,. \tag{5.47}$$

The unnormalized density matrix $\hat{\rho}$ satisfies the equation

$$\frac{\partial \hat{\rho}}{\partial \beta} = -\hat{\rho}\hat{H} = -\hat{H}\hat{\rho} \tag{5.48}$$

subjected to the initial condition $\hat{\rho}\big|_{\beta=0} = \hat{\mathrm{I}}$, where $\hat{\mathrm{I}}$ is the identity operator. Equation (5.48) is referred to as the Bloch equation for the density matrix of a canonical ensemble [26]. Making the Wigner-Weyl transformation [27] of Eq. (5.48), one obtains [2,28] (cf. Eq. (5.41))

$$\frac{\partial W_{st}(x,p)}{\partial \beta} = -\varepsilon(x,p)\cos(\hbar\Theta/2)W_{st}(x,p) \tag{5.49}$$

where $W_{st}(x,p) = \tilde{\rho}$, $\varepsilon(x,p) = \tilde{H}$, and $\tilde{F}$ denotes the Wigner-Weyl transformation of the operator $\hat{F}$, viz.,

$$\tilde{F}(x,p) = \int e^{ipz/\hbar} \left\langle x - z/2 \middle| \hat{F} \middle| x + z/2 \right\rangle dz\,. \tag{5.50}$$

The initial condition for Eq. (5.49) is

$$W_{st}(x,p)\big|_{\beta=0} = 1\,. \tag{5.51}$$

This is the Wigner interpretation of the Bloch equation, which was intensively studied by many authors and was first derived in this form by Oppenheim and Ross [29]. Equation (5.49) can be simplified to yield [3]

$$\frac{\partial W_{st}(x,p)}{\partial \beta} = \left[2V(x)\sin^2\left(\frac{\hbar}{4}\frac{\overleftarrow{\partial}}{\partial x}\frac{\vec{\partial}}{\partial p} \right) - \varepsilon(x,p) + \frac{\hbar^2}{8m}\frac{\partial^2}{\partial x^2} \right] W_{st}(x,p). \tag{5.52}$$

This equation was originally given by Alastuey and Jancovici [30].

In order to find the stationary probability function $W_{st}(x,p)$ from Eq. (5.52) by perturbation methods, we develop $W_{st}(x,p)$ in a power series

$$W_{st}(x,p) = W_0(x,p) + \sum_{r=1}^{\infty} \hbar^{2r} W_{2r}(x,p) \tag{5.53}$$

where

$$W_0(x,p) = e^{-\beta\varepsilon(x,p)}\,. \tag{5.54}$$

By substituting Eq. (5.53) into Eq. (5.52) and equating the coefficients of the different powers of $\hbar$, we have in the n^{th} order of perturbation theory

$$\frac{\partial W_{2n}}{\partial \beta} = -\varepsilon W_{2n} + \frac{\hbar^2}{8m}\frac{\partial^2 W_{2n-2}}{\partial x^2} - \sum_{k=1}^{n} \frac{(-\hbar^2)^k}{(2k)!2^{2k}}\frac{\partial^{2k} V}{\partial x^{2k}}\frac{\partial^{2k} W_{2(n-k)}}{\partial p^{2k}}.$$

(5.55)

The solution of Eq. (5.55) satisfying the condition

$$W_{2n}\big|_{\beta=0} = 0 \tag{5.56}$$

is

$$W_{2n} = e^{-\beta\varepsilon}\int_0^\beta \left\{\frac{1}{8m}\frac{\partial^2 W_{2n-2}}{\partial x^2} - \sum_{k=1}^{n}\frac{(-1)^k}{(2k)!2^{2k}}\frac{\partial^{2k} V}{\partial x^{2k}}\frac{\partial^{2k} W_{2(n-k)}}{\partial p^{2k}}\right\} e^{\lambda\varepsilon} d\lambda.$$

(5.57)

The analogous solution for a different distribution function was obtained by Kirkwood [31]. One of the earliest applications was to quantum corrections of the classical equations of state and related corrections to chemical reaction rates [6,7]. They have been extensively used in statistical mechanics ever since (see, for example, Oppenheim and Ross [29] and Nienhuis [32]).

As an example of application of the above formalism, we calculate the Wigner function of a canonical ensemble of harmonic oscillators at temperature T [33]. Here

$$V(x) = V(x_0) + \frac{m\omega_0^2 x^2}{2}$$

and

$$V''(x) = m\omega_0^2$$

so that Eq. (5.52) becomes

$$\frac{\partial W_{st}(x,p)}{\partial \beta} = \left[-\varepsilon(x,p) + \frac{\hbar^2}{8}\left(\frac{1}{m}\frac{\partial^2}{\partial x^2} + m\omega_0^2\frac{\partial^2}{\partial p^2}\right)\right] W_{st}(x,p).$$

(5.58)

To solve Eq. (5.58) we make the *ansatz* (following Hillery et al. [2])

$$W_{st}(x,p) = e^{-A(\beta)\left[\varepsilon(x,p) - V(x_0)\right] + B(\beta) - \beta V(x_0)} \tag{5.59}$$

where $A(0) = B(0) = 0$. Substituting this into Eq. (5.58) yields

$$\left[\varepsilon(x,p) - V(x_0)\right]\left[1 - \frac{dA}{d\beta} - \left(\frac{\hbar\omega_0}{2}A\right)^2\right] + \frac{dB}{d\beta} + \left(\frac{\hbar\omega_0}{2}\right)^2 A = 0.$$

(5.60)

Noting that the solution of the coupled differential equations

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

and

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

is given by

$$A(\beta)=\frac{2}{\hbar\omega_0}\tanh\left(\frac{\beta\hbar\omega_0}{2}\right)$$

and

$$B(\beta)=-\ln\cosh\left(\frac{\beta\hbar\omega_0}{2}\right),$$

we have finally

$$W_{st}(x,p)=e^{-\beta V(x_0)}\operatorname{sech}\left(\beta\hbar\omega_0/2\right)e^{-2[\varepsilon(x,p)-V(x_0)]\tanh(\beta\hbar\omega_0/2)/(\hbar\omega_0)}.$$

(5.61)

The normalized Wigner function is then given by

$$\begin{aligned}W_{norm}(x,p)&=\frac{W_{st}(x,p)}{Z}\\&=(\pi\hbar)^{-1}\tanh\left(\beta\hbar\omega_0/2\right)e^{-2[\varepsilon(x,p)-V(x_0)]\tanh(\beta\hbar\omega_0/2)/(\hbar\omega_0)},\end{aligned}$$

(5.62)

where

$$\begin{aligned}Z&=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}W_{st}(x,p)dxdp\\&=\frac{\pi\hbar e^{-\beta V(x_0)}}{\sinh\left(\beta\hbar\omega_0/2\right)}.\end{aligned}\qquad(5.63)$$

We remark that the Wigner function $W_{norm}(x,p)$ for the mixed states of a harmonic oscillator is a superposition of the Wigner functions for the pure states $W_n(x,p)$, viz., [2,4]

$$W_{norm}(x,p) = \frac{\sum_{n=0}^{\infty} W_n(x,p) e^{-\beta\hbar\omega_0(n+1/2)}}{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega_0(n+1/2)}}$$
$$= (\pi\hbar)^{-1} \tanh\left(\beta\hbar\omega_0/2\right) e^{-2[\varepsilon(x,p)-V(x_0)]\tanh(\beta\hbar\omega_0/2)/(\hbar\omega_0)}.$$

(5.64)

Here $W_n(x,p)$ is defined as

$$W_n(x,p) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \psi_n(x-y/2)\psi_n^*(x+y/2)e^{-ipy/\hbar}dy$$
$$= \frac{(-1)^n}{\pi\hbar} e^{-\left(p^2+m^2\omega_0^2x^2\right)/(m\hbar\omega_0)} L_n\left[\frac{2\left(p^2+m^2\omega_0^2x^2\right)}{m\hbar\omega_0}\right],$$

(5.65)

where

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega_0}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega_0 x^2}{2\hbar}\right) H_n\left(x\sqrt{\frac{m\omega_0}{\hbar}}\right) \quad (5.66)$$

is an eigenfunction of the harmonic oscillator, where $H_n(z)$ and $L_n(z)$ are the Hermite and Laguerre polynomials, respectively [5]. Other examples of Wigner functions for simple quantum systems such as the Morse oscillator and the particle in an infinite square well potential can be found in Ref. [3].

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CHAPTER VI

Master equation for the Wigner function

VI.I Wigner function for open systems

The results we have given in Chapter V apply to closed quantum systems apart from the supposition that for intermediate damping just as its classical counterpart the quantum TST rate provides a good approximation to the Kramers escape rate at temperatures greater than the critical temperature. Now, as already mentioned in Chapter I and as demonstrated by Caldeira and Leggett [1], the Wigner formalism [2,3] may also be applied to *open* quantum systems [4]. In particular, it provides a useful tool for introducing quantum corrections to classical models of dissipation such as many body collisions or Brownian motion [1,5-8]. In this context as we have seen the one-dimensional quantum Brownian motion of a particle of mass m moving in a potential $V(x)$ is usually studied by regarding the Brownian particle as bi-linearly coupled to a bath of harmonic oscillators in thermal equilibrium at temperature T [1,8-16]. The most convenient way (see Chapter II, Appendix II.I) of characterizing the bath effect is by means of the *spectral density* characterising the coupling parameters to the j^{th} oscillator, which is cut off in some manner at high frequencies. (Little information about the coupling constants is usually available and introduction of the spectral density with a given high frequency cutoff should therefore be regarded [17] as a phenomenological way to account for environmental effects). The oscillators constituting the string or transmission line represent the normal modes of the bath. We remark that the effect of friction is regarded as entirely equivalent to the bilinear coupling to these normal modes. Quantization of the bath of oscillators [1] then yields the semiclassical master equation [1,8-16]

$$\frac{\partial W}{\partial t} + \hat{M}_W W = \hat{M}_D W \,, \tag{6.1}$$

where the operator $\hat{M}_W$ is defined by Eq.(4.26) viz.,

$$\hat{M}_W W = \frac{p}{m}\frac{\partial W}{\partial x} - \frac{1}{i\hbar}\left[V\left(x + \frac{i\hbar}{2}\frac{\partial}{\partial p}\right) - V\left(x - \frac{i\hbar}{2}\frac{\partial}{\partial p}\right)\right] W$$
$$= \frac{p}{m}\frac{\partial W}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial W}{\partial p} - \sum_{r=1}^{\infty}\frac{(i\hbar/2)^{2r}}{(2r+1)!}\frac{\partial^{2r+1}V}{\partial x^{2r+1}}\frac{\partial^{2r+1}W}{\partial p^{2r+1}} \tag{6.2}$$

and the operator $\hat{M}_D$ is given by

$$\hat{M}_D W = \frac{\partial}{\partial p}\left[D_p p W + D_{pp}\frac{\partial W}{\partial p} + D_{xp}\frac{\partial W}{\partial x}\right]. \tag{6.3}$$

Here $D_p, D_{pp},$ and D_{xp} are coordinate, momentum, and time dependent parameters which are to be determined. The left hand side of Eq. (6.1) is the quantum analogue of the Liouville equation, while $\hat{M}_D W$ characterizes the interaction of the Brownian particle with the thermal bath at temperature *T*; the term $\hat{M}_D W$ being the analogue of the collision kernel (*stosszahlansatz*) in the classical kinetic theory. In general Eq. (6.3) has the form of a Kramers-Moyal expansion truncated at the second term, which is to be expected on intutitive grounds given that the Wigner distribution should closely approximate the classical one (as discussed in Chapter I). This point has also been emphasized by Gross and Lebowitz [18] who state that "appropriate quantum kernels are suggested by requiring that the Wigner distribution function satisfy an integrodifferential equation (e.g. Boltzmann's collision integral) with a stochastic kernel which is the same as that obeyed by the classical distribution function." Conditions for the validity of the master Eq. (6.1) are discussed elsewhere (e.g., Refs. 19 and 20). We remark that in general the kernel $\hat{M}_D W$ contains quantum correction terms [15] additional to those given by Caldeira and Leggett. Most of these terms can be incorporated in the present treatment, e.g. the term $\partial_p D_{xp} \partial_x$ in Eq. (6.3) absent in the original Caldeira–Leggett equation [1] is included in $\hat{M}_D W$ explicitly as in Ref. [15] (this term describes quantum mechanical coupled *p-x* diffusion).

Being in possession of the functional form of the master Eq. (6.1) for the Brownian particle, the crucial step is to determine the coefficients $D_p, D_{pp},$ and D_{xp}. In the classical limit, $\hbar \to 0$, the coefficients $D_p, D_{pp},$ and D_{xp} become (as shown, e.g., in [24,63])

$$D_p = \gamma,\ D_{pp} = \gamma m/\beta,\ \ D_{xp} = 0\,, \tag{6.4}$$

where γ is a dissipation parameter. Equation (6.1) then reduces to the Klein-Kramers (Fokker-Planck) Eq. (2.51). As we have already mentioned the classical Klein-Kramers equation has been extensively applied to the Brownian motion in a potential [21,22].

Hitherto calculations of $D_p, D_{pp},$ and D_{xp} in the quantum case have usually been undertaken for a Brownian harmonic oscillator (see, for example, Refs. 10-14). As far as semiclassical treatments of the Brownian motion in an anharmonic potential $V(x)$ are concerned little in the way of solution of Eq. (6.1) apart from the pioneering work of Wigner (on quantum corrections to the classical distribution function in the closed system summarized in the previous Chapter) has appeared. Undoubtedly, many methods of determining these coefficients exist. However, we now suggest a simple heuristic method of determining D_p, D_{pp}, D_{xp} for an *arbitrary* potential $V(x)$. For simplicity, we evaluate D_p, D_{pp}, D_{xp} in the approximation of frequency independent damping, where D_p, D_{pp}, D_{xp} in Eq. (6.1) are *independent* of the time [12,13]. In the high temperature limit, this approximation may be used in a wide range of the model parameters both in the limits of weak and strong damping [23]. For the range of parameters, where such an approximation is not valid (e.g., throughout the very low temperature region), other methods should be used (a detailed discussion of the validity of this approximation is given by Grabert [23]). We have also chosen the approximation of frequency independent damping because that underlies the classical Brownian motion and so is appropriate here. Our objective being merely to understand how quantum effects treated in semiclassical fashion alter the classical Brownian motion in a potential.

In order to determine the explicit form of D_p, D_{pp}, D_{xp} in Eq. (6.1), we use Wigner's results for the unnormalized equilibrium distribution $W_{st}(x, p)$ from Eq. (5.6) viz.

$$W_{st}(x,p)=e^{-\beta\varepsilon(x,p)}\left\{1+\Lambda\left(\frac{\beta p^2}{m}V''-3V''+\beta V'^2\right)\right.$$
$$+3\Lambda^2\left[\frac{p^4}{m^2}\left(\frac{(\beta V'')^2}{6}-\frac{\beta V^{(4)}}{10}\right)\right.$$
$$+\frac{p^2}{m}\left(V^{(4)}-\frac{2\beta V'''V'}{5}+\frac{V''(\beta V')^2}{3}-\frac{9\beta V''^2}{5}\right)$$
$$\left.\left.+\frac{\beta^2V'^4}{6}+\frac{5V''^2}{2}-\frac{9\beta V''V'^2}{5}+2V'''V'-\frac{3V^{(4)}}{2\beta}\right]+\ldots\right\}. \tag{6.5}$$

The equilibrium Wigner distribution $W_{st}(x,p)$ satisfies Wigner's Eq. (5.1), namely

$$\frac{\partial W}{\partial t}+\hat{M}_W W=0 \tag{6.6}$$

to $o\left(\hbar^4\right)$ [2]. On the other hand, $W_{st}(x,p)$ must also be the equilibrium solution of the generic master Eq. (6.1), i.e., it must also satisfy $\hat{M}_D W_{st}=0$. By seeking a solution for D_p, D_{xp}, D_{pp} in the form

$$D_p=\gamma+\hbar^2 d_2^p(x,p)+\hbar^4 d_4^p(x,p)+\cdots,$$

$$D_{pp}=\frac{\gamma m}{\beta}+\hbar^2 d_2^{pp}(x,p)+\hbar^4 d_4^{pp}(x,p)+\cdots$$

and

$$D_{xp}=\hbar^2 d_2^{xp}(x,p)+\hbar^4 d_4^{xp}(x,p)+\cdots$$

and by substituting Eq. (6.5) into Eq. (6.1), one then finds if $W_{st}(x,p)$ is a solution of $\hat{M}_D W_{st}=0$, that the coefficients D_p and D_{xp} must remain as in Eq. (6.4) and only D_{pp} must be altered to read

$$D_{pp}=\frac{m\gamma}{\beta}\left\{1+2\Lambda V''(x)-\frac{2\Lambda^2}{5}\left[6V'''(x)V'(x)+2V''(x)^2+3V^{(4)}(x)\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]+\ldots\right\}. \tag{6.7}$$

Thus the explicit form of the master Eq. (6.1) containing the terms up to $o\left(\hbar^4\right)$ is

$$\frac{\partial W}{\partial t}+\frac{p}{m}\frac{\partial W}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}+\frac{\hbar^2}{24}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3}-\frac{\hbar^4}{1920}\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5}+\ldots$$

$$=\gamma\frac{\partial}{\partial p}\left[pW+\frac{m}{\beta}\left\{1+\frac{\hbar^2\beta^2}{12m}V''-\frac{\hbar^4\beta^4}{1440m^2}\left[6V'''V'+2V''^2+3V^{(4)}\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right]+\ldots$$

(6.8)

The imposition of the Wigner phase space distribution $W_{st}(x,p)$ as the equilibrium solution of the master Eq. (6.1) so yielding a potential dependent diffusion coefficient D_{pp} appears to be the exact analogue of the *ansatz* of a Maxwell-Boltzmann stationary distribution used by Einstein, Smoluchowski, Langevin, Klein and Kramers [21,22] in order to calculate diffusion coefficients in the Fokker-Planck equation of the classical theory of the Brownian motion. Furthermore, the condition

$$\widehat{M}_D W_0 = 0$$

is entirely equivalent to the property of the collision kernel $St(f)$ in the classical kinetic theory, whereby the equilibrium distribution function

$$f_0(x,p) \sim \exp[-\beta\varepsilon(x,p)]$$

always satisfies the condition

$$St(f_0)=0\,.$$

Here $f(x,p,t)$ is the phase space distribution function obeying the kinetic equation

$$\frac{\partial f}{\partial t}+\frac{p}{m}\frac{\partial f}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial f}{\partial p}=St(f)\,.$$

In particular, this is so for the Klein-Kramers equation (2.51), where

$$St(f)=\gamma\frac{\partial}{\partial p}\left[pf+\frac{m}{\beta}\frac{\partial f}{\partial p}\right].$$

In the quantum case, this idea has been used before, e.g., by Gross and Lebowitz [18] in their formulation of quantum kinetic models of impulsive collisions. According to [18], for a system with a time dependent Hamiltonian $\widehat{H}$, the equation governing the time behaviour of the density matrix ρ is

$$\frac{\partial\rho}{\partial t}+\frac{i}{\hbar}\left[\widehat{H},\rho\right]=\widehat{Q}\rho\,, \tag{6.9}$$

where the collision kernel operator $\widehat{Q}$ satisfies the condition

$$\hat{Q}\rho_0 = 0$$

where

$$\rho_0 = \frac{e^{-\beta \hat{H}_0}}{\mathrm{Tr}\left(e^{-\beta \hat{H}_0}\right)}$$

is the equilibrium density matrix and $\hat{H}_0$ is the time independent Hamiltonian. Our condition $\hat{M}_D W_0 = 0$ is entirely analogous to the Gross-Lebowitz condition $\hat{Q}\rho_0 = 0$. The condition $\hat{Q}\rho_0 = 0$; has also been used by Redfield [24] in the calculation of the matrix elements of the relaxation operator $\hat{Q}$ in the context of his (second-order) perturbation theory of relaxation processes. We also mention that the modification of the diffusion coefficients in the classical Fokker-Planck equation caused by quantum effects has been anticipated by Zwanzig [25].

By way of comparison with previous results we note that the master equation Eq. (6.8) can be used for an arbitrary potential $V(x)$. For illustration, we consider a harmonic potential

$$V(x) = \frac{m\omega_0^2 x^2}{2},$$

which is of the utmost importance as the quantum Brownian oscillator model is ubiquitous in physics and chemistry. Here the calculation can be considerably simplified as the normalized equilibrium Wigner function is available in the simple exact form Eq. (5.16). Noting Eqs. (5.16) and (5.20), we can readily evaluate D_{pp} for a quantum oscillator in closed form. Thus we have from our perturbation procedure

$$\begin{aligned} D_{pp} &= \frac{m\gamma}{\beta}\left(1 + \frac{\hbar^2\beta^2\omega_0^2}{12} - \frac{\hbar^4\beta^4\omega_0^4}{720} + \ldots\right) \\ &= \gamma \frac{m\hbar\omega_0}{2} \coth\frac{\beta\hbar\omega_0}{2} \\ &= \gamma\left\langle p^2 \right\rangle, \end{aligned} \tag{6.10}$$

where $\left\langle p^2 \right\rangle$ is given by Eq.(5.18), so that Eq. (6.8) becomes

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial W}{\partial p} = \gamma \frac{\partial}{\partial p}\left[pW + \left\langle p^2 \right\rangle \frac{\partial W}{\partial p} \right]. \tag{6.11}$$

The master Eq. (6.11) coincides in all respects with that of Agarwal [10], who first developed a detailed theory of Brownian motion of a quantum oscillator (see his Eq. (2.11) with $\lambda = 0$) in the weak coupling limit. It is known, however, that according to the already available theory of quantum dissipation, in a quantum Brownian oscillator, the equilibrium distribution as well as the equilibrium averages $\langle x^2 \rangle$ and $\langle p^2 \rangle$ *depend on damping* (appropriate equations are given in Chapter 6 of [26]). In the approximation of Ohmic damping with Drude's regularization, these equations read

$$\langle x^2 \rangle = \frac{1}{m\beta} \sum_{n=-\infty}^{\infty} \frac{1}{\omega_0^2 + v_n^2 + \gamma\omega_D /(1 + \omega_D / |v_n|)} \tag{6.12}$$

and

$$\langle p^2 \rangle = \frac{m}{\beta} \sum_{n=-\infty}^{\infty} \frac{\omega_0^2 + \gamma\omega_D /(1 + \omega_D / |v_n|)}{\omega_0^2 + v_n^2 + \gamma\omega_D /(1 + \omega_D / |v_n|)}, \tag{6.13}$$

where

$$|v_n| = \frac{2\pi |n|}{\hbar\beta}$$

and ω_D is a cutoff frequency (a Drude regularization is necessary as in pure Ohmic damping $\langle p^2 \rangle$ diverges [27]). However, according to [27], these equations reduce to Eqs. (5.17)and (5.18) either for vanishing damping ($\gamma \to 0$) or in the high temperature limit ($\beta\hbar\omega_0 \to 0$). Moreover, the difference between the damping dependent and damping independent equations is negligible for $\gamma / \omega_0 < 0.1$ (which is, in fact, the condition for the existence of damped oscillations and/or narrow spectral lines) for all $\beta\hbar\omega_0$ (see Figure VI.I below). Thus for $\beta\hbar\gamma \le 1$, Eq. (6.11) (i.e., the Agarwal model) may be used as an approximate description of the kinetics of a quantum oscillator.

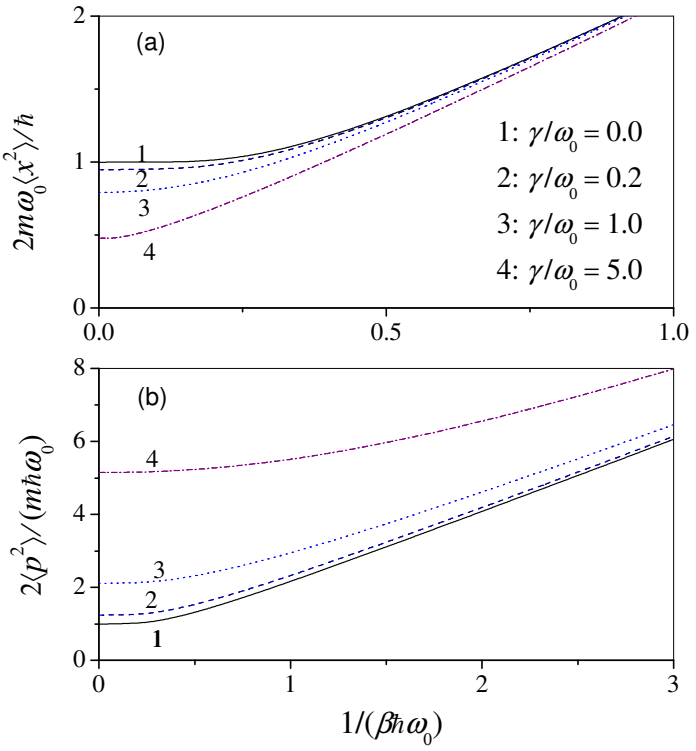

Figure VI.I. The normalized equilibrium averages $2m\omega_0\left\langle x^2\right\rangle/\hbar$ and $2\left\langle p^2\right\rangle/m\hbar\omega_0$ vs. temperature, $1/(\beta\hbar\omega_0)$ for various values of the normalized damping γ/ω_0: 0 (curves 1), 0.2 (2), 1.0 (3), and 5.0 (4). The calculations are from Eqs. (6.12) and (6.13); a Drude model with the cutoff frequency $\omega_D = 10\omega_0$. (After U. Weiss [27] and Grabert et al. [28]).

We remark that our procedure can be generalized for the harmonic oscillator by simply using the corresponding damped equations for $\left\langle x^2\right\rangle$ and $\left\langle p^2\right\rangle$ from Eqs. (6.12) and (6.13). Noting that for the stationary distribution (Eq. (5.16)) the condition $\hat{M}_D W_{st} = 0$ is fulfilled and seeking the additional terms needed in order to satisfy the Wigner Eq. (6.6), leads to the master equation given by Grabert [23]

$$\frac{\partial W}{\partial t}+\frac{p}{m}\frac{\partial W}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}=\gamma\frac{\partial}{\partial p}\left[pW+\left\langle p^2\right\rangle\frac{\partial W}{\partial p}\right]$$
$$-\frac{\partial^2}{\partial p\partial q}\left(\frac{\left\langle p^2\right\rangle}{m}-m\omega_0^2\left\langle x^2\right\rangle\right)W. \tag{6.14}$$

Equation (6.14) differs from the Agarwal Eq. (6.11) by the last term in the right hand side. The principal difference between Eqs. (6.11) and (6.14) is that because of this additional term, Eq. (6.14) is not a bona fide Fokker-Planck equation since one of the eigenvalues of the diffusion matrix is negative [23]. This is related to the fact that the equilibrium averages $\left\langle x^2\right\rangle$ and $\left\langle p^2\right\rangle$ depend on the damping parameter γ.

VI.II Quantum Smoluchowski equation

Here we demonstrate how the quantum Smoluchowski equation for the configuration space distribution function which is valid in the high dissipation or noninertial limit can be obtained from the master Eq. (6.1) by using Brinkman's method [29] which we have summarized in Chapter II. We shall show how (a) his method of solution of the Klein-Kramers equation may be transparently extended to the quantum case to yield quantum differential recurrence relations in configuration space and how (b) a quantum Smoluchowski equation (having as equilibrium solution the Wigner configuration space distribution) follows directly from the quantum Brinkman recurrence relations. We recall first that Brinkman [29] showed by expanding the momentum part of the solution of the Klein-Kramers equation (Eq. (2.51)), $W(x,p)$ in an orthonormal basis $\{D_n\}$ of Weber (harmonic oscillator) functions $D_n(y)$, viz., [30]

$$W(x,p,t)=e^{-\beta p^2/4m}\sum_{n=0}^{\infty}D_n\left(p\sqrt{\frac{\beta}{m}}\right)\varphi_n(x,t), \tag{6.15}$$

where

$$D_n(y)=2^{-n/2}e^{-y^2/4}H_n\left(\frac{y}{\sqrt{2}}\right)$$

and $H_n(z)$ is the Hermite polynomial of order n [31], that Eq.(2.51) becomes a partial three-term differential recurrence relation in the distribution functions

$\varphi_n(x,t)$, $n \geq 0$ (see Chapter II.IV). In particular, $\varphi_0(x,t)$ yields the configuration space distribution function

$$P(x,t) = \int W(x,p,t)dp \equiv \varphi_0(x,t)$$

Thus one may assume [15,16] (just as in the classical case) that the momentum dependence of the Wigner function W may be expanded in the Weber functions D_n in the form of Eq. (6.15). By substituting Eq. (6.15) into the master equation with the collision kernel, Eq. (6.8), one then finds on utilizing the orthogonality and recurrence properties of D_n that the quantum Brinkman equations for the functions $\varphi_n(x,t)$ are

$$\frac{\partial \varphi_n}{\partial t} + n\gamma\varphi_n + \frac{1}{\sqrt{\beta m}}\left[\frac{\partial \varphi_{n-1}}{\partial x} + (n+1)\frac{\partial \varphi_{n+1}}{\partial x}\right] + \sqrt{\frac{\beta}{m}}\frac{\partial V}{\partial x}\varphi_{n-1} = \Lambda\left(2\gamma\frac{\partial^2 V}{\partial x^2}\varphi_{n-2} + \frac{1}{\sqrt{\beta m}}\frac{\partial^3 V}{\partial x^3}\varphi_{n-3}\right). \tag{6.16}$$

(for simplicity we limit the calculation to $o(\hbar^2)$). In the classical limit ($\Lambda = 0$), Brinkman's recurrence Eq. (6.16) has been solved for a wide variety of potentials using matrix continued fraction methods as described in [21,22]. As the semiclassical Eq. (6.16) constitutes a partial differential recurrence relation, essentially similar to the classical one, Brinkman's original method may also be applied here. Equation (6.16) then yields to first order in $\hbar^2$, quantum corrections to the nonequilibrium configuration space functions $\varphi_n(x,t)$. In effect, Eq. (6.16) generalizes Wigner's perturbation procedure, his Eq. (23) of Ref. [2] to non-equilibrium dynamics governed by the Brownian motion *stosszahlansatz* allowing one to study the nonequilibrium quantum-classical correspondence.

Now our objective along with calculating diffusion coefficients for the quantum Fokker-Planck equation in phase space is to show (guided everywhere by Brinkman's classical calculation [29]) how one can derive from Eq. (6.16) a semiclassical Smoluchowski equation. In order to accomplish this we note that in the noninertial or high damping limit ($m \to 0$ or $\gamma = \zeta/m >> 1$), the ratio

$$\dot{\varphi}_n/\gamma \approx 0, \quad n \geq 1. \tag{6.17}$$

Hence we have from Eqs. (6.16) and (6.17) the following hierarchy

$$\frac{\partial \varphi_0}{\partial t} = -\frac{1}{\sqrt{\beta m}} \frac{\partial \varphi_1}{\partial x}, \tag{6.18}$$

$$\varphi_1 = -\frac{1}{\gamma\sqrt{\beta m}} \left(\frac{\partial \varphi_0}{\partial x} + 2\frac{\partial \varphi_2}{\partial x} + \beta V' \varphi_0 \right), \tag{6.19}$$

$$\varphi_2 = -\frac{1}{2\gamma\sqrt{\beta m}} \left(\frac{\partial \varphi_1}{\partial x} + 3\frac{\partial \varphi_3}{\partial x} + \beta V' \varphi_1 \right) + \Lambda V'' \varphi_0, \tag{6.20}$$

etc. The time derivative in Eq. (6.18) cannot be neglected as that equation is a constitutive relation. If we now close the set by supposing $\varphi_3 = 0$ then the first two terms on the right hand side of Eq. (6.20) vanish when $m \to 0$ as is easily shown and we have in the non-inertial (or high friction) limit

$$\varphi_2 = \varphi_0 \Lambda V''(x).$$

The system of Eqs. (6.18)-(6.20) is now closed and can be readily rearranged to yield an equation for the configuration space distribution function $P(x,t) = \varphi_0(x,t)$, viz.,

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{P}{\zeta} \frac{\partial V}{\partial x} + \frac{\partial}{\partial x}(DP) \right\}. \tag{6.21}$$

Here

$$\zeta = \gamma m$$

and

$$D = \frac{\left[1 + 2\Lambda V''(x)\right]}{\zeta\beta}$$

have the meaning of friction and diffusion coefficients, respectively. Equation (6.21) reduces to the classical Smoluchowski equation for the configuration space distribution function $P(x,t)$ if $\Lambda = 0$. The closure assumption we have used may be justified rigorously by solving the quantum Brinkman Eqs. (6.16) by iteration to arbitrary order in *n* and then taking the noninertial limit as illustrated in the classical case in Chapter II.IV. The advantage of the Smoluchowski equation is that it is much easier to solve than the Brinkman equations. We remark that Eq. (6.21) can also be obtained from Eq. (6.1) by using an heuristic approach due to Kramers [32] just as in the classical case (see Appendix VI.I at the end of this Chapter).

The semiclassical Smoluchowski Eq. (6.21) is equivalent to classical Brownian motion in the potential $V(x)$ with coordinate dependent diffusion coefficient $D(x)$. The corresponding Langevin equation in the Stratonovich interpretation [21,22] reads

$$\dot{x}(t) = -\frac{1}{\zeta}\frac{\partial}{\partial x}\left\{V\left[x(t)\right] + \frac{\zeta}{2}D\left[x(t)\right]\right\} + \sqrt{\frac{\beta}{\zeta}D\left[x(t)\right]}\lambda(t)\,. \quad (6.22)$$

Here the dot denotes the time derivative and $\lambda(t)$ is a random force with the Gaussian white noise properties

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

(the overbar means the statistical average over the realizations of the random force). Just as in the classical case, the semiclassical Smoluchowski Eq. (6.21) may be applied to the study of the long time (or low frequency) relaxational behavior of a system [21,22].

We emphasize that it is often preferable to write the diffusion coefficient D in the equivalent form

$$D = \left\{\zeta\beta\left[1 - 2\Lambda V''(x)\right]\right\}^{-1} + o(\hbar^4)\,. \quad (6.23)$$

The diffusion coefficient so written ensures that Eq. (6.21) will not violate the second law of thermodynamics irrespective of the nature of the potential [33]. For example, the diffusion coefficient so written for an arbitrary *asymmetric* periodic ratchet potential $V(x)$ at *zero*-external bias ensures a *vanishing probability* current j for any order of $\hbar^2$ (and not only to $o(\hbar^4)$) as evidenced by Machura *et al.* [33] in their discussion of the semiclassical Smoluchowski equation proposed by Ankerhold *et al.* [34,35]. The quantum Smoluchowski equation deduced by Ankerhold et al. [34,35] (via the path integral formulation of quantum dissipative systems) is *very similar* but not *identical* to Eq. (6.21). That equation reads in our notation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left\{\frac{P}{\zeta}\frac{\partial V_{ef}}{\partial x} + \frac{\partial\left[D_A P\right]}{\partial x}\right\}, \quad (6.24)$$

where

$$V_{ef} = V(x) + \frac{\lambda V''(x)}{2},$$

$$D_A = \frac{[1+\beta\lambda V''(x)]}{\zeta\beta}$$

and

$$\lambda = \frac{12\Lambda}{\pi^2\beta}\sum_{n=1}^{\infty}\left(n^2 + \frac{\hbar\gamma\beta}{2\pi}n\right)^{-1}$$

is the quantum parameter as used by them [34,35]. Noting that, $\sum_{n=1}^{\infty} n^{-2} = \pi^2/6$, $\lambda \to 2\Lambda/\beta$ and $D_A \to D$ in the high temperature limit $\hbar\gamma\beta << 2\pi$; we see that Eq. (6.24) differs from Eq. (6.21) only by the additional term $(\lambda/2)V''$ in V_{ef}. However, this difference is important, because the stationary solution of Eq. (6.24) in the high temperature limit is [34,35]

$$P_A(x) \sim e^{-\beta V(x)}\left[1+\Lambda\left(\beta V'(x)^2 - 3V''(x)\right)+...\right],$$

which is similar to the coordinate dependent part of the Wigner phase space distribution $W_{st}(x,p)$ [resulting from omitting the p^2 term in Eq. (6.8)]. However, the *true* Wigner equilibrium distribution in configuration space $P_{st}(x)$ [2]

$$P_{st}(x) \sim e^{-\beta V(x)}\left\{1+\Lambda\left[\beta V'(x)^2 - 2V''(x)\right]+...\right\} \qquad (6.25)$$

(which includes by integration with respect to *p* the contribution of the p^2 term in Eq. (6.8)), does not coincide with $P_A(x)$ and so *does not satisfy* Eq. (6.24). Moreover, only the first order term (with respect to Λ) of the quantum correction factor Ξ Eq. (5.28) to the classical TST escape rate formula in the very high damping limit is yielded correctly by Eq. (6.24) (in order to evaluate the factor Ξ one needs only $P_{st}(x)$ and $D(x)$; see Section III below, where the factor Ξ is calculated from the Smoluchowski Eq. (6.21)). Nevertheless, in order to satisfy these two conditions, one may easily modify the Ankerhold *et al.* Eq. (6.24) by simply replacing V_{ef} by V and λ by $2\Lambda/\beta$ in that equation.

Equation (6.21) is written explicitly to $o\left(\hbar^4\right)$. In like manner higher order quantum correction terms to the diffusion coefficient *D* may be calculated. However, a much more simple approach to the evaluation of *D* exists. Namely by

using the explicit form of the equilibrium distribution function in configuration space

$$P_{st}(x) = \int W_{st}(x, p)\, dp$$

given by Eq. (5.9), combined with the stationary equation

$$\frac{\partial}{\partial x}\left\{ \frac{P_{st}}{\zeta}\frac{\partial V}{\partial x} + \frac{\partial (DP_{st})}{\partial x} \right\} = 0$$

so that we have the next term in the perturbation expansion of the diffusion coefficient D in Eq. (6.21), viz.,

$$D(x) = \frac{1}{\zeta\beta}\left[1 + 2\Lambda V''(x) - \frac{4\Lambda^2}{5}\left(3V'''(x)V'(x) + V''(x)^2 - 3\beta^{-1}V^{(4)}(x) \right) + ... \right]$$
$$= \left\{ \zeta\beta\left[1 - 2\Lambda V''(x) + \frac{12\Lambda^2}{5}\left(V'''(x)V'(x) + 2V''(x)^2 - \beta^{-1}V^{(4)}(x) \right) + ... \right] \right\}^{-1}. \tag{6.26}$$

We remark that for a quantum oscillator, the diffusion coefficient D is independent of x and is given by

$$D = \frac{\hbar\omega_0}{2\zeta}\coth\frac{\beta\hbar\omega_0}{2}. \tag{6.27}$$

Here we have noted that according to Eqs. (5.16) and (5.17) the equilibrium distribution in configuration space $P_{st}(x)$ for a quantum oscillator is

$$P_{st}(x) \sim \exp\left[-\frac{V(x)\tanh(\beta\hbar\omega_0/2)}{\hbar\omega_0/2} \right]$$

where $V(x) = m\omega_0^2 x^2/2$.

VI.III. Escape rate in the very high damping limit

As a simple application of the above results, we demonstrate how a semiclassical correction to the Kramers escape rate Γ (see chapter II) of a Brownian particle over a potential barrier in the very high damping limit (VHD) and at high temperatures $T>T_c$ [17,21,27] can be calculated from Eq. (6.21). First we note that Eq. (6.21) is a continuity equation namely

$$\frac{\partial P}{\partial t} + \frac{\partial j}{\partial x} = 0,$$

where the probability current j is given by

$$j = -\left[\frac{P}{\zeta}\frac{\partial V}{\partial x} + \frac{\partial (DP)}{\partial x}\right]. \tag{6.28}$$

Substitution of the stationary Wigner distribution $P_{st}(x)$ from Eq. (5.9) into Eq. (6.28) renders $j = 0$ [with accuracy $o\left(\hbar^4\right)$] for any well behaved $V(x)$, so verifying that

$$P_0(x) = \frac{P_{st}(x)}{\int P_{st}(x)dx}$$

is a stationary solution of our semiclassical quantum Smoluchowski Eq. (6.21). The second stationary solution of Eq. (6.21) j=constant refers to steady probability current flow over the potential barrier generated by $V(x)$. This solution allows one to evaluate the escape rate $\Gamma \approx j/N$ from a potential well with a minimum at $x = x_a$ over a single potential barrier at $x = x_c$ the nonequilibrium effects arise because unlike in TST Maxwell's demon does not replace the particles lost by diffusion over the barrier. The normalization factor N is given by the well population and the probability current j is evaluated in the vicinity of the barrier top [22]. First we note that the inverse escape rate Γ^{-1} may by approximated as ([22], Section 5.10)

$$\Gamma^{-1} \sim \int_{top} D^{-1}(x)P_{st}^{-1}(x)dx \int_{well} P_{st}(x)dx. \tag{6.29}$$

The well integral can be evaluated just as in the TST case described in Chapter V from the harmonic oscillator equations

$$\begin{aligned} I_{well} &= \int_{well} P_{st}(x)dx \\ &= \int_{well}\int W_{st}(x,p)dpdx \\ &= Z_a \\ &= \pi\hbar e^{-\beta V(x_a)}\left[\sinh\left(\hbar\omega_a\beta/2\right)\right]^{-1}. \end{aligned} \tag{6.30}$$

Regarding the calculation of the integral in the vicinity of the barrier

$$I_{top} = \int_{top} D^{-1}(x)P_{st}^{-1}(x)dx,$$

we recall that within the approximation of the potential near the barrier top by an inverted parabola, the diffusion coefficient $D(x)$ near the top (point c) is independent of x and is given by Eq. (6.27) with $\omega_0 = i\omega_c$, viz.,

$$D = \left(\hbar\omega_c / 2\zeta\right)\cot\left(\beta\hbar\omega_c / 2\right). \tag{6.31}$$

Furthermore the equilibrium distribution function in configuration space near the top is

$$\begin{aligned} P_{st}(x) &= \int_{top} W_c(x,p)dp \\ &= \sqrt{\frac{2\pi\hbar m\omega_c}{\sin\hbar\omega_c\beta}}\, e^{-\beta V(x_c)+m\omega_c x^2\tan(\hbar\omega_c\beta/2)/\hbar} \end{aligned}, \tag{6.32}$$

where $W_c(x,p)$ is defined by Eq. (5.61) with $\omega_0 = i\omega_c$. Noting Eqs. (6.31) and (6.32), we can evaluate the integral I_{top} near the barrier top as

$$\begin{aligned} I_{top} &= \int_{top} D^{-1}(x)P_{st}^{-1}(x)dx \\ &= \frac{2\zeta\sin\left(\hbar\beta\omega_c/2\right)}{m\hbar\omega_c^2}\, e^{\beta V(x_c)}. \end{aligned} \tag{6.33}$$

Hence we have

$$\begin{aligned} \Gamma &\sim \left(I_{top}I_{well}\right)^{-1} \\ &= \frac{\omega_c^2\sinh(\hbar\beta\omega_a/2)}{2\pi\gamma\sin(\hbar\beta\omega_c/2)}\, e^{-\beta\Delta V} \\ &= \frac{\omega_c\omega_a}{2\pi\gamma}\,\Xi e^{-\beta\Delta V}. \end{aligned} \tag{6.34}$$

The form of Eq. (6.34) which is the classical VHD Kramers rate

$$\Gamma_{VHD} \sim \frac{\omega_c\omega_a e^{-\beta\Delta V}}{2\pi\gamma}$$

multiplied by the quantum correction factor

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

reinforces our contention that we are essentially treating our system as a quantum particle at $T>T_c$ 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 effect of very high dissipation is to reduce the tunnelling contribution to the reaction rate just as such dissipation reduces the thermal

reaction rate below that predicted by the classical TST. The quantum correction terms in Eq. (6.34) are (as they must be) in complete agreement with Wigner's quantum TST calculation of the escape rate [36] given in Chapter IV which assumes that equilibrium prevails in the vicinity of the barrier (see also [37]). This semiclassical rate is increased due to tunnelling compared to the classical Kramers rate ($\hbar \to 0$) because the tunnelling *decreases* the effective barrier height which occurs in the exponential part of Eq. (6.34). The result we have given should hold at relatively high temperatures $T>T_c$ and when classically the energy dissipated per cycle of the almost periodic motion of a particle having the saddle point energy is much greater than the thermal energy.

VI.IV. Escape rate in the intermediate to high damping region

Here we consider intermediate to high damping which includes small inertial effects and which has the foregoing result as a particular limit. Guided by the classical case the solution will obtain when the energy loss per cycle is significantly greater than kT. In other words when the region of nonequilibrium of the distribution function near the top of the barrier does not exceed in spatial extent the region where the potential may be represented as an inverted harmonic oscillator potential [21]. This calculation illustrates the link between the exact solution of the IHD quantum Kramers escape rate for finite temperatures $T>T_c$ (given by Wolynes [38] and later by Pollak [39]) and the present perturbative semiclassical approach. Wolynes used a path integral evaluation of the reactive flux correlation function. On the other hand Pollak [39] started from the equivalence of the generalized Langevin equation for a Brownian particle to the equation of motion of a particle moving in a potential $V(x)$ bilinearly coupled to a bath of harmonic oscillators already alluded to. This procedure (which demonstrates using normal mode analysis that classically the IHD Kramers rate is equivalent to a harmonic multidimensional TST rate) may be extended to the quantum case by quantizing the system plus bath Hamiltonian consisting at the transition state of an assembly of real oscillators and one with imaginary frequency of oscillation representing the unstable barrier crossing mode. It leads to Wolynes' result without using path integrals. Other calculations [17] based on extensions of Langer's imaginary part of the free energy method to include

quantum effects also yield that result. The objective of all these calculations was to predict the temperature dependence of the quantum Kramers escape rate in condensed phases at finite temperatures.

We proceed from Eq. (6.1) using our perturbative method as follows. Adapting the procedure described for the classical case in [40-42], we need the number of particles n_a in the potential well at point *a* and the current j_c across the barrier top at point *c* (or in general the saddle point current) in order to calculate the escape rate

$$\begin{aligned} \Gamma_{IHD} &= \frac{j_c}{n_a} \\ &= \frac{\int_{top} (p/m) W(x_c, p) dp}{\int_{well} W(x, p) dp dx}. \end{aligned} \tag{6.35}$$

Note that Eq. (6.35) is of course the same flux over barrier definition as used by Wigner (cf. Eq (5.21)) however the difference is that *W* occurring in the numerator is now the nonequilibrium distribution near the barrier top.

The number of particles is $n_a = Z_a$, where Z_a is given by Eq. (5.25). In order to calculate the barrier current j_c, one needs the Wigner stationary solution *near the top* (point *c*). Here the Wigner function is approximated by the harmonic oscillator Eq. (5.61) with $\omega_0 = i\omega_c$ and is given by

$$W(x', p') = e^{-\beta V(x_c)} \sec\left(\beta\hbar\omega_c/2\right) e^{-m\left(p'^2 - \omega_c^2 x'^2\right)\tan(\beta\hbar\omega_c/2)/(\hbar\omega_c)}, \tag{6.36}$$

where $p' = p/m$ and $x' = x - x_c$. Furthermore, near the top we have from Eq. (6.1)

$$p'\frac{\partial W_c}{\partial x'} + \omega_c^2 x'\frac{\partial W_c}{\partial p'} = \frac{\partial}{\partial p'}\left[\gamma p' W_c + D_{p'p'}\frac{\partial W_c}{\partial p'}\right], \tag{6.37}$$

where $D_{p'p'} = D_{pp}/m^2$. The diffusion coefficient D_{pp} is independent of *x* and is given by Eq. (6.10) with $\omega_0 = i\omega_c$, so that

$$D_{p'p'} = (\gamma\hbar\omega_c/2m)\cot(\beta\hbar\omega_c/2).$$

Equation (6.36) has the form of a Boltzmann distribution and satisfies Eq. (6.37). This fact allows us to write following Kramers [32,41,42] the nonequilibrium solution $W(x', p')$ near the barrier as

$$W_c(x',p') = CF(x',p')e^{-\beta'\left(p'^2-\omega_c^2 x'^2\right)}, \tag{6.38}$$

where $C = e^{-\beta V(x_c)}\sec\left(\hbar\omega_c\beta/2\right)$ and $\beta' = m\tan\left(\hbar\omega_c\beta/2\right)/(\hbar\omega_c)$. The function $F(x',p')$ is a crossover function which has the equilibrium distribution in the depths of the well, varies very rapidly in the vicinity of the barrier and vanishes beyond the barrier as in the classical Kramers case [32,41,42]. Consequently that function must satisfy the boundary conditions

$$F(x',p') \to \begin{cases} 1, & x' \to \infty \\ 0, & x' \to -\infty \end{cases}. \tag{6.39}$$

By substituting Eq. (6.38) into Eq. (6.37) and noting that $D_{p'p'}\beta' = \gamma/2$, we have the differential equation for the crossover function as in the classical case [32,40-42]

$$p'\frac{\partial F}{\partial x'} + \omega_c^2 x'\frac{\partial F}{\partial p'} = D_{p'p'}\frac{\partial^2 F}{\partial p'^2} - \gamma p'\frac{\partial F}{\partial p'}. \tag{6.40}$$

The solution of Eq. (6.40) is of the form

$$F(x',p') = F(p'-ax').$$

By substituting $F(p'-ax')$ into Eq. (6.40) and introducing $p'-ax' = \xi$, we have

$$\left[(a-\gamma)p' - \omega_c^2 x'\right]\frac{\partial F}{\partial \xi} + D_{p'p'}\frac{\partial^2 F}{\partial \xi^2} = 0. \tag{6.41}$$

Equation (6.41) simplifies to an ordinary differential equation if

$$\omega_c^2 = (a-\gamma)a$$

or

$$a-\gamma = \sqrt{\frac{\gamma^2}{4}+\omega_c^2} - \frac{\gamma}{2}$$

(this is the condition that the eigenvalue associated with the unstable barrier crossing mode is real) namely

$$(a-\gamma)\xi\frac{\partial F}{\partial \xi} + D_{p'p'}\frac{\partial^2 F}{\partial \xi^2} = 0. \tag{6.42}$$

The solution of Eq. (6.42) satisfying the boundary conditions Eq. (6.39) is

$$F(\xi) = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\xi\sqrt{(a-\gamma)/2D_{p'p'}}} e^{-y^2}dy. \tag{6.43}$$

The current j_c is then given by

$$
\begin{aligned}
j_c &= m\int_{-\infty}^{\infty} p' W_c(0,p')dp' \\
&= \frac{mC}{\sqrt{\pi}}\int_{-\infty}^{\infty} p' e^{-\beta' p'^2} \int_{-\infty}^{p'\sqrt{(a-\gamma)/2D_{p'p'}}} e^{-y^2} dy dp' \qquad (6.44)\\
&= \frac{\hbar}{2\sin(\hbar\beta\omega_c/2)}\left(\sqrt{\frac{\gamma^2}{4}+\omega_c^2}-\frac{\gamma}{2}\right)e^{-\beta V(x_c)}.
\end{aligned}
$$

Thus the escape rate Γ_{IHD} from Eq. (6.35) is given by

$$
\Gamma_{IHD} = \Xi\frac{\omega_a}{2\pi\omega_c}\left(\sqrt{\frac{\gamma^2}{4}+\omega_c^2}-\frac{\gamma}{2}\right)e^{-\beta\Delta V}, \qquad (6.45)
$$

where the quantum enhancement factor Ξ is again given by the Wigner quantum TST factor Eq. (5.28). In the very high damping limit, Eq. (6.45) reduces to Eq. (6.34). Equation (6.45) appears to describe a quantum Brownian particle 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. The simple form of the results obtained are a consequence of the exact solution for the Wigner function for the harmonic oscillator given in [20,43].

In the context of solutions of the IHD quantum Kramers rate, we remark that the analysis of Wolynes [38] as well as that of Pollak [39] involves quantization of *both* bath and particle just as methods [17] based on Langer's analytical continuation of the free energy. The quantum mechanical enhancement factor Ξ yielded by all these calculations is for Ohmic friction [27,38]

$$
\Xi_W = \prod_{n=1}^{\infty}\frac{\omega_a{}^2+(2\pi n/\hbar\beta)^2+2\pi n\gamma/\hbar\beta}{-\omega_c{}^2+(2\pi n/\hbar\beta)^2+2\pi n\gamma/\hbar\beta}. \qquad (6.46)
$$

If the condition $\hbar\gamma\beta << 2\pi$ is fulfilled, we have the TST result as $\lim_{\hbar\beta\gamma\to 0}\Xi_W = \Xi$ [27], thus recovering our result embodied in Eq. (6.45). In this particular instance the *damping independent* Ξ is a fair approximation to Ξ_W. 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. A comprehensive analysis of Eq. (6.46) has been made by Hänggi *et al*. [44] and also by Weiss [27], where it is shown how the product Eq. (6.46) may be written

in terms of gamma functions consequently Wigner's original quantum correction is recovered when $T>>(\gamma/\omega_c)^2 T_c$.

VI.V Escape rate for all values of the dissipation

The escape rate Γ^{IHD} in the IHD regime discussed in Section VI.IV is extremely important, because exactly as in the classical case it appears in a general expression for escape rate valid for all values of dissipation. As already mentioned in Chapter II.III, Mel'nikov [45,46] and Rips and Pollak [47] have extended the bridging integral method for mechanical particles to account for quantum tunnelling in a semiclassical way. They attempt to generalize the classical formulae given by Kramers to all escape rate regimes and the bridging integral to include quantum effects by incorporating in their derivation the quantum tunnelling factor for a parabolic barrier. They showed that the quantum rate Γ above the crossover temperature may be written just as in the classical case as [47]

$$\Gamma = \Gamma_{IHD} \Upsilon , \tag{6.47}$$

where Γ_{IHD} is the quantum escape rate in the IHD regime and Υ is the quantum depopulation factor defined as

$$\Upsilon = \exp\left\{ \frac{\lambda \sin\lambda}{\pi} \int_{-\infty}^{\infty} \frac{\ln\left[1-\tilde{P}(x-i/2)\right]}{\cosh(2x\lambda)-\cos\lambda} dx \right\}. \tag{6.48}$$

Here

$$\lambda = \frac{\beta\hbar\Omega}{2},$$

with

$$\Omega = \sqrt{\frac{\gamma^2}{4}+\omega_c^2} - \frac{\gamma}{2}$$

is the characteristic frequency of the unstable barrier crossing mode (in the Ohmic damping limit), and

$$\tilde{P}(is) = \int_{-\infty}^{\infty} P\left(\varepsilon\middle|\varepsilon'\right) e^{-s(\varepsilon-\varepsilon')} dx ,$$

where $P\left(\varepsilon\middle|\varepsilon'\right)$ is the probability kernel expressing the probability that a particle with energy ε' leaving the barrier region will return to the barrier with an energy between ε and $\varepsilon + d\varepsilon$. The quantum rate

$$\Gamma = \int_{-\infty}^{\infty} [1 - R(\varepsilon)] f(\varepsilon) d\varepsilon$$

is found by solving (using the Wiener-Hopf method) an integral equation

$$f(\varepsilon) = \int_{-\infty}^{\infty} P\left(\varepsilon \middle| \varepsilon'\right) R(\varepsilon') f(\varepsilon') d\varepsilon' \tag{6.49}$$

for the population per unit time of particles $f(\varepsilon)$ at the top of the barrier; here $R(\varepsilon)$ is the quantum reflection probability for a parabolic barrier. The explicit forms of $\tilde{P}(is)$ are given elsewhere [47-49]. In particular, in Refs. 48 and 49 explicit equations for the escape rate are given for quantum Brownian motion in the periodic potential

$$V(x) = -V_0 \cos(x / x_0) . \tag{6.50}$$

(x_0 is a characteristic length) which will be used in Chapter VI. In the classical limit, Eq. (6.48) reduces to the known result of Mel'nikov [45,46]

$$\Upsilon = \exp\left[\frac{1}{\pi} \int_0^{\infty} \frac{\ln\{1 - \exp[-\gamma\delta(x^2 + 1/4)]\}}{x^2 + 1/4} dx \right],$$

where δ is the dimensionless action variable.

Just as in the classical case, the validity of Eq. (6.47) may be confirmed by direct comparison with the escape rate evaluated from the master equation (6.1) describing the evolution of the Wigner distribution function in phase space. Here the escape rate can be calculated by the matrix continued fraction method [21,22]. As we have stated García-Palacios and Zueco [15,16] have shown how the classical matrix continued fraction Risken method [22] could be extended to the quantum regime. Using this approach, Coffey et al. [50,51] have evaluated the escape rate Γ by solving Eq. (6.8) for the cosine potential Eq. (6.50) via matrix continued fractions.

VI. VI Conclusions

We have shown in this Chapter how the quantum master Eq. (6.1) which we have proposed may be used to incorporate the dissipation to the heat bath in quantum reaction rate theory in the intermediate to high damping limit. These results will be compared with the exact escape rates yielded by the matrix continued fraction method in Chapter VII. In that Chapter the quantum master equation for a cosine potential will be solved in detail to order $\hbar^2$ and a brief

sketch will also be given for a 2-4 bistable potential will also be given. Moreover it will also be demonstrated how the quantum generalization of the Meshkov-Melnik'ov depopulation factor combined with the quantum IHD Kramers rate which we have derived here agrees closely with the exact results. This is a rather important test of the Wigner function approach as quantum reaction rate theory has been extensively verified by computer simulations obtained by the molecular dynamics method [52,53] which calculates numerically time correlation functions etc. in the Wigner representation of quantum statistical mechanics.

APPENDIX VI

Appendix VI.I: Kramers's method applied to the derivation of the quantum Smoluchowski equation

In the classical theory of the Brownian motion for the purpose of deriving the Smoluchowski equation from the Klein-Kramers equation, Kramers proceeded by splitting the Klein-Kramers equation into two parts, consisting of the Smoluchowski operator acting on the phase space distribution and a remainder. Next by integrating along a straight line $x + p/\gamma = x_0$ (constant) in phase space and taking the high damping limit he demonstrates that the contribution of the remainder to the configuration space distribution is approximately zero while the first part reduces to the Smoluchowski equation.

In order to derive a quantum Smoluchowski equation from the quantum Klein-Kramers Eq. (6.8) in analogous fashion we first rewrite Eq. (6.8) in the form (with m = 1 following Kramers [32])

$$\frac{\partial W}{\partial t} = \gamma\left(\frac{\partial}{\partial p} - \frac{1}{\gamma}\frac{\partial}{\partial x}\right)\left(pW + \frac{1}{\beta}\left[1 + 2\Lambda\frac{\partial^2 V}{\partial x^2}\right]\frac{\partial W}{\partial p} + \frac{1}{\gamma}\frac{\partial V}{\partial x}W + \frac{1}{\beta\gamma}\frac{\partial}{\partial x}\left\{\left[1 + 2\Lambda\frac{\partial^2 V}{\partial x^2}\right]W\right\}\right)$$
$$+\frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial x}W + \frac{1}{\beta}\frac{\partial}{\partial x}\left\{\left[1 + 2\Lambda\frac{\partial^2 V}{\partial x^2}\right]W\right\}\right) - \frac{\Lambda}{\beta}\left(\frac{\partial}{\partial p} - \frac{1}{\gamma}\frac{\partial}{\partial x}\right)\frac{\partial^3 V}{\partial x^3}\frac{\partial^2 W}{\partial p^2}$$
$$-\frac{\Lambda}{\gamma\beta}\frac{\partial}{\partial x}\left(\frac{\partial}{\partial p} - \frac{1}{\gamma}\frac{\partial}{\partial x}\right)\frac{\partial^3 V}{\partial x^3}\frac{\partial W}{\partial p} - \frac{\Lambda}{\beta\gamma^2}\frac{\partial^2}{\partial x^2}\left(\frac{\partial}{\partial p} - \frac{1}{\gamma}\frac{\partial}{\partial x}\right)\frac{\partial^3 V}{\partial x^3}W - \frac{\Lambda}{\beta\gamma^3}\frac{\partial^3}{\partial x^3}\left(\frac{\partial^3 V}{\partial x^3}W\right). \tag{6.51}$$

This can be checked most easily by directly rewriting Eq. (6.51) in the form of Eq.(6.8) up to the terms $O(\hbar^4)$. We now integrate both sides of this equation (with respect to the momentum) along a straight line in phase space $x + p/\gamma = x_0$ (constant). The integration extends over all possible momentum values from $p = -\infty$ to $p = +\infty$. Note

$$\frac{\partial}{\partial x} = \frac{\partial x_0}{\partial x}\frac{\partial}{\partial x_0} = \frac{\partial}{\partial x_0}$$

and

$$\frac{\partial}{\partial p} = \frac{\partial x_0}{\partial p}\frac{\partial}{\partial x_0} = \frac{1}{\gamma}\frac{\partial}{\partial x_0}$$

whence

$$\frac{\partial}{\partial p} - \frac{1}{\gamma}\frac{\partial}{\partial x}$$

is the zero operator along this line. If we denote the integral of W along this line by $P(x_0, t)$, we obtain:

$$\begin{aligned}\frac{\partial P}{\partial t} &= \int_{x+p/\gamma=x_0} \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial x}W + \frac{1}{\beta}\frac{\partial}{\partial x}\left\{\left[1 + 2\Lambda\frac{\partial^2 V}{\partial x^2}\right]W\right\}\right)ds \\ &\approx \int_{x+p/\gamma=x_0} \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial x}W + \frac{1}{\beta}\frac{\partial}{\partial x}\left\{\left[1 + 2\Lambda\frac{\partial^2 V}{\partial x^2}\right]W\right\}\right)dp \\ &= \frac{\partial}{\partial x}\left\{\frac{P}{\zeta}\frac{\partial V}{\partial x} + \frac{\partial}{\partial x}(DP)\right\}.\end{aligned}$$

(6.52)

where ds is the element of arc length along the line in question. However, since $ds^2 = dx^2 + dp^2$ and $dp/dx = -\gamma$ or $dp = -\gamma dx$ and also, since we let $\gamma \to \infty$, (i.e., we take the high friction limit) we can approximate $ds \approx dp$. Thus; the position coordinate has the value $x \approx x_0$ along the line $x + p/\gamma = x_0$. We also use the fact that

$$\int_{x+p/\gamma=x_0} \frac{\partial W}{\partial t} ds = \frac{\partial}{\partial t} \int_{x+p/\gamma=x_0} W ds$$
$$= \frac{\partial}{\partial t} P(x_0, t) \tag{6.53}$$

By letting $\gamma \to \infty$ and $x_0 \to x$ we again obtain Eq. (6.21).

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CHAPTER VII

Solution of the quantum master equation

In the previous chapters we have proposed a quantum master equation for the Brownian motion of a particle in a potential $V(x)$ [1-4]. Specifically we have demonstrated how the Wigner stationary distribution for closed systems can be used to *formally* establish a semiclassical master equation allowing one to study the quantum-classical correspondence. Here we show *in detail* [2,3] how to solve this master equation for *particular* quantum systems. In order to illustrate this we consider a particle moving in the periodic potential

$$V(x) = -V_0 \cos(x / x_0) \tag{7.1}$$

where x is the position of the particle and x_0 is a characteristic length. Both the classical and quantum Brownian motion in periodic potentials have been used, e.g., to model the diffusion in solids, premelting films, and surfaces (see, for example, Refs. [5-7]). Furthermore, Brownian motion in periodic potentials arises in a number of other important physical applications. We mention the current-voltage characteristics of the Josephson junction [8], mobility of superionic conductors [9], a laser with injected signal [10], phase-locking techniques in radio engineering [11], dielectric relaxation of molecular crystals [12], the dynamics of a charged density wave condensate in an electric field [13], ring-laser gyroscopes [14], stochastic resonance [15,16], etc.

Analytical approaches to the problem are usually based on the ingenious asymptotic method originally devised by Kramers [17] (as described in Chapter II) in connection with thermally activated escape of particles from a potential well. His method allows one to determine closed form asymptotic equations for the escape rate in the limits of very low and relatively high dissipation to the heat bath. In this context we must remark that the Kramers escape rate problem in a periodic potential is qualitatively different from that for a metastable well because the periodic potential is multistable. Thus the particle having escaped a particular well may again be trapped due to the 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 [18]. Furthermore we have mentioned that the Kramers idea was later elaborated upon by Mel'nikov [19,20] and Mel'nikov and Meshkov [21]. They proposed, based on a Wiener-Hopf equation, a universal formula (that is valid for all values of the dissipation) for the escape rate. Thus they solved the problem of the Kramers turnover between very low and relatively high dissipation, i.e., the calculation of the escape rate Γ from a potential well for all values of the damping. Later Grabert [22] and Pollak *et al.* [23] presented a complete solution of the classical Kramers turnover problem showing that the Mel'nikov turnover formula for the escape rate can be obtained without his *ad hoc* interpolation between the weak and strong damping regimes. We remark that the theory of Pollak et al. [23] is also applicable to an arbitrary memory friction and not just in the "white noise" (memoryless) limit. A detailed comparison of numerical and analytical approaches to the Brownian motion in the cosine periodic and tilted cosine periodic potentials has been given by Ferrando et al. [18] and Coffey et al. [24]. Moreover, in order to estimate the quantum decay rate for all values of damping, Mel'nikov [19,20] and Rips and Pollak [25] have further extended the classical method of evaluation of the escape rate Γ to account for quantum tunnelling in a semiclassical way. By applying this approach to a cosine periodic potential, Georgievskii and Pollak [26] have obtained a universal expression for the quantum rate Γ above the crossover temperature between tunneling and thermal activation for the quantum Brownian dynamics in that potential.

Here we solve the semiclassical master equation for the quantum Brownian dynamics in a periodic potential Eq. (6.50). In particular we evaluate the dynamic structure factor. This factor allows one to evaluate various physical parameters [18,27] including of course the escape rate. One of the most important characteristics associated with the Brownian motion in either a single- or a multi-well potential is the friction and temperature dependence of the greatest (overbarrier) relaxation time τ (or the inverse of the escape rate). The results of exact solutions yielded by the continued fraction method for the damping dependence of τ will be compared here with those of the Mel'nikov universal equation for the quantum Kramers rate. Such a comparison is yet another purpose

of this Chapter. Thus the validity of the semiclassical approach may be ascertained.

VII.I. Representation of the quantum master equation as a differential recurrence equation

The quantum master equation is

$$\begin{aligned}&\frac{\partial W}{\partial t}+\frac{p}{m}\frac{\partial W}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}+\frac{\hbar^2}{24}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3}+\ldots\\&=\gamma\frac{\partial}{\partial p}\left[pW+\frac{m}{\beta}\left\{1+\frac{\hbar^2\beta^2}{12m}\frac{\partial^2 V}{\partial x^2}+\ldots\right\}\frac{\partial W}{\partial p}\right].\end{aligned}\tag{7.2}$$

In order to represent the quantum master equation as a differential recurrence relation for the statistical moments, we make the following rescaling in Eq. (7.2) so to render that equation in non dimension form

$$\begin{aligned}x' &= x/x_0,\\ p' &= \frac{p\eta}{mx_0},\\ t' &= t/\eta,\\ U(x') &= -g\cos x',\\ \Lambda &= \frac{\beta^2\hbar^2}{48\eta^2},\\ g &= \beta V_0,\\ \gamma' &= \eta\gamma,\\ \eta &= \sqrt{\frac{\beta m x_0^2}{2}}.\end{aligned}$$

We then have in the first order of perturbation theory, (second order perturbations will be considered in Chapter VIII)

$$\begin{aligned}&\frac{\partial W}{\partial t'}+p'\frac{\partial W}{\partial x'}-\frac{1}{2}\frac{\partial U}{\partial x'}\frac{\partial W}{\partial p'}+\frac{\Lambda}{4}\frac{\partial^3 U}{\partial x'^3}\frac{\partial^3 W}{\partial p'^3}\\&=\frac{\gamma'}{2}\frac{\partial}{\partial p'}\left[2p'W+\left(1+2\Lambda\frac{\partial^2 U}{\partial x'^2}\right)\frac{\partial W}{\partial p'}\right].\end{aligned}\tag{7.3}$$

To investigate the process whereby the particle traverses the periodic potential we must obtain the nonperiodic solution of Eq. (7.3) [27]. Thus we make the *ansatz* [27]

$$W(x',p',t')=\int_{-1/2}^{1/2} w(k,x',p',t')e^{-ikx'}dk\,,\tag{7.4}$$

where w is periodic in x' with period 2π and it is assumed that k is restricted to the first Brillouin zone, -1/2 ≤ k ≤ 1/2. The periodic function w can then be expanded in a Fourier series in x and in orthogonal Hermite functions $H_n(p')$ in p' [18,27], viz., (this particular form of the orthogonal expansion is chosen because the resulting differential recurrence relation is more amenable to numerical calculation than the one generated by an expansion in harmonic oscillator functions as used in our discussion of the Brinkman equations)

$$w(k,x',p',t') = \frac{e^{-p'^2 - U(x')/2}}{2\pi^{3/2}} \sum_{n=0}^{\infty} \sum_{q=-\infty}^{\infty} \frac{c_{n,q}(k,t')}{\sqrt{2^n n!}} H_n(p') e^{-iqx'}. \quad (7.5)$$

By substituting Eq. (7.5) into Eq. (7.4), we obtain from Eq. (7.3) after some algebra that the Fourier coefficients $c_{n,q}(k,t')$ satisfy the eleven term differential recurrence relation

$$\begin{aligned} &\frac{d}{dt'} c_{n,q} + \gamma' \left[n c_{n,q} - \Lambda g \sqrt{n(n-1)} \left(c_{n-2,q+1} + c_{n-2,q-1} \right) \right] \\ &= i\sqrt{n/2} \left[(q+k) c_{n-1,q} + g \left(c_{n-1,q+1} - c_{n-1,q-1} \right)/4 \right] \\ &+ i\sqrt{(n+1)/2} \left[(q+k) c_{n+1,q} - g \left(c_{n+1,q+1} - c_{n+1,q-1} \right)/4 \right] \\ &+ i\Lambda g \sqrt{n(n-1)(n-2)/8} \left(c_{n-3,q+1} - c_{n-3,q-1} \right). \end{aligned} \quad (7.6)$$

By invoking the general method for solving matrix differential-recurrence equations [28,29], we have the solution of Eq. (7.6) for the spectra

$$\tilde{c}_{n,q}(k,\omega) = \int_0^{\infty} c_{n,q}(k,t) e^{-i\omega t} dt \quad (7.7)$$

in terms of matrix continued fractions (details of this solution are given in Appendix VII.I).

VII.II. Calculation of the observables

Just as in the classical case, having determined $c_{n,q}(k,t)$, we can evaluate the dynamic structure factor $\tilde{S}(k,\omega)$ defined as

$$\tilde{S}(k,\omega) = \int_0^{\infty} S(k,t) e^{-i\omega t} dt, \quad (7.8)$$

where

$$S(k,t) = \left\langle e^{ik[x(t)-x(0)]} \right\rangle_0$$

is the characteristic function of the random variable $x(t)-x(0)$, i.e., the displacement of the particle as it wanders through the wells, and the angular brackets $\langle\ \rangle_0$ mean equilibrium ensemble averaging. The dynamic structure factor plays a major role in neutron and light scattering experiments [27]. In the present context various physical parameters such as the escape rate, diffusion coefficient, etc., can be evaluated from $\tilde{S}(k,\omega)$. The characteristic function $S(k,t')$ is calculated in a manner analogous to the classical case [18,27]

$$\begin{aligned} S(k,t') &= \left\langle e^{ik[x'(t')-x'(0)]} \right\rangle_0 \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{ik(x'-x_0')} W(x',p',x_0',p_0',t)\,dx'\,dx_0'\,dp'\,dp_0' \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{ik(x'-x_0')} \int_{-1/2}^{1/2} e^{-ik_1(x'-x_0')} w(k_1,x',p',x_0',p_0',t)\,dk_1\,dx'\,dx_0'\,dp'\,dp_0'. \end{aligned}$$

(here $x'(0)=x_0'$, $x'(t)=x'$). The function

$$W(x',p',x_0',p_0',t) = \int_{-1/2}^{1/2} e^{-ik(x'-x_0')} w(k,x',p',x_0',p_0',t)\,dk$$

satisfies Eq. (7.3) with the initial condition

$$W(x',p',x_0',p_0',0) = W_{st}(x_0',p_0'). \tag{7.9}$$

where $W_{st}(x_0',p_0')$ is the equilibrium Wigner distribution function (which is a stationary solution of the master equation (7.2) [1,2]; see Appendix VII.I, Eq. (7.30)]. Noting that for a periodic function $f(x)$ and $-1/2 \le k,\ k_1 \le 1/2$ [27]

$$\int_{-\infty}^{\infty} e^{i(k-k_1)x} f(x)\,dx = \delta(k-k_1)\int_0^{2\pi} f(x)\,dx,$$

and utilizing Eq. (7.5) and the orthogonality properties of the Hermite functions H_n, the characteristic function $S(k,t')$ becomes a series of the Fourier coefficients $c_{0,q}(k,t')$ as [27]

$$\begin{aligned} S(k,t') &= \int_0^{2\pi}\int_0^{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} w(k,x',p',x_0',p_0',t)\,dx'\,dx_0'\,dp'\,dp_0' \\ &= \int_0^{2\pi}\int_{-\infty}^{\infty} w(k,x',p',t')\,dx'\,dp' \\ &= \sum_{q=-\infty}^{\infty} a_q c_{0,q}(k,t'), \end{aligned}$$

where

$$a_q = \frac{1}{2\pi}\int_0^{2\pi} e^{-iqx - U(x')/2}dx'$$

and

$$w(k,x',p',t') = \int_0^{2\pi}\int_{-\infty}^{\infty} w(k,x',p',x_0',p_0',t)dx_0'dp_0'.$$

Thus the dynamic structure factor $\tilde{S}(k,\omega)$ then becomes a series of the $\tilde{c}_{0,q}(k,\omega)$, viz.,

$$\tilde{S}(k,\omega) = \sum_{q=-\infty}^{\infty} a_q \tilde{c}_{0,q}(k,\omega)\cdot \tag{7.10}$$

Thus having calculated $\tilde{S}(k,\omega)$, we may evaluate the escape (jump) rate Γ as follows [18]. The function $S(k,t)$ can be approximated at long times by an exponential

$$S(k,t) = h(k)e^{-t/\tau(k)}. \tag{7.11}$$

The characteristic (longest) relaxation time $\tau(k)$ can then be extracted by representing Eq. (7.11) in the frequency domain as [18]

$$\tau(k) = \lim_{\omega\to 0}\frac{\tilde{S}(k,0) - \tilde{S}(k,\omega)}{i\omega\tilde{S}(k,\omega)}.$$

The escape (jump) rate Γ is given by

$$\Gamma \approx 2\int_0^{1/2} \tau^{-1}(k)dk \tag{7.12}$$

allowing one to estimate the average longest relaxation time of the system since $\tau \sim \Gamma^{-1}$. Now $\tau^{-1}(k)$ can be expressed in terms of the jump rate Γ and the jump length probabilities P_n (the probability of a jump of length $|n|x_0/2\pi$) as the trigonometric series [18]

$$\tau^{-1}(k) = \Gamma\sum_{n=1}^{\infty} P_n\left[1 - \cos(2\pi nk)\right]. \tag{7.13}$$

Thus the jump-length probabilities P_n may then be obtained in integral form as the Fourier coefficients of the Fourier expansion of $\tau^{-1}(k)$ as detailed in [18]

$$P_n = -2\Gamma^{-1}\int_0^{1/2} \tau^{-1}(k)\cos(2\pi nk)dk\,. \tag{7.14}$$

For high potential barriers, in the jump diffusion limit, the jump-length probabilities P_n allow one to evaluate both the mean-square jump length $\langle l^2 \rangle$ and the diffusion coefficient *D* as [18]

$$\langle l^2 \rangle = 4\pi^2 x_0^2 \sum_{n=1}^{\infty} n^2 P_n \,, \tag{7.15}$$

$$D \approx (\Gamma/2)\langle l^2 \rangle \,. \tag{7.16}$$

The above equations describe in detail the diffusion process in the periodic potential.

VII.III Application of Mel'nikov's universal equation

As already mentioned, Mel'nikov [20] has extended his solution of the classical Kramers turnover problem to include quantum effects in a semiclassical way. He did this by simply inserting 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 derived a universal formula for the quantum rate Γ^M valid for all values of damping above the crossover temperature between tunneling and thermal activation

$$\Gamma^M = \Gamma_{IHD} \Upsilon \,. \tag{7.17}$$

Here Γ_{IHD} is the quantum escape rate in the intermediate to high damping (IHD) region ($\gamma' \geq 1$) and Υ is the quantum depopulation factor. Furthermore Larkin and Ovchinnikov [30] have generalized Mel'nikov's approach to a system coupled to a bath with Johnson-Nyquist quantum thermal noise spectrum and Mel'nikov and Sütö [31] have applied this method to quantum Brownian motion in a tilted cosine potential [the zero tilt case corresponds to Eq. (6.50)]. Later Rips and Pollak [25] gave a consistent solution of the quantum Kramers turnover problem demonstrating how the Mel'nikov universal Eq. (7.17) can be obtained without his *ad hoc* interpolation between the weak and strong damping regimes. Finally Georgievskii and Pollak [26] treated the escape rate problem in a periodic cosine potential showing that the quantum depopulation factor Υ in Eq. (7.17) is

$$\Upsilon = 4\int_0^1 \sin^2(\pi k) F(k) dk \,. \tag{7.18}$$

The function $F(k)$ is (in our notation)

$$F(k)=\exp\left\{\frac{a\sin a}{\pi}\int_{-\infty}^{\infty}\ln\left[\frac{1-e^{-2R(x)}}{1+e^{-2R(x)}-2e^{-R(x)}\cos(2\pi k)}\right]\frac{dx}{\cosh(2ax)-\cos a}\right\},$$

(7.19)

with

$$R(x)=\frac{\pi\gamma'}{\sqrt{3\Lambda}}\int_{-\infty}^{\infty}\frac{\cosh(\sqrt{\Lambda}y)-\cos(2\sqrt{\Lambda}xy)}{y\sinh(\sqrt{\Lambda}y)\cosh^2[\pi y/(2\sqrt{6g})]}dy\,. \quad (7.20)$$

Here $a=\sqrt{3\Lambda}\left(\sqrt{\gamma'^2+2g}-\gamma'\right)$ and $\delta=8\gamma'\sqrt{2g}$. If absolute precision is unnecessary the function $R(x)$ from Eq. (7.20) can be replaced by its classical limit $R(x)\approx\delta\left(x^2+1/4\right)$. We may now estimate using the Wigner function method the quantum escape rate Γ_{IHD} [and thus Γ^M via Eq. (7.17)] by adapting results of the classical Kramers escape rate theory [17] (see Section VI.IV). The quantum escape rate Γ_{IHD} is then

$$\Gamma_{IHD}=\frac{\Xi}{2\pi\eta}\left(\sqrt{\gamma'^2+2g}-\gamma'\right)e^{-2g}\,, \quad (7.21)$$

where

$$\Xi=\frac{\omega_c\sinh(\hbar\beta\omega_a/2)}{\omega_a\sin(\hbar\beta\omega_c/2)}=1+2g\Lambda+\ldots \quad (7.22)$$

is the quantum correction factor (in full agreement with quantum transition state theory [32]),

$$\begin{aligned}\omega_c&=\sqrt{|V''(x_c)|/m}\\&=\omega_a\\&=\sqrt{V''(x_a)/m}.\end{aligned}$$

The form of Eq. (6.45) appears to be consistent with our (Chapter II) 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. The simple result follows from the exact solution for the Wigner equilibrium distribution function for the harmonic oscillator given in Refs. [33-35] which we have described earlier.

Finally the jump-length probabilities can be estimated as [18]

$$P_n^M = -\frac{\int_0^{1/2} \sin^2(\pi k)\, F(k) \cos(2\pi n k)\, dk}{\int_0^{1/2} \sin^2(\pi k)\, F(k)\, dk}, \qquad (7.23)$$

where $F(k)$ is defined by Eq. (7.19) and the superscript M denotes analytical calculation (as in Ref. [18]).

The results yielded by the analytical theory may now be compared with the matrix continued fraction solution.

VII.IV Results and discussion

The real and imaginary parts of the normalized dynamic structure factor

$$\frac{\tilde{S}(k,\omega)}{\tilde{S}(k,0)}$$

are shown in Figure VII.I for various barrier heights g with the damping parameter $\gamma' = 10$, and wave number k = 0.2. For comparison, we also show in this figure the pure Lorentzian spectra

$$\frac{\tilde{S}(k,\omega)}{\tilde{S}(k,0)} = \frac{1}{1 + i\omega\tau_k}, \qquad (7.24)$$

where the relaxation time $\tau_k = \tau_M(k)$ is related to the escape Γ^M from the universal Eq. (7.17) via

$$\Gamma^M = 2\int_0^{1/2} \tau_M^{-1}(k)\, dk\,.$$

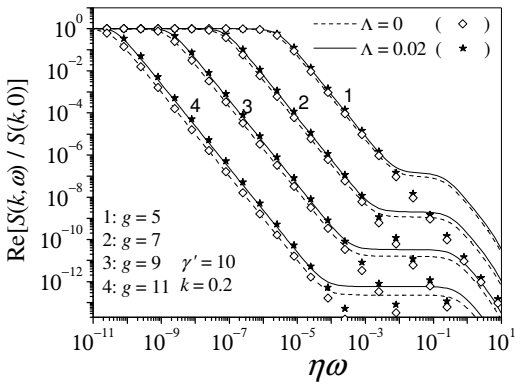

Figure VII.I (a). The real part of the normalized dynamic structure factor $\tilde{S}(k,\omega)/\tilde{S}(k,0)$ vs $\omega\eta$ for various values of barrier parameter g = 5, 7, 9, and 11; the damping coefficient γ' = 10 and k = 0.2. Solid and dashed lines: the matrix continued fraction solution with Λ = 0.02 and Λ = 0 (classical case), respectively. Stars and open diamonds: Eq. (7.24) with Λ = 0.02 and Λ = 0, respectively.

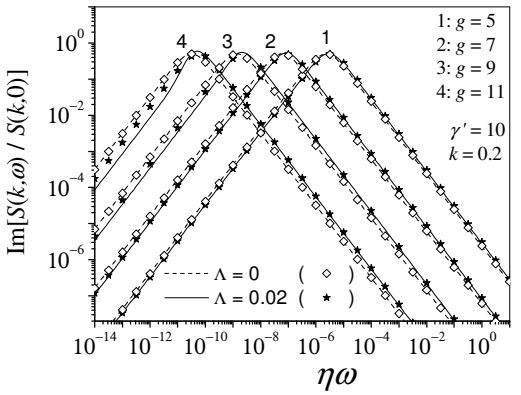

Figure VII.I (b). The imaginary part of the normalized dynamic structure factor $\tilde{S}(k,\omega)/\tilde{S}(k,0)$ vs $\omega\eta$ for various values of barrier parameter g = 5, 7, 9, and 11; the damping coefficient γ' = 10 and k = 0.2. Solid and dashed lines: the matrix continued fraction solution with Λ = 0.02 and Λ = 0 (classical case), respectively. Stars and open diamonds: Eq. (7.24) with Λ = 0.02 and Λ = 0, respectively.

Apparently the simple Eq. (7.24) describes perfectly the low frequency part of the normalized dynamic structure factor $\tilde{S}(k,\omega)/\tilde{S}(k,0)$.

The greatest relaxation time $\tau = \Gamma^{-1}$ predicted by the turnover formula Eq. (7.17) and the inverse decay rate calculated numerically by matrix continued fractions are shown in Figure VII.II as functions of the damping parameter γ' for various values of the quantum parameters Λ (the curves and open circles corresponding to $\Lambda = 0$ are the classical results). The IHD [Eq. (6.45)], asymptotes for τ are also shown for comparison. Using the Wigner stationary distribution W_{st} and imposing the condition $\widehat{M}_D W_{st} = 0$ gives the correct dependence of the escape rate on the quantum parameter Λ (τ decreases with increasing Λ). If the condition $\widehat{M}_D W_{st} = 0$ is not fulfilled (for example, the diffusion coefficient D_{pp} is regarded as a constant), the behaviour of the decay rate *is not reproduced at all* (see Figure VII.II). The quantitative agreement in damping behaviour may be explained as follows. The escape rate as a function of the barrier height parameter g for large g is approximately Arrhenius-like and arises from an *equilibrium* property of the system (namely the stationary distribution at the bottom of the well). On the other hand the damping dependence of the escape rate is due to *nonequilibrium* (dynamical) properties of the system so that the Mel'nikov approach [19,20] should yield the relaxation time for all values of the damping. The greatest relaxation time τ predicted by the Mel'nikov universal Eq. (7.17) and the inverse decay rate calculated numerically via matrix continued fractions are shown in Figure VII.III as functions of γ' for various barrier heights. The IHD [Eq.(6.45)] asymptotes for τ are also shown for comparison. The higher the barrier parameter g the more pronounced is the quantum correction in agreement with Wigner's original prediction [36] based on equilibrium considerations.

The results of calculations of the jump-length probabilities P_n and P_n^M from Eqs. (7.14) and (7.23) are shown in Figure VII.IV for $\Lambda = 0$ (classical case) and $\Lambda = 0.02$. The numerical results are consistent with an asymptotic exponential decay of the P_n^M. However, for large n and small friction parameter, γ' deviations from the exponential behaviour may appear [18].

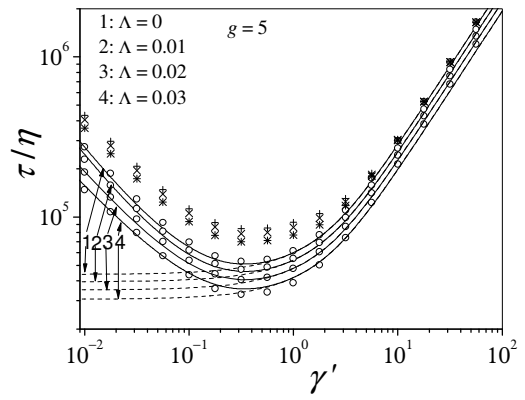

Figure VII.II. The normalized longest relaxation time τ/η vs. γ' for the barrier parameter $g = 5$ and various values of the quantum parameter $\Lambda = 0$ (classical case), 0.01, 0.02, and 0.03. Solid lines: the universal Eq. (7.17). Dashed lines: the IHD Eq.(6.45). Open circles: the matrix continued fraction solution of the master Eq.(7.3). Symbols: the matrix continued fraction solution of Eq. (7.3) with the constant diffusion coefficient $D_{pp} = \gamma m / \beta$.

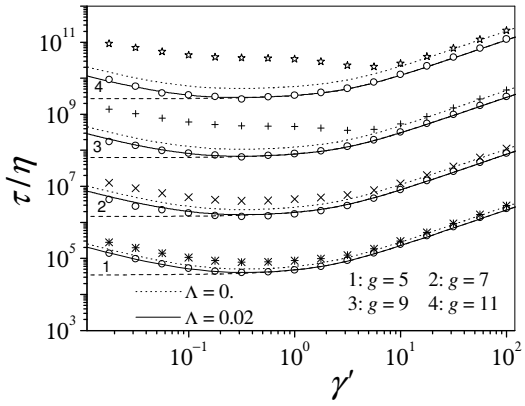

Figure VII.III. τ/η vs. γ' for various values of the barrier parameter $g = 5$, 7, 9, and 11. Solid and dotted lines: the universal Eq. (7.17) for $\Lambda = 0.02$ and $\Lambda = 0$ (classical case), respectively. Dashed lines: the IHD Eq. (6.45) for $\Lambda = 0.02$. Open circles: the matrix continued fraction solution of Eq. (7.3). Symbols: the matrix continued fraction solution of Eq. (7.3) with the constant diffusion coefficient $D_{pp} = \gamma m / \beta$.

In spite of the very good agreement between the numerical results and the universal Eq. (7.17) for $\Lambda<0.03$, a difference between numerical and analytical results exists in the IHD region for larger values of Λ. The disagreement indicates that in order to improve the accuracy for these values of Λ, additional terms of the

order of Λ^2, etc. should be included in the master equation. These higher order quantum correction terms to the master Eq. (7.2), may be calculated, in principle, to any desired degree r of $\hbar^{2r}$. However, with increasing r, the correction terms become more complicated. In particular, the explicit form of the master Eq. (6.1) containing the terms up to $o\left(\hbar^4\right)$ is (the derivation is given in detail in Chapter VIII)

$$\frac{\partial W}{\partial t}+\frac{p}{m}\frac{\partial W}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}+\frac{\hbar^2}{24}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3}-\frac{\hbar^4}{1920}\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5}+...$$
$$=\gamma\frac{\partial}{\partial p}\left[pW+\frac{m}{\beta}\left\{1+\frac{\hbar^2\beta^2}{12m}V''-\frac{\hbar^4\beta^4}{1440m^2}\left[6V'''V'+2V''^2+3V^{(4)}\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right]+... \tag{7.25}$$

We emphasize that we use the equilibrium Wigner function $W_{st}(x,p)$ for vanishing damping ($\gamma\to 0$). In quantum systems, however, the equilibrium distribution $W_\gamma(x,p)$ is often regarded as damping dependent [32]. The damping dependence of $W_\gamma(x,p)$ is unknown for arbitrary $V(x)$. However, $W_\gamma(x,p)$ always reduces to $W_{st}(x,p)$ in the high temperature limit. Moreover, the difference between $W_\gamma(x,p)$ and $W_{st}(x,p)$ may be negligible in a large range of variation of the model parameters. Thus one would expect that the evolution Eq. (7.2) is a reasonable approximation for the kinetics of a quantum Brownian particle in a potential $V(x)$ when $\beta\hbar\gamma\le 1$.

The justification of the master Eq. (7.2) for the quantum Brownian motion of a particle in a periodic (cosine) potential (by showing that the solution of that equation for the greatest relaxation time is in agreement with that predicted by quantum rate theory) and the successful extension to the quantum case of the matrix continued fraction methods associated with the classical Fokker-Planck equation are our main results. **In particular the dependence of the diffusion coefficient on the derivatives of the potential (with consequent lowering of the potential barrier) arising from the *ansatz* of a Wigner stationary distribution for the equilibrium solution of the open system successfully reproduces escape rates predicted by the quantum generalization of the Kramers escape rate theory and its various extensions to the turnover region as applied to the**

cosine potential. Furthermore, the successful extension of the classical matrix continued fraction method [27,37] to the semiclassical quantum master equation allows one to accurately calculate in semiclassical fashion quantum corrections to the appropriate dynamical quantities such as correlation functions and susceptibilities (cf. the calculation of the dynamic structure factor). This is in general impossible using quantum reaction rate theory since that theory as presently formulated does not involve an explicit master equation. We further remark that the agreement obtained between escape rates calculated from quantum reaction rate theory in the manner of Georgievskii and Pollak [26] and those from the master Eq. (7.2) (cf. Figures VII.II and VII.III) also constitutes a verification of quantum rate theory for the potential in question. The above considerations suggest it is obviously worthwhile extending the present study of Eq. (7.2) to other quantum systems such as the Brownian motion in a periodic potential with tilt, the double-well potential, etc. This will allow one to study the interplay of quantum tunnelling, thermal fluctuations and dissipation in such systems. In particular one will be able to evaluate in semiclassical fashion quantum effects in the spectra of relevant dynamical quantities and the influence of quantum tunnelling on the relatively high temperature behaviour of their spectra. **We reiterate that the dependence of the diffusion coefficient on the derivatives of the potential arising from the imposition of the Wigner stationary distribution is crucial. If this dependence is not taken into account, e.g. considering the diffusion coefficient as constant, 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 the quantum reaction rate theory.**

Our calculations which have been outlined for mechanical systems with separable and additive Hamiltonians may also be extended to particular (nonseparable) spin systems such as a single domain ferromagnetic particle since the giant spin Hamiltonian of the particle may be mapped onto an equivalent single mechanical particle Hamiltonian. This transformation is of particular importance concerning the existence of macroscopic quantum tunnelling phenomena in such ferromagnetic particles [38] and also in the discussion of the crossover region between reversal of magnetization by thermal agitation and

reversal by macroscopic quantum tunnelling which is of current topical interest [39].

The calculations we have given are in the first order of perturbation theory and consequently apply to small values of the small values of the parameter Λ. The purpose of the following Chapter is to extend them to second order in Λ. In this way at some time in the future it will be possible to assess the accuracy of the first order perturbation theory results.

APPENDIX VII

Appendix VII.I : Matrix continued fraction solution

First we introduce the column vectors

$$\mathbf{C}_n(t) = \begin{pmatrix} \vdots \\ c_{n-1,-1}(k,t') \\ c_{n-1,0}(k,t') \\ c_{n-1,1}(k,t') \\ \vdots \end{pmatrix}.$$

Hence the scalar multi-term recurrence Eq. (7.6) can be rearranged as the five term matrix differential recurrence relation

$$\begin{aligned} \frac{d}{dt}\mathbf{C}_n(t') = \mathbf{Q}_n^{-}\mathbf{C}_{n-1}(t') - \gamma'(n-1)\mathbf{C}_n(t') \\ +\mathbf{Q}_n^{+}\mathbf{C}_{n+1}(t') + \Lambda\left[\mathbf{q}_n\mathbf{C}_{n-2}(t') + \mathbf{r}_n\mathbf{C}_{n-3}(t')\right], \end{aligned} \tag{7.26}$$

where the matrix elements of $\mathbf{Q}_n^{\pm}, \mathbf{q}_n, \mathbf{r}_n$ are given by

$$\left[\mathbf{Q}_n^{\pm}\right]_{q,p} = i\sqrt{\frac{2n-1\pm 1}{4}}\left[(q+k)\delta_{q,p} \mp \frac{g}{4}\left(\delta_{q,p-1} - \delta_{q,p+1}\right)\right],$$

$$\left[\mathbf{r}_n\right]_{q,p} = ig\sqrt{\frac{(n-1)(n-2)(n-3)}{8}}\left(\delta_{q,p-1} - \delta_{q,p+1}\right),$$

$$\left[\mathbf{q}_n\right]_{q,p} = g\gamma'\sqrt{(n-1)(n-2)}\left(\delta_{q,p-1} + \delta_{q,p+1}\right),$$

and $\delta_{q,p}$ is Kronecker's delta. Next we use perturbation theory to find the solution of Eq. (7.26) treating Λ as the customary small parameter so that we seek a solution as

$$\mathbf{C}_n(t') = \mathbf{C}_n^0(t') + \Lambda\mathbf{C}_n^1(t') \tag{7.27}$$

Substituting Eq. (7.27) into Eq. (7.26), we have the matrix three-term differential recurrence relation for $\mathbf{C}_n^0(t')$ in the zero-order of perturbation theory

$$\frac{d}{dt'}\mathbf{C}_n^0(t') = \mathbf{Q}_n^-\mathbf{C}_{n-1}^0(t') - \gamma'(n-1)\mathbf{C}_n^0(t') + \mathbf{Q}_n^+\mathbf{C}_{n+1}^0(t') \quad (7.28)$$

and in the first order of perturbation theory the forced matrix three-term differential recurrence relation for $\mathbf{C}_n^1(t')$, viz.,

$$\begin{aligned}\frac{d}{dt'}\mathbf{C}_n^1(t') = \mathbf{Q}_n^-\mathbf{C}_{n-1}^1(t') - \gamma'(n-1)\mathbf{C}_n^1(t') + \mathbf{Q}_n^+\mathbf{C}_{n+1}^1(t') \\ +\mathbf{R}_n(t')\end{aligned} \quad (7.29)$$

where

$$\mathbf{R}_n(t') = \mathbf{q}_n\mathbf{C}_{n-2}^0(t') + \mathbf{r}_n\mathbf{C}_{n-3}^0(t').$$

By invoking the general method [27,37,40,41] for solving three term matrix recursion equations, we have the exact solution for the zero order spectrum

$$\tilde{\mathbf{C}}_n^0(s) = \int_0^\infty \mathbf{C}_n^0(t)e^{-st}dt$$

in terms of a matrix continued fraction, viz.

$$\tilde{\mathbf{C}}_1^0(s) = \mathbf{\Delta}_1(s)\mathbf{C}_1^0(0),$$

$$\tilde{\mathbf{C}}_n^0(s) = \mathbf{S}_n^-\mathbf{C}_{n-1}^0(s) = \mathbf{S}_n^-\mathbf{S}_{n-1}^-...\mathbf{S}_2^-\mathbf{\Delta}_1(s)\mathbf{C}_1^0(0),$$

where

$$\mathbf{S}_n^- = \mathbf{\Delta}_n(s)\mathbf{Q}_n^-$$

and the matrix continued fraction $\mathbf{\Delta}_n(k,s)$ is defined by the recurrence equation

$$\mathbf{\Delta}_n(s) = \left\{\left[s+\gamma'(n-1)\right]\mathbf{I} - \mathbf{Q}_n^+\mathbf{\Delta}_{n+1}(s)\mathbf{Q}_{n+1}^-\right\}^{-1}.$$

In like manner, we also have the exact solution for the first order spectrum $\tilde{\mathbf{C}}_1^1(k,s)$ in terms of a matrix continued fraction, viz.,

$$\tilde{\mathbf{C}}_1^1(s) = \mathbf{\Delta}_1(s)\mathbf{C}_1^1(0) + \mathbf{\Delta}_1(s)\mathbf{S}_2^+\mathbf{S}_3^+[\mathbf{C}_3^1(0)+\mathbf{F}],$$

where $\mathbf{S}_n^+ = \mathbf{Q}_{n-1}^+\mathbf{\Delta}_n(s)$ and

$$\mathbf{F} = \left[\mathbf{q}_3 + \sum_{n=4}^{\infty}\mathbf{S}_4^+...\mathbf{S}_n^+\left(\mathbf{q}_n\mathbf{S}_{n-2}^- + \mathbf{r}_n\right)\mathbf{S}_{n-3}^-...\mathbf{S}_2^-\right]\mathbf{\Delta}_1(s)\mathbf{C}_1^0(0).$$

Here we have noted that $\mathbf{C}_n^0(0) = \mathbf{0},\ n \geq 2$ and $\mathbf{C}_2^1(0) = \mathbf{0},\ \mathbf{C}_n^1(0) = \mathbf{0},\ n \geq 4$.

The initial condition vectors $\mathbf{C}_n^0(0)$ and $\mathbf{C}_n^1(0)$ can be calculated just as in the classical case [27] by using the initial condition at $t = 0$ for

$$W(x', p', x_0', p_0', 0) = W_{st}(x_0', p_0'),$$

Eq. (7.9). However, instead of the Maxwell-Boltzmann distribution of the classical theory, the equilibrium Wigner distribution function $W_{st}(x_0', p_0')$ now has the form [1,2] (see note at the end of this Appendix)

$$W_{st}(x_0', p_0') = Z^{-1} e^{-p_0'^2 - U(x_0')} \left\{ 1 + \Lambda \left[U'^2(x_0') + \left(2p_0'^2 - 3 \right) U''(x_0') \right] \right\} \tag{7.30}$$

where the partition function Z is given by

$$\begin{aligned} Z &= \sqrt{\pi} \int_0^{2\pi} \left\{ 1 + \Lambda \left(U'(x_0') \right)^2 - 2\Lambda U''(x_0') \right\} e^{-U(x_0')} dx_0' \\ &= Z_{cl} \left[1 - \Lambda g \frac{I_1(g)}{I_0(g)} \right]. \end{aligned}$$

Here

$$Z_{cl} = 2\pi^{3/2} I_0(g)$$

is the classical partition function and $I_0(x)$ and $I_1(x)$ are modified Bessel functions of the first kind. Equations (7.4), (7.5), (7.9), and (7.30) yield the initial conditions for $c_{n,q}(t)$ as

$$c_{n,q}(0) = \frac{1}{\sqrt{2^n n!}} \left\langle H_n\left(p_0' \right) e^{iqx_0' + U(x_0')/2} \right\rangle_0,$$

where the brackets $\langle \ \rangle_0$ mean the average over $W_{st}(x_0', p_0')$. By representing $c_{n,q}(0)$ via perturbation theory as

$$c_{n,q}(0) = c_{n,q}^0(0) + \Lambda c_{n,q}^1(0),$$

we have the initial conditions for $c_{n,q}^0(0)$ and $c_{n,q}^1(0)$, viz.,

$$\begin{aligned} c_{0,q}^0(0) &= \sqrt{\pi} Z_{cl}^{-1} \int_0^{2\pi} e^{iqx_0' - U(x_0')/2} dx_0' \\ &= 2\pi^{3/2} Z_{cl}^{-1} I_{|q|}(g/2), \end{aligned}$$

$$c_{0,q}^{1}(0)=\sqrt{\pi}Z_{cl}^{-1}\int_{0}^{2\pi}\left[U'^{2}(x_0')-2U''(x_0')+\frac{gI_1(g)}{I_0(g)}\right]e^{iqx_0'-U(x_0')/2}dx_0'$$

$$=-2\pi^{3/2}Z_{cl}^{-1}\left[4q^2-g\frac{I_1(g)}{I_0(g)}\right]I_{|q|}(g/2),$$

$$c_{2,q}^{1}(0)=\sqrt{2\pi}Z_{cl}^{-1}\int_{0}^{2\pi}U''(x')e^{iqx_0'-U(x_0')/2}dx_0'$$

$$=\frac{g}{\sqrt{2}}\left[c_{0,q+1}^{0}(0)+c_{0,q-1}^{0}(0)\right].$$

We now demonstrate how we obtained the initial condition $c_{0,q}^{1}(0)$. Firstly,

$$W_{st}(x_0',p_0')=\frac{e^{-p_0'^2-U(x_0')}}{Z}\left\{1+\Lambda\left[U'^{2}(x_0')+\left(2p_0'^{2}-3\right)U''(x_0')\right]\right\}$$

(7.31)

where Z is

$$Z(x_0')=\sqrt{\pi}\int_{0}^{2\pi}e^{-U(x_0')}\left\{1+\Lambda\left(U'^{2}(x_0')-2U''(x_0')\right)\right\}dx_0' \quad (7.32)$$

i.e.

$$W_{st}(x_0',p_0')=\frac{e^{-p_0'^2-U(x_0')}\left\{1+\Lambda\left[U'^{2}(x_0')+\left(2p_0'^{2}-3\right)U''(x_0')\right]\right\}}{\sqrt{\pi}\int_{0}^{2\pi}e^{-U(x_0')}\left\{1+\Lambda\left(U'^{2}(x_0')-2U''(x_0')\right)\right\}dx_0'}.$$

(7.33)

We calculated Z for the potential $U\left(x_0'\right)=-g\cos x_0'$. i.e.

$$Z=Z_{cl}\left[1-\Lambda\frac{gI_1(g)}{I_0(g)}\right]. \quad (7.34)$$

Therefore

$$W_{st}(x_0',p_0')=\frac{e^{-p_0'^2-U(x_0')}\left\{1+\Lambda\left[U'^{2}(x_0')+\left(2p_0'^{2}-3\right)U''(x_0')\right]\right\}}{Z_{cl}\left[1-\Lambda\frac{gI_1(g)}{I_0(g)}\right]},$$

(7.35)

which by Taylor's theorem is

$$W_{st}(x_0', p_0') = \frac{e^{-p_0'^2 - U(x_0')}}{Z_{cl}} \left\{1 + \Lambda\left[U'^2(x_0') + \left(2p_0'^2 - 3\right)U''(x_0')\right]\right\}\left[1 + \Lambda \frac{gI_1(g)}{I_0(g)}\right]$$

(7.36)

and with $H_0 = 1$ and $H_2 = 4p^2 - 2$ can be written as

$$W_{st}(x_0', p_0') = \frac{e^{-p_0'^2 - U(x_0')}}{Z_{cl}} \left\{1 + \Lambda\left[U'^2 - 2U'' + \frac{gI_1(g)}{I_0(g)}\right]H_0 + \frac{\Lambda}{2}U''H_2\right\}$$

(7.37)

From Eq. (7.5) viz.,

$$w(k, x', p', t') = \frac{e^{-p'^2 - U(x')/2}}{2\pi^{3/2}} \sum_{n=0}^{\infty} \sum_{q=-\infty}^{\infty} \frac{c_{n,q}(k,t')}{\sqrt{2^n n!}} H_n(p') e^{-iqx'}$$

(7.38)

we can write Eq. (7.37) as

$$W_{st}(x_0', p_0') = \frac{e^{-p_0'^2 - U(x_0')/2}}{2\pi^{3/2}} \sum_{q=-\infty}^{\infty} \left\{c_{0,q} H_0 + \frac{c_{2,q}}{2\sqrt{2}} H_2\right\} e^{-iqx_0'}. \quad (7.39)$$

Equating the coefficients of the H_n in Eq. (7.39) with Eq. (7.37) we obtain,

$$\frac{e^{-U(x_0')/2}}{Z_{cl}} \left\{1 + \Lambda\left[U'^2 - 2U'' + \frac{gI_1(g)}{I_0(g)}\right]\right\} = \frac{1}{2\pi^{3/2}} \sum_{q=-\infty}^{\infty} c_{0,q} e^{-iqx_0'}$$

(7.40)

and which by the orthogonality property of the circular function yields

$$c_{0,q}^1(0) = \sqrt{\pi} Z_{cl}^{-1} \int_0^{2\pi} \left[U'^2(x_0') - 2U''(x_0') + \frac{gI_1(g)}{I_0(g)}\right] e^{iqx_0' - U(x_0')/2} dx_0'.$$

(7.41)

In like manner we obtain the result for $c_{2,q}^1(0)$. Having determined $\tilde{\mathbf{C}}_1(k,s) = \tilde{\mathbf{C}}_1^0(s) + \Lambda\tilde{\mathbf{C}}_1^1(s)$, we can evaluate the dynamic structure factor $\tilde{S}(k,\omega)$ in terms of $\tilde{c}_{n,q}(k,\omega)$ as

$$\tilde{S}(k,\omega) = \frac{Z_{cl}}{2\pi^{3/2}} \sum_{q=-\infty}^{\infty} c_{0,q}^0(0) \tilde{c}_{0,q}(k,\omega) \cdot$$

A note on initial conditions:

As far as the first order of perturbation theory is concerned the solution of the master equation is of the form

$$\mathbf{C}_n(t') = \mathbf{C}_n^0(t') + \Lambda \mathbf{C}_n^1(t') . \tag{7.42}$$

Moreover we saw that the initial condition vectors $\mathbf{C}_n^0(0)$ and $\mathbf{C}_n^1(0)$ can be calculated just as in the classical case [27] by using the initial condition at $t = 0$ for

$$W(x', p', x_0', p_0', 0) = W_{st}(x_0', p_0') . \tag{7.43}$$

The notation is exactly that of Wang and Uhlenbeck [42] as used in classical problems, in other words we first solve the Fokker-Planck equation for sharp initial conditions and then average the result over a Maxwell-Boltzmann distribution of initial values of x_0, p_0 in order to determine the solution for equilibrium initial conditions. This procedure amounts to finding the Green function of the Fokker-Planck equation and then weighting it with the Maxwell-Boltzmann distribution. For example Wang and Uhlenbeck calculate the mean and mean square positions and momenta for a harmonic oscillator for sharp initial conditions. If the mean positions and momenta as a function of time so calculated are multiplied by the sharp initial values of these quantities and then averaged for a second time over a Maxwell-Boltzmann distribution the quantities that result (by stationarity, i.e. invariance under a shift of the time axis) are the position and momentum autocorrelation and crosscorrelation functions of the oscillator. Alternatively if one wished to calculate these functions one can simply proceed by postulating the Maxwell-Boltzmann distribution as the initial condition and disregard the Green function or one can as in Chapter II in deriving the Smoluchowski equation from the Brinkman equations postulate an initial condition in the form of a Maxwellian distribution of velocities or momenta times an arbitrary function of position. By analogy we suppose that the procedure carries over to the quantum master equation in the context of Wigner's quasi phase space approach so that one effectively replaces the Maxwell-Boltzmann initial condition by Wigner's stationary distribution in phase space. If one chooses to proceed via direct calculation of the Green function some care must be taken into what is exactly meant by a delta function initial distribution in phase space on account of the limitations imposed by the uncertainty principle. Furthermore the phase space averages calculated by imposing the Wigner stationary distribution as initial condition will no longer necessarily have the meaning of correlation

functions due to the non commutative operator algebra characteristic of quantum mechanics.

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CHAPTER VIII

Inclusion of higher order corrections in $\hbar^2$ in the quantum Brownian motion in a cosine potential

VIII.I Brief outline

In Chapter II we have shown how in principle how one may calculate diffusion coefficients to any order in $\hbar^2$ in the quantum master equation resulting from the ansatz that one may truncate a Kramers-Moyal like expansion at the second order term. Moreover we have solved the particular problem of the quantum Brownian motion in a cosine potential, viz.

$$V(x) = -V_0 \cos(x/x_0)\,. \tag{8.1}$$

In order to investigate the convergence of the perturbation expansion or to consider cases where the quantum parameter is not necessarily small it is necessary to outline how higher order terms can be included in the ordinary differential recurrence relations. We shall illustrate the methodology for the cosine potential problem of the previous chapter. In order to achieve maximum clarity for the reader we shall proceed by first giving the partial differential recurrence relations or the Brinkman equations for a general potential in the basis defined by the Fourier expansion [1,2]

$$W(k,x',p',t') = \frac{e^{-p'^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{C_n(k,x',t')}{\sqrt{2^n n!}} H_n(p') \tag{8.2}$$

where the orthogonality relation for the Hermite polynomials, $H_n(p)$, is given by

$$\int_{-\infty}^{\infty} e^{-p^2} H_m(p) H_n(p) dp = 2^n n! \sqrt{\pi}\,\delta_{m,n}\,. \tag{8.3}$$

We shall then specialize these equations to the cosine potential by expanding the spatial part $C_n(k,x',t')$ in a Fourier series like in the previous Chapter. Just as in

that Chapter the basis is chosen in the form of Eq. (8.2) rather than the $\varphi_n(x,t)$ used for the Brinkman equations used in Chapters II and VI, because the above form yields optimum convergence of the ordinary differential recurrence relations.

VIII.II The quantum master equation to the 2nd order in $\hbar^2$ and its solution

In Chapter VI we showed that the evolution equation of the Wigner distribution function for an open system is,

$$\frac{\partial W}{\partial t}+\hat{M}_W W=\hat{M}_D W\,, \tag{8.4}$$

and to $O(\hbar^4)$

$$\frac{\partial W}{\partial t}+\frac{p}{m}\frac{\partial W}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}+\frac{\hbar^2}{24}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3}-\frac{\hbar^4}{1920}\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5}\cdots$$
$$=\gamma\frac{\partial}{\partial p}\left[pW+\frac{m}{\beta}\left\{1+\frac{\hbar^2\beta^2}{12m}V''-\frac{\hbar^4\beta^4}{1440m^2}\left[6V'''V'+2V''^2+3V^{(4)}\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right]+\ldots \tag{8.5}$$

and on transposing terms from the left hand side we have

$$\frac{\partial W}{\partial t}=-\frac{p}{m}\frac{\partial W}{\partial x}+\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}-\frac{\hbar^2}{24}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3}+\frac{\hbar^4}{1920}\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5}\cdots$$
$$+\gamma\frac{\partial}{\partial p}\left[pW+\frac{m}{\beta}\left\{1+\frac{\hbar^2\beta^2}{12m}V''-\frac{\hbar^4\beta^4}{1440m^2}\left[6V'''V'+2V''^2+3V^{(4)}\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right]+\ldots \tag{8.6}$$

In terms of Λ where

$$\Lambda=\frac{\hbar^2\beta^2}{24m} \tag{8.7}$$

is the characteristic quantum parameter the evolution equation ($O(\Lambda^2)\equiv O(\hbar^4)$) becomes

$$\frac{\partial W}{\partial t}=-\frac{p}{m}\frac{\partial W}{\partial x}+\frac{\partial V}{\partial x}\frac{\partial W}{\partial p}-\frac{m}{\beta^2}\Lambda\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3}+\frac{3m^2}{10\beta^4}\Lambda^2\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5}\cdots$$
$$+\gamma\frac{\partial}{\partial p}\left[pW+\frac{m}{\beta}\left\{1+2\Lambda V''-\frac{2\Lambda^2}{5}\left[6V'''V'+2V''^2+3V^{(4)}\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right]+\ldots \tag{8.8}$$

The first order terms in Λ are obviously the same as before and since Eq. (8.8) is linear we can simply add on the second order terms in Λ, i.e. to $O(\hbar^4)$, are

$$+\frac{\hbar^4}{1920}\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5} \equiv +\frac{3m^2}{10\beta^4}\Lambda^2\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5} \tag{8.9}$$

from the right hand side of Eqs.(8.6) (or (8.8)), and the dissipative term is

$$\begin{aligned}&+\gamma\frac{\partial}{\partial p}\left[\frac{m}{\beta}\left\{-\frac{\hbar^4\beta^4}{1440m^2}\left[6V'''V'+2V''^2+3V^{(4)}\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right]\\ &\equiv +\gamma\frac{\partial}{\partial p}\left[\frac{m}{\beta}\left\{-\frac{2\Lambda^2}{5}\left[6V'''V'+2V''^2+3V^{(4)}\left(\frac{p^2}{m}-\frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right].\end{aligned} \tag{8.10}$$

Λ has units of T^2M^{-1} or area per Joule. $\hbar\beta$ has units of time.

In order to represent the quantum master equation as a differential recurrence relation for the statistical moments we again introduce the following normalized variables [1,2],

$$\begin{aligned}p &\to \frac{mx_0}{\eta}p'\\ t &\to \eta t'\\ x &\to x_0 x'\\ V(x) &\to \frac{1}{\beta}U(x')\end{aligned} \tag{8.11}$$

where

$$\eta = \sqrt{\frac{\beta m {x_0}^2}{2}} \tag{8.12}$$

and

$$g = \beta V_0 \tag{8.13}$$

After some simple algebra, we obtain the following rescaled master equation,

$$\begin{aligned}&\frac{\partial W}{\partial t'} = -p'\frac{\partial W}{\partial x'}+\frac{1}{2}\frac{\partial U}{\partial x'}\frac{\partial W}{\partial p'}-\frac{\Lambda}{4}\frac{\partial^3 U}{\partial x'^3}\frac{\partial^3 W}{\partial p'^3}+\frac{3}{80}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\frac{\partial^5 W}{\partial p'^5}\\ &+\frac{\gamma'}{2}\frac{\partial}{\partial p'}\left[2p'W+\left\{1+2\Lambda\frac{\partial^2 U}{\partial x'^2}-\frac{2}{5}\Lambda^2\left[6\frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'}+2\left(\frac{\partial^2 U}{\partial x'^2}\right)^2+3\frac{\partial^4 U}{\partial x'^4}\left(2p^2-5\right)\right]\right\}\frac{\partial W}{\partial p'}\right]\end{aligned} \tag{8.14}$$

where we have introduced

$$\gamma' = \gamma\eta \tag{8.15}$$

and the *new* quantum parameter (note the difference in this and (8.7))

$$\Lambda = \frac{\hbar^2 \beta}{24 m x_0{}^2} \tag{8.16}$$

which are dimensionless damping and quantum parameters, respectively.

To investigate the process whereby the particle traverses the periodic potential we must obtain the nonperiodic solution of Eq. (8.14) [1,2] as in Chapter VII. Thus we again make the *ansatz* [1,2]

$$W(x', p', t') = \int_{-1/2}^{1/2} w(k, x', p', t') e^{-ikx'} dk \tag{8.17}$$

where w is periodic in x with period 2π and it is assumed that k is restricted to the first Brillouin zone, $-1/2 \le k \le 1/2$. The periodic function w can then be expanded in a Fourier series in x and in orthogonal Hermite functions $H_n(p')$ in p' as before, viz.,

$$w(k, x', p', t') = \frac{e^{-p'^2 - U(x')/2}}{2\pi^{3/2}} \sum_{n=0}^{\infty} \sum_{q=-\infty}^{\infty} \frac{c_{n,q}(k, t')}{\sqrt{2^n n!}} H_n(p') e^{-iqx'}. \tag{8.18}$$

For the moment for purpose of illustration we shall just take the classical part of our second order quantum master equation (8.14) i.e. (let $\Lambda = 0$)

$$\frac{\partial W}{\partial t'} = -p' \frac{\partial W}{\partial x'} + \frac{1}{2} \frac{\partial U}{\partial x'} \frac{\partial W}{\partial p'} + \frac{\gamma'}{2} \frac{\partial}{\partial p'} \left[2p' W + \frac{\partial W}{\partial p'} \right]. \tag{8.19}$$

By substituting Eq. (8.18) into Eq. (8.17), (i.e. Eq. (8.2))

$$W(k, x', p', t') = \frac{e^{-p'^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{C_n(k, x', t')}{\sqrt{2^n n!}} H_n(p') \tag{8.20}$$

and on substitution of this expansion we have

$$\begin{aligned}
&\frac{e^{-p'^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{\partial C_n(k, x', t')}{\partial t'} \frac{1}{\sqrt{2^n n!}} H_n(p') = \\
&-\frac{e^{-p'^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{\partial C_n(k, x', t')}{\partial x'} \frac{1}{\sqrt{2^n n!}} p' H_n(p') \\
&+\frac{1}{2} \frac{\partial U}{\partial x'} \frac{\partial}{\partial p'} \left[\frac{e^{-p'^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{C_n(k, x', t')}{\sqrt{2^n n!}} H_n(p') \right] \\
&+\frac{\gamma}{2} \frac{\partial}{\partial p'} \left[\frac{e^{-p'^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{C_n(k, x', t')}{\sqrt{2^n n!}} \left(2p' H_n(p') + \frac{\partial H_n(p')}{\partial p'} \right) \right].
\end{aligned} \tag{8.21}$$

We use the following recurrence relations of the $H_n(p)$ (we have dropped the $'$ for ease of notation)

$$\begin{aligned} 2\,p\,H_n(p) &= H_{n+1}(p) + 2n\,H_{n-1}(p) \\ \frac{d\,H_n(p)}{dp} &= 2n\,H_{n-1}(p). \end{aligned} \tag{8.22}$$

Notice that,

$$\begin{aligned} \frac{\partial W}{\partial p'} &= \frac{\partial}{\partial p'}\left\{\frac{e^{-p'^2}}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{C_n(k,x',t')}{\sqrt{2^n n!}}H_n(p')\right\} \\ &= \frac{e^{-p'^2}}{\sqrt{\pi}}\left[\sum_{n=0}^{\infty}\frac{C_n(k,x',t')}{\sqrt{2^n n!}}\left(\frac{dH_n(p')}{dp'} - 2p'H_n(p')\right)\right] \end{aligned} \tag{8.23}$$

and on using the recurrence relations (Eqs. (8.22)) we have

$$\frac{\partial W}{\partial p'} = \frac{e^{-p'^2}}{\sqrt{\pi}}\left[\sum_{n=0}^{\infty}\frac{C_n(k,x',t')}{\sqrt{2^n n!}}\left(-H_{n+1}(p')\right)\right], \tag{8.24}$$

i.e. on differentiation of *W* with respect to p' we just change sign and increase the counter of $H_n(p)$ by one, hence

$$\frac{\partial^2 W}{\partial p'^2} = \frac{e^{-p'^2}}{\sqrt{\pi}}\left[\sum_{n=0}^{\infty}\frac{C_n(k,x',t')}{\sqrt{2^n n!}}\left(+H_{n+2}(p')\right)\right]. \tag{8.25}$$

Therefore Eq. (8.21) can be written as

$$\begin{aligned} \sum_{n=0}^{\infty}\frac{\partial C_n(k,x',t')}{\partial t'}\frac{1}{\sqrt{2^n n!}}H_n(p') = &-\sum_{n=0}^{\infty}\frac{\partial C_n(k,x',t')}{\partial x'}\frac{1}{\sqrt{2^n n!}}\left[\frac{1}{2}H_{n+1}(p') + nH_{n-1}(p')\right] \\ &+\frac{1}{2}\frac{\partial U}{\partial x'}\sum_{n=0}^{\infty}\frac{C_n(k,x',t')}{\sqrt{2^n n!}}\left(-H_{n+1}(p')\right) \\ &+\frac{\gamma}{2}\sum_{n=0}^{\infty}\frac{C_n(k,x',t')}{\sqrt{2^n n!}}\left(-nH_n(p')\right); \end{aligned} \tag{8.26}$$

(we divided out $\frac{e^{-p'^2}}{\sqrt{\pi}}$). We now apply the orthogonality relation of the $H_n(p)$ i.e.

$$\int_{-\infty}^{\infty} e^{-p^2}H_m(p)H_n(p)\,dp = 2^n n!\sqrt{\pi}\delta_{m,n} \tag{8.27}$$

to obtain the following set of partial differential recurrence equations

$$\frac{\partial C_n(k,x',t')}{\partial t'} = -n\gamma C_n - \sqrt{\frac{n}{2}}\left(\frac{\partial C_{n-1}}{\partial x'} + \frac{\partial U}{\partial x'} C_{n-1}\right) - \sqrt{\frac{n+1}{2}}\frac{\partial C_{n+1}}{\partial x'} \tag{8.28}$$

which are simply the classical Brinkman equations written in the basis defined by Eq. (8.20). We next expand $C_n(k,x',t')$ in the form

$$C_n(k,x',t') = \frac{1}{2\pi} e^{-\frac{U(x')}{2}} \sum_{q=-\infty}^{\infty} c_{n,q}(k,t') e^{-i(q+k)x' + ikx'(0)} . \tag{8.29}$$

We substitute this equation into Eq. (8.28) in order to obtain

$$\begin{aligned}
&\frac{1}{2\pi} e^{-\frac{U(x')}{2}} \sum_{q=-\infty}^{\infty} \frac{dc_{n,q}(k,t')}{dt'} e^{-i(q+k)x' + ikx'(0)} = -n\gamma \frac{1}{2\pi} e^{-\frac{U(x')}{2}} \sum_{q=-\infty}^{\infty} c_{n,q}(k,t') e^{-i(q+k)x' + ikx'(0)} \\
&-\sqrt{\frac{n}{2}}\left(-\frac{1}{2\pi} e^{-\frac{U(x')}{2}} \left\{ \sum_{q=-\infty}^{\infty} \left[i(q+k) + \frac{1}{2}\frac{\partial U}{\partial x'} \right] c_{n-1,q}(k,t') e^{-i(q+k)x' + ikx'(0)} \right\} \right. \\
&\qquad \left. + \frac{\partial U}{\partial x'} \cdot \frac{1}{2\pi} e^{-\frac{U(x')}{2}} \sum_{q=-\infty}^{\infty} c_{n-1,q}(k,t') e^{-i(q+k)x' + ikx'(0)} \right) \\
&-\sqrt{\frac{n+1}{2}} \left\{ -\frac{1}{2\pi} e^{-\frac{U(x')}{2}} \sum_{q=-\infty}^{\infty} \left[i(q+k) + \frac{1}{2}\frac{\partial U}{\partial x'} \right] c_{n+1,q}(k,t') e^{-i(q+k)x' + ikx'(0)} \right\}.
\end{aligned} \tag{8.30}$$

Letting $r = q + k$, say, we can divide across both sides of Eq. (8.30) to give

$$\begin{aligned}
\sum_{q=-\infty}^{\infty} \frac{dc_{n,q}(k,t')}{dt'} e^{-irx'} &= -n\gamma \sum_{q=-\infty}^{\infty} c_{n,q}(k,t') e^{-irx'} + \sqrt{\frac{n}{2}} \sum_{q=-\infty}^{\infty} \left[ir - \frac{1}{2}\frac{\partial U}{\partial x'} \right] c_{n-1,q}(k,t') e^{-irx'} \\
&\quad + \sqrt{\frac{n+1}{2}} \sum_{q=-\infty}^{\infty} \left[ir + \frac{1}{2}\frac{\partial U}{\partial x'} \right] c_{n+1,q}(k,t') e^{-irx'} .
\end{aligned} \tag{8.31}$$

Thus with the potential given by Eq. (8.1) namely

$$U(x') = -g\cos(x') \tag{8.32}$$

and its derivative expressed in exponential form

$$\begin{aligned}
\frac{\partial U}{\partial x'} &= g\sin x' \\
&= -\frac{ig}{2}\left(e^{ix'} - e^{-ix'} \right),
\end{aligned} \tag{8.33}$$

Eq. (8.31) becomes

$$\sum_{q=-\infty}^{\infty}\frac{dc_{n,q}(k,t')}{dt'}e^{-irx'}=-n\gamma\sum_{q=-\infty}^{\infty}c_{n,q}(k,t')e^{-irx'}$$
$$+\sqrt{\frac{n}{2}}\sum_{q=-\infty}^{\infty}\left[ir+\frac{ig}{4}\left(e^{ix'}-e^{-ix'}\right)\right]c_{n-1,q}(k,t')e^{-irx'}$$
$$+\sqrt{\frac{n+1}{2}}\sum_{q=-\infty}^{\infty}\left[ir-\frac{ig}{4}\left(e^{ix'}-e^{-ix'}\right)\right]c_{n+1,q}(k,t')e^{-irx'}$$

(8.34)

so that we can apply the orthogonality property of the trigonometrical functions namely

$$\frac{1}{2\pi}\int_0^{2\pi}e^{\pm i(r-s)x}dx=\delta_{r,s} \tag{8.35}$$

to obtain the following set of ordinary differential recurrence equations

$$\frac{d}{dt'}c_{n,q}=-n\gamma' c_{n,q}+\sqrt{\frac{n}{2}}\left[i(q+k)c_{n-1,q}+\frac{ig}{4}\left(c_{n-1,q+1}-c_{n-1,q-1}\right)\right]$$
$$+\sqrt{\frac{n+1}{2}}\left[i(q+k)c_{n+1,q}-\frac{ig}{4}\left(c_{n+1,q+1}-c_{n+1,q-1}\right)\right].$$

(8.36)

These are simply the Brinkman equations for a cosine potential written in a form which will yield the nonperiodic solution.

Now in order to find the quantum corrections (since the master equation is linear) we can take one term at a time and add the results of our calculations to the relevant equations. We initially take the first order in Λ and then proceed to Λ^2. We have already carried out the calculation for $O(\Lambda)$ and we give the results below. The set of partial differential equations to $O(\Lambda)$ are

$$\frac{\partial C_n(k,x',t')}{\partial t'}=-n\gamma C_n-\sqrt{\frac{n}{2}}\left(\frac{\partial C_{n-1}}{\partial x'}+\frac{\partial U}{\partial x'}C_{n-1}\right)-\sqrt{\frac{n+1}{2}}\frac{\partial C_{n+1}}{\partial x'}$$
$$+\Lambda\sqrt{n(n-1)}\left\{\sqrt{\frac{n-2}{2}}\frac{\partial^3 U}{\partial x'^3}C_{n-3}+2\gamma\frac{\partial^2 U}{\partial x'^2}C_{n-2}\right\}.$$

(8.37)

The corresponding set of ordinary differential recurrence equations have been given in Chapter VII (namely Eq. (7)) and are

$$\frac{d}{dt'}c_{n,q} = -n\gamma' c_{n,q} + \sqrt{\frac{n}{2}}\left[i(q+k)c_{n-1,q} + \frac{ig}{4}\left(c_{n-1,q+1} - c_{n-1,q-1}\right)\right]$$
$$+\sqrt{\frac{n+1}{2}}\left[i(q+k)c_{n+1,q} - \frac{ig}{4}\left(c_{n+1,q+1} - c_{n+1,q-1}\right)\right]$$
$$+\Lambda g\sqrt{n(n-1)}\left[\gamma'\left(c_{n-2,q+1} + c_{n-2,q-1}\right) + \frac{i}{2}\sqrt{\frac{n-2}{2}}\left(c_{n-3,q+1} - c_{n-3,q-1}\right)\right].$$

(8.38)

VIII.III The quantum master equation to the second order in $\hbar^2$ and its solution

The second order terms in Λ in the conservative part of the master equation (cf. Eq. (8.6)), i.e. to $O(\hbar^4)$, are after rescaling

$$+\frac{\hbar^4}{1920}\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5} \equiv +\frac{3m^2}{10\beta^4}\Lambda^2\frac{\partial^5 V}{\partial x^5}\frac{\partial^5 W}{\partial p^5}$$
$$\rightarrow +\frac{3}{80}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\frac{\partial^5 W}{\partial p'^5} \tag{8.39}$$

while the dissipative term becomes

$$\gamma\frac{\partial}{\partial p}\left[\frac{m}{\beta}\left\{-\frac{\hbar^4\beta^4}{1440m^2}\left[6V'''V' + 2V''^2 + 3V^{(4)}\left(\frac{p^2}{m} - \frac{5}{\beta}\right)\right]\right\}\frac{\partial W}{\partial p}\right]$$
$$\rightarrow \frac{\gamma'}{2}\frac{\partial}{\partial p'}\left[-\frac{2}{5}\Lambda^2\left[6\frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'} + 2\left(\frac{\partial^2 U}{\partial x'^2}\right)^2 + 3\frac{\partial^4 U}{\partial x'^4}\left(2p^2 - 5\right)\right]\frac{\partial W}{\partial p'}\right].$$

(8.40)

Thus written in full the rescaled master equation reads (cf. Eq. (8.14) above)

$$\frac{\partial W}{\partial t'} = -p'\frac{\partial W}{\partial x'} + \frac{1}{2}\frac{\partial U}{\partial x'}\frac{\partial W}{\partial p'} - \frac{\Lambda}{4}\frac{\partial^3 U}{\partial x'^3}\frac{\partial^3 W}{\partial p'^3} + \frac{3}{80}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\frac{\partial^5 W}{\partial p'^5}$$
$$+\frac{\gamma'}{2}\frac{\partial}{\partial p'}\left[2p'W + \left\{1 + 2\Lambda\frac{\partial^2 U}{\partial x'^2} - \frac{2}{5}\Lambda^2\left[6\frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'} + 2\left(\frac{\partial^2 U}{\partial x'^2}\right)^2 + 3\frac{\partial^4 U}{\partial x'^4}\left(2p^2 - 5\right)\right]\right\}\frac{\partial W}{\partial p'}\right].$$

(8.41)

Taking the correction to the conservative term first, namely

$$+\frac{3}{80}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\frac{\partial^5 W}{\partial p'^5}, \tag{8.42}$$

we apply Eq. (8.24) so that expression (8.42) becomes

$$+\frac{3}{80}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\frac{e^{-p'^2}}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{C_n(k,x',t')}{\sqrt{2^n n!}}\left(-H_{n+5}(p')\right). \qquad (8.43)$$

Divide across by $\frac{e^{-p'^2}}{\sqrt{\pi}}$ and apply the orthogonality relation Eq. (8.27) to get

$$-\frac{3}{80}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\frac{C_{n-5}(k,x',t')2^n n!\sqrt{\pi}}{\sqrt{2^{n-5}(n-5)!}}. \qquad (8.44)$$

To get our first order of perturbation theory the partial differential equation (Eq. (8.37) above) we multiplied across by $\left(2^n n!\right)^{-1/2}\sqrt{\pi}$ and we must do the same for our new term (8.44) which becomes

$$-\frac{3\sqrt{2}}{20}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\sqrt{n(n-1)(n-2)(n-3)(n-4)}C_{n-5}. \qquad (8.45)$$

Our second order expression for the dissipative part of the master equation requires a much lengthier calculation. This term is

$$+\frac{\gamma'}{2}\frac{\partial}{\partial p'}\left[-\frac{2}{5}\Lambda^2\left[6\frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'}+2\left(\frac{\partial^2 U}{\partial x'^2}\right)^2+3\frac{\partial^4 U}{\partial x'^4}\left(2p^2-5\right)\right]\frac{\partial W}{\partial p'}\right]$$

(8.46)

which also may be written

$$-\frac{\gamma'\Lambda^2}{5}\left[\left(6\frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'}+2\left(\frac{\partial^2 U}{\partial x'^2}\right)^2-15U^{(4)}\right)\frac{\partial^2 W}{\partial p'^2}+6U^{(4)}\frac{\partial}{\partial p'}\left(p'^2\frac{\partial W}{\partial p'}\right)\right].$$

(8.47)

In writing (8.47) we have used the identity

$$\frac{\partial}{\partial p'}\left(p'^2\frac{\partial W}{\partial p'}\right)=p'^2\frac{\partial^2 W}{\partial p'^2}+2p'\frac{\partial W}{\partial p'}. \qquad (8.48)$$

Now from the recurrence relations of the Hermite polynomials (cf. Eq. (8.22)) we have

$$\begin{aligned}p^2H_{n+1}(p)=&\frac{1}{4}H_{n+3}(p)+\frac{2n+3}{2}H_{n+1}(p)\\&+n(n+1)H_{n-1}(p).\end{aligned} \qquad (8.49)$$

We use this and the ladder type property of the derivative of *W* with respect to p' given in Eq. (8.24) and follow the same procedure as for the conservative term to obtain

$$-\frac{2\gamma'\Lambda^2}{5}\sqrt{n(n-1)}\left\{3\sqrt{(n-2)(n-3)}\,\frac{\partial^4 U}{\partial x'^4}C_{n-4}\right.$$
$$\left.+2\left[3\frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'}+\left(\frac{\partial^2 U}{\partial x'^2}\right)^2+3(n-3)\frac{\partial^4 U}{\partial x'^4}\right]C_{n-2}+3\frac{n(n+1)}{\sqrt{n(n-1)}}\frac{\partial^4 U}{\partial x'^4}C_n\right\}.$$

(8.50)

The foregoing equations allow one to write the quantum Brinkman equations correct to second order in Λ, these are the seven term partial differential recurrence relation which however in reality again constitute a *forced* three term partial differential recurrence relation in accordance with perturbation theory in Λ;

$$\frac{\partial C_n(k,x,t)}{\partial t}=-n\gamma C_n-\sqrt{\frac{n}{2}}\left(\frac{\partial C_{n-1}}{\partial x}+\frac{\partial V}{\partial x}C_{n-1}\right)-\sqrt{\frac{n+1}{2}}\frac{\partial C_{n+1}}{\partial x}$$
$$+\Lambda\sqrt{n(n-1)}\left\{\sqrt{\frac{n-2}{2}}\frac{\partial^3 V}{\partial x^3}C_{n-3}+2\gamma\frac{\partial^2 V}{\partial x^2}C_{n-2}\right\}$$
$$-\frac{2\Lambda^2}{5}\sqrt{n(n-1)}\left\{\frac{3\sqrt{2}}{8}\sqrt{(n-2)(n-3)(n-4)}\,\frac{\partial^5 V}{\partial x^5}C_{n-5}+3\gamma\sqrt{(n-2)(n-3)}\,\frac{\partial^4 V}{\partial x^4}C_{n-4}\right.$$
$$\left.+2\gamma\left[3\frac{\partial^3 V}{\partial x^3}\frac{\partial V}{\partial x}+\left(\frac{\partial^2 V}{\partial x^2}\right)^2+3(n-3)\frac{\partial^4 V}{\partial x^4}\right]C_{n-2}+3\gamma\frac{n(n+1)}{\sqrt{n(n-1)}}\frac{\partial^4 V}{\partial x^4}C_n\right\}.$$

(8.51)

Now our potential is $U(x')=-g\cos x'$. Take the first term i.e. (8.45) and our expansion of $C_n(k,x',t')$, namely

$$C_n(k,x',t')=\frac{1}{2\pi}e^{-\frac{U(x')}{2}}\sum_{q=-\infty}^{\infty}c_{n,q}(k,t')e^{-i(q+k)x'+ikx'(0)}, \quad (8.52)$$

we get the fifth derivative of U and express it in exponential form, i.e.

$$\frac{\partial^5 U}{\partial x'^5}=U^{(5)}=-\frac{ig}{2}\left(e^{ix}-e^{-ix}\right), \quad (8.53)$$

so that

$$-\frac{3\sqrt{2}}{20}\Lambda^2\frac{\partial^5 U}{\partial x'^5}\sqrt{n(n-1)(n-2)(n-3)(n-4)}C_{n-5}$$
$$\to+\frac{ig3\sqrt{2}}{40}\Lambda^2\sqrt{n(n-1)(n-2)(n-3)(n-4)}\sum_{q=-\infty}^{\infty}c_{n-5,q}(k,t')\left(e^{ix'}-e^{-ix'}\right)e^{-irx'}$$
$$=\frac{ig3\sqrt{2}}{40}\Lambda^2\sqrt{n(n-1)(n-2)(n-3)(n-4)}\sum_{q=-\infty}^{\infty}c_{n-5,q}(k,t')\left(e^{i(r-1)x'}-e^{-i(r+1)x'}\right). \tag{8.54}$$

As before we apply the orthogonality property of the circular functions to give

$$+\frac{ig3\sqrt{2}}{40}\Lambda^2\sqrt{n(n-1)(n-2)(n-3)(n-4)}\left(c_{n-5,q+1}(k,t')-c_{n-5,q-1}(k,t')\right). \tag{8.55}$$

The recurrence relations resulting from the dissipation term involves quite an amount of algebra but the method is exactly the same. In this case we have some products of different orders of derivatives of the potential e.g. $\frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'}$ which results in different effects on the q-counter. Some useful results:

$$\begin{aligned}\frac{\partial^4 U}{\partial x'^4}&=-\frac{g}{2}\left(e^{ix}-e^{-ix}\right)\\ \frac{\partial^3 U}{\partial x'^3}\frac{\partial U}{\partial x'}&=\frac{g^2}{4}\left(e^{i2x}+e^{-i2x}-2\right).\\ \left(\frac{\partial^2 U}{\partial x'^2}\right)^2&=\frac{g^2}{4}\left(e^{i2x}+e^{-i2x}+2\right)\end{aligned} \tag{8.56}$$

After the procedure described above the second order dissipative term can be written as

$$+\frac{3\Lambda^2 g}{5}\sqrt{n(n-1)}\left\{\gamma'\sqrt{(n-2)(n-3)}\left(c_{n-4,q+1}+c_{n-4,q-1}\right)+\gamma'\frac{n(n+1)}{\sqrt{n(n-1)}}\left(c_{n,q+1}+c_{n,q-1}\right)\right.$$
$$\left.+\frac{4}{3}g\gamma'(c_{n-2,q}-c_{n-2,q+2}-c_{n-2,q-2})+2\gamma'(n-3)\left(c_{n-2,q+1}+c_{n-2,q-1}\right)\right\}. \tag{8.57}$$

The complete set of differential recurrence relations for the nonperiodic solution for the cosine potential is then

$$\frac{d}{dt'}c_{n,q}=-n\gamma' c_{n,q}+\sqrt{\frac{n}{2}}\left[i\left(q+k\right)c_{n-1,q}+\frac{ig}{4}\left(c_{n-1,q+1}-c_{n-1,q-1}\right)\right]$$
$$+\sqrt{\frac{n+1}{2}}\left[i\left(q+k\right)c_{n+1,q}-\frac{ig}{4}\left(c_{n+1,q+1}-c_{n+1,q-1}\right)\right]$$
$$+\Lambda g\sqrt{n(n-1)}\left[\gamma'\left(c_{n-2,q+1}+c_{n-2,q-1}\right)+\frac{i}{2}\sqrt{\frac{n-2}{2}}\left(c_{n-3,q+1}-c_{n-3,q-1}\right)\right]$$
$$+\frac{3\Lambda^2 g}{5}\sqrt{n(n-1)}\left\{\frac{i}{4}\sqrt{\frac{(n-2)(n-3)(n-4)}{2}}\left(c_{n-5,q+1}-c_{n-5,q-1}\right)\right.$$
$$+\gamma'\left(\sqrt{(n-2)(n-3)}\left(c_{n-4,q+1}+c_{n-4,q-1}\right)+\frac{n(n+1)}{\sqrt{n(n-1)}}\left(c_{n,q+1}+c_{n,q-1}\right)\right.$$
$$\left.\left.+\frac{4}{3}g(c_{n-2,q}-c_{n-2,q+2}-c_{n-2,q-2})+2(n-3)\left(c_{n-2,q+1}+c_{n-2,q-1}\right)\right)\right\}.$$

(8.58)

Again Eq. (8.58) in accordance with perturbation theory constitutes the classical ordinary differential recurrence relation for the cosine potential forced by the quantum terms, for example in order to solve Eq. (8.58) we first calculate the solution of the classical problem i.e. Eq. (8.58) without the quantum terms which is the zero order perturbation theory or unperturbed solution. Having determined this solution (via matrix continued fractions) it is substituted into Eq. (8.58) and all terms $O(\Lambda^2)$ and higher are neglected. This is the first order perturbation solution we have calculated in Chapter VII. The second order perturbation solution is then calculated by substitution of the first order perturbation solution into Eq. (8.58) and then ignoring terms $O(\Lambda^4)$ and higher. The perturbation method is entirely analogous to that used by Wigner in 1932 for the solution of the Wigner-Liouville equation for the closed quantum system. We shall now arrange Eq. (8.58) in matrix continued fraction form as we did for the first order perturbation solution in Chapter VII.

VIII.IV Matrix continued fraction solution for second order perturbation theory in the quantum parameter

We introduce as in the previous Chapter, the column vectors (we use here *t* instead *t'*)

$$\mathbf{C}_n(t)=\begin{pmatrix}\vdots\\ c_{n-1,-1}(k,t)\\ c_{n-1,0}(k,t)\\ c_{n-1,1}(k,t)\\ \vdots\end{pmatrix}. \tag{8.59}$$

which allow us to suppress the q dependence, Eq.(8.58) can be ostensibly rearranged as the set of matrix seven-term recurrence equations (which of course is simply a forced three term matrix recurrence equation because of the structure of the perturbation expansion)

$$\frac{d}{dt}\mathbf{C}_n(t)=\mathbf{Q}_n^{-}\mathbf{C}_{n-1}(t)-\left[\gamma'(n-1)-\Lambda^2\mathbf{u}_n\right]\mathbf{C}_n(t)+\mathbf{Q}_n^{+}\mathbf{C}_{n+1}(t)+\Lambda\left[\mathbf{q}_n+\Lambda\mathbf{q}_n'\right]\mathbf{C}_{n-2}(t)$$
$$+\Lambda\mathbf{r}_n\mathbf{C}_{n-3}(t)+\Lambda^2\mathbf{s}_n\mathbf{C}_{n-4}(t)+\Lambda^2\mathbf{t}_n\mathbf{C}_{n-5}(t) \tag{8.60}$$

where

$$\mathbf{Q}_n^{-}=i\sqrt{\frac{n-1}{2}}\begin{pmatrix}\ddots & \vdots & \vdots & \vdots & \iddots\\ \cdots & k-1 & g/4 & 0 & \cdots\\ \cdots & -g/4 & k & g/4 & \cdots\\ \cdots & 0 & -g/4 & k+1 & \cdots\\ \iddots & \vdots & \vdots & \vdots & \ddots\end{pmatrix},$$

$$\mathbf{Q}_n^{+}=i\sqrt{\frac{n}{2}}\begin{pmatrix}\ddots & \vdots & \vdots & \vdots & \iddots\\ \cdots & k-1 & -g/4 & 0 & \cdots\\ \cdots & g/4 & k & -g/4 & \cdots\\ \cdots & 0 & g/4 & k+1 & \cdots\\ \iddots & \vdots & \vdots & \vdots & \ddots\end{pmatrix},$$

$$\mathbf{q}_n=\gamma' g\sqrt{(n-1)(n-2)}\begin{pmatrix}\ddots & \vdots & \vdots & \vdots & \iddots\\ \cdots 1 & 0 & 1 & 0 & 0\cdots\\ \cdots 0 & 1 & 0 & 1 & 0\cdots\\ \cdots 0 & 0 & 1 & 0 & 1\cdots\\ \iddots & \vdots & \vdots & \vdots & \ddots\end{pmatrix},$$

$$\mathbf{q}'_n = \frac{6}{5}\gamma' g\sqrt{(n-1)(n-2)}\left\{\frac{2g}{3}\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 1 & 0 & -1 & \cdots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & -1 & 0 & 1 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} + (n-4)\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & 1 & 0 & 1 & \cdots \\ \cdots & 0 & 1 & 0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}\right\} \tag{8.61}$$

$$\mathbf{r}_n = ig\sqrt{\frac{(n-1)(n-2)(n-3)}{8}}\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & -1 & 0 & 1 & \cdots \\ \cdots & 0 & -1 & 0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{u}_n = \frac{2\gamma' gn(n-1)}{5}\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & 0 & 0 & 1 & \cdots \\ \cdots & 1 & 0 & 0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{8.62}$$

$$\mathbf{s}_n = \frac{3\gamma' g\sqrt{(n-1)(n-2)(n-3)(n-4)}}{5}\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & 1 & 0 & 1 & \cdots \\ \cdots & 0 & 1 & 0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

(8.63)

$$\mathbf{t}_n = \frac{i3g\sqrt{(n-1)(n-2)(n-3)(n-4)(n-5)}}{20}\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & -1 & 0 & 1 & \cdots \\ \cdots & 0 & -1 & 0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

(8.64)

In accordance with perturbation theory it is anticipated that the solution will be of the form

$$\mathbf{C}_n(t) = \mathbf{C}_n^0(t) + \Lambda\mathbf{C}_n^1(t) + \Lambda^2\mathbf{C}_n^2(t), \tag{8.65}$$

where the superscripts denote the power of Λ used. Having written our set Eq. (8.58) in matrix form we must also determine the initial conditions to second

order of perturbation theory. In the time and resources allotted to this project it has only been possible to treat the partition function to second order in Λ. I propose to solve the problem completely at a later stage and to present a full numerical analysis and comparison with the first order solution.

We saw that the Wigner stationary distribution (before rescaling) is

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

(8.66)

where

$$\varepsilon(x,p) = \frac{p^2}{2m} + V(x)$$

and (in this unrescaled notation) where

$$\Lambda = \frac{\hbar^2\beta^2}{24m}$$

is the characteristic quantum parameter. The reader should not confuse this Λ ($\Lambda = \hbar^2\beta^2/(24m)$) with the Λ which we will soon redefine. We will rescale Eq. (8.66) as before using:

$$x \to x_0 x' \tag{8.67}$$

$$p \to \frac{m x_0}{\eta} p' \tag{8.68}$$

$$V(x) \to \frac{1}{\beta} U(x'). \tag{8.69}$$

Therefore Eq. (8.66) becomes (with the new and dimensionless parameter $\Lambda = \frac{\hbar^2\beta}{24 m x_0^2}$)

$$W_{st}(x',p') = e^{-p'^2-U(x')}\left\{1+\Lambda\left((2p'^2-3)U''+U'^2\right)\right.$$
$$+3\Lambda^2\left[2p'^4\left(\frac{U''^2}{3}-\frac{U^{(4)}}{5}\right)+2p'^2\left(U^{(4)}-\frac{2U'''U'}{5}+\frac{U''U'^2}{3}-\frac{9U''^2}{5}\right)\right.$$
$$\left.\left.+\frac{U'^4}{6}+\frac{5U''^2}{2}-\frac{9U''U'^2}{5}+2U'''U'-\frac{3U^{(4)}}{2}\right]+O(\Lambda^3)+...\right\}.$$

(8.70)

This distribution must again be normalized. To $O(\Lambda)$ i.e. the first quantum correction to the Maxwell-Boltzmann distribution which we now call the Wigner distribution, we have the following:

$$W_{st}(x',p') = \frac{e^{-p'^2-U(x')}\left\{1+\Lambda\left[2p'^2U''-3U''+U'^2\right]\right\}}{\int_{-\infty}^{\infty}\int_{0}^{2\pi} e^{-p'^2-U(x')}\left\{1+\Lambda\left[2p'^2U''-3U''+U'^2\right]\right\}dx'dp'}$$
$$= \frac{e^{-p'^2-U(x')}\left\{1+\Lambda\left[2p'^2U''-3U''+U'^2\right]\right\}}{Z}$$

(8.71)

where Z is the partition function as we saw in Chapter VII,

$$Z(x',p') = \int_{-\infty}^{\infty}\int_{0}^{2\pi} e^{-p'^2-U(x')}\left\{1+\Lambda\left[2p'^2U''-3U''+U'^2\right]\right\}dx'dp'.$$

(8.72)

Including the next correction gives

$$W_{st}(x',p') = Z^{-1}e^{-p'^2-U(x')}\left\{1+\Lambda\left((2p'^2-3)U''+U'^2\right)\right.$$
$$+3\Lambda^2\left[2p'^4\left(\frac{U''^2}{3}-\frac{U^{(4)}}{5}\right)+2p'^2\left(U^{(4)}-\frac{2U'''U'}{5}+\frac{U''U'^2}{3}-\frac{9U''^2}{5}\right)\right.$$
$$\left.\left.+\frac{U'^4}{6}+\frac{5U''^2}{2}-\frac{9U''U'^2}{5}+2U'''U'-\frac{3U^{(4)}}{2}\right]\right\}$$

(8.73)

where the partition function is now given by

$$Z(x',p') = \int_{-\infty}^{\infty}\int_{0}^{2\pi} e^{-p'^2-U(x')}\left\{1+\Lambda\left((2p'^2-3)U''+U'^2\right)\right.$$
$$+3\Lambda^2\left[2p'^4\left(\frac{U''^2}{3}-\frac{U^{(4)}}{5}\right)+2p'^2\left(U^{(4)}-\frac{2U'''U'}{5}+\frac{U''U'^2}{3}-\frac{9U''^2}{5}\right)\right.$$
$$\left.\left.+\frac{U'^4}{6}+\frac{5U''^2}{2}-\frac{9U''U'^2}{5}+2U'''U'-\frac{3U^{(4)}}{2}\right]\right\}dx'dp'.$$

(8.74)

On integrating out the momentum we get

$$Z(x') = \sqrt{\pi}\int_{0}^{2\pi} e^{-U(x')}\left\{1+\Lambda\left(U'^2-2U''\right)\right.$$
$$\left.+\Lambda^2\frac{1}{5}\left[\frac{5U'^4}{2}+18U''^2-22U''U'^2+24U'''U'-12U^{(4)}\right]\right\}dx'dp'.$$

(8.75)

The potential is

$$U(x') = -g\cos x' \tag{8.76}$$

and therefore the partition function maybe expressed [3] in terms of the modified Bessel functions [4] as

$$Z = Z_{cl}\left[1-\Lambda g\frac{I_1(g)}{I_0(g)}+\Lambda^2 g\left(\frac{7}{10}g-\frac{I_1(g)}{5I_0(g)}\right)\right]. \tag{8.77}$$

Here

$$Z_{cl} = 2\pi^{3/2}I_0(g) \tag{8.78}$$

is the classical partition function and $I_0(x)$ and $I_1(x)$ are modified Bessel functions of the first kind [4].

Equation (8.77) can be found by using the recurrence relations of the modified Bessel functions, namely

$$I_{v-1}(x) - I_{v+1}(x) = \frac{2v}{x}I_v(x)\,. \tag{8.79}$$

The Wigner stationary distribution is now

$$W_{st}(x',p') = e^{-p'^2-U(x')}\left\{1+\Lambda\left((2p'^2-3)U''+U'^2\right)\right.$$
$$+3\Lambda^2\left[2p'^4\left(\frac{U''^2}{3}-\frac{U^{(4)}}{5}\right)+2p'^2\left(U^{(4)}-\frac{2U'''U'}{5}+\frac{U''U'^2}{3}-\frac{9U''^2}{5}\right)\right.$$
$$\left.\left.+\frac{U'^4}{6}+\frac{5U''^2}{2}-\frac{9U''U'^2}{5}+2U'''U'-\frac{3U^{(4)}}{2}\right]\right\}$$
$$\times\frac{1}{Z_{cl}\left[1-\Lambda g\frac{I_1(g)}{I_0(g)}+\Lambda^2 g\left(\frac{7}{10}g-\frac{I_1(g)}{5I_0(g)}\right)\right]}. \tag{8.80}$$

Having determined the partition function the Fourier coefficients $c_{n,q}$ maybe calculated in the same way as the first order approximation.

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CHAPTER IX

Conclusions

We have outlined in this Thesis how Wigner's method of obtaining quantum mechanical corrections to the Maxwell-Boltzmann distribution and applying to closed quantum systems may be extended to a canonical ensemble of Brownian particles in a potential $V(x)$ at temperature T. Throughout the calculation the bath is described classically while the tagged particle is treated quantum mechanically using Wigner's quasiprobablity representation of the density operator for the single particle distribution function. The advantage of such a formalism as emphasized by Gross and Lebowitz [1] is that the connection between classical and quantum collision kernels, (i.e. in classical mechanics the *Stosszahlanzatz* used in the Boltzmann equation) is much more transparent if one is familiar with the classical case than in the density operator formalism. Indeed according to Gross and Lebowitz [1] in their discussion of quantum dielectric relaxation using the quantum generalization of the so called strong collision model [2,3] (following earlier work of Karplus and Schwinger [4] on a full quantum mechanical treatment of the Van Vleck-Weisskopf model [5] for the shape of collision broadened absorption lines) "appropriate quantum kernels are suggested by requiring that the Wigner distribution satisfy an integrodifferential equation (of the form of a Boltzmann equation) with a stochastic kernel which is the same as that obeyed by the classical distribution function. Then one expresses the Wigner function in terms of the density matrix." (cf. Baker's [6] remark "the (quasiprobability) distribution is imagined to be concentrated about the classical point, so that a crude measurement will be unable to differentiate between the two theories"). These considerations led us to postulate since the *Stosszahlansatz* underlying the theory of the classical Brownian motion is that the collisions are frequent but weak a Kramers–Moyal like expansion truncated at the second term (leading of course in the classical limit to the Fokker-Planck equation) as the phase space representation of the collision operator. The diffusion coefficients in the resulting quantum master equation may then be determined by requiring that

the equilibrium quasiprobability distribution in the representation space renders the collision term zero. The most important result is that the bath-particle interaction causes the various diffusion coefficients in the semiclassical quantum master equation for the single particle distribution function in phase (representation) space to become position and momentum dependent; a result which had already been anticipated by Zwanzig (1958) [7]. He suggested that the diffusion coefficients in the classical Fokker-Planck equation should be modified by quantum effects. He was led to this conclusion by considering a model of Montroll and Shuler [8] for the relaxation from an initial nonequilibrium distribution of energy of a system of harmonic oscillators immersed in a heat bath. They gave a relaxation equation for the fraction of quantum oscillators in a given quantum state at any time. Zwanzig rewrote this relaxation equation in terms of the appropriate von Neumann evolution equation for the elements of the nonequilibrium density matrix which reduces to the Schrödinger equation for zero dissipation. Next he expressed the von Neumann equation in phase space form using Wigner's definition of his function as a particular Fourier transform of the density matrix as we have used throughout the Thesis. Thus, he arrived at a quantum master equation analogous to the Fokker-Planck equation which clearly shows that the diffusion coefficients are altered by quantum effects.

Now on expansion of the momentum dependence of the time dependent Wigner distribution function in phase space in Weber or oscillator functions (orthogonal Hermite polynomials) and substitution into our quantum master equation, the form of the classical Brinkman hierarchy of partial differential recurrence relations for the configuration space distribution function is essentially preserved as we saw in Chapters V-VIII. Thus all the methods of solution of the Brinkman equations for the classical Fokker-Planck equation such as matrix continued fractions may also be applied to the quantum master equation. The explicit calculations we have presented in Chapters VII and VIII constitute an example of the solution of the semiclassical Klein-Kramers equation for the Brownian motion in a periodic potential. The approach, which is grounded in continued fraction methods, clearly indicates how many existing results of the classical theory of Brownian motion in a potential (double well, tilted periodic, etc.) may be extended to the semiclassical case. In addition in the high damping (or noninertial) limit, Brinkman's method of derivation of a partial differential

equation (Smoluchowski equation) governing the behaviour of the configuration space distribution function may also be used to derive from the quantum Brinkman hierarchy a quantum Smoluchowski equation for the configuration space distribution function without using path integral methods.

By way of illustration of our results we have demonstrated how our calculation of the diffusion coefficient yields the known master equation for the time dependent Wigner function for the quantum Brownian harmonic oscillator originally obtained by Agarwal [9]. In addition we have demonstrated how our procedure yields a closed form solution for the quantum Kramers IHD escape rate showing clearly that the nature of our dynamical model is that of a quantum particle embedded in a classical bath with the bath particle interaction giving rise to a dependence of the diffusion coefficients on the derivatives of the potential and on the momentum. The solution so obtained reduces to Wigner's previously known solution given by his extension of TST to quantum systems described in Chapter V. This is in effect the intermediate damping case of the quantum IHD result. We remark that the theory we have presented yields in the manner of the classical Fokker-Planck equation exact numerical solutions (within the limitations of the semiclassical approach) for various system parameters such as the quantum Kramers escape rate. These may be used as a benchmark in order to evaluate the accuracy and range of validity of various asymptotic expressions for that quantity as we have shown in Chapter VII. We have illustrated methods of calculating escape rates in the context of the Wigner function approach without detailed treatment of the very low damping case. In general, in order to consider the VLD case, it may be easier to use semiclassical functional-integral methods [10,11]. However, since the objective of the Thesis is the formulation of appropriate quantum mechanical evolution equations rather than the calculation of quantum mechanical escape rates, we have refrained from considering the low damping case although that is the most interesting from a quantum mechanical point of view as one would expect the largest quantum effects to manifest themselves in the VLD regime. In view of these considerations the existence of the universal escape rate ($\Gamma = \Gamma_{IHD}\Upsilon$ where Υ is the depopulation factor) valid for all values of damping [12-14] is a most useful tool as it will automatically yield the correct escape rate for all values of the damping from a knowledge of the IHD rate.

Our approach which has been outlined for mechanical systems with separable and additive Hamiltonians may also be extended to spin systems such as single domain ferromagnetic particles in the presence of an external magnetic field. This is accomplished using Stratonovich's generalization of Moyal's quantization procedure to spins in order to construct a Wigner function for spin systems. We recall (Chapter IV) that mindful that Moyal's definition of the characteristic function is not periodic as it must be so if applicable to spins. Stratonovich introduced a quasiprobability density function on the sphere which he defined as the trace of the product of the system density matrix and the irreducible tensor operators having matrix elements in the spherical basis representation given by the Clebsch-Gordan coefficients. Hence the average value of a quantum spin operator may be calculated just as the corresponding classical function from the Weyl symbol of the operator. We have briefly illustrated this in Chapter IV. There we briefly outlined for the purpose of completeness a calculation made by Kalmykov and so presented the equilibrium quasiprobabililty function representation of the density operator for the spin Hamiltonian corresponding to a spin under the influence of an internal uniaxial anisotropy field and an applied uniform field parallel to the anisotropy field. The Wigner-Stratonovich method is capable of great generalization and it has been very recently been shown [15-17] that a knowledge of the phase space representation of the equilibrium density matrix coupled with a truncated Kramers-Moyal like representation (as we have illustrated for particles in Chapter V) of the collision operator for spins allows one to determine the diffusion coefficients in that expansion so that spin problems may be treated in essentially the same way as we have outlined for particles.

The main part of the Thesis assumes that Wigner's evolution equation for particles is truncated at terms of the order of the square of Planck's constant. In Chapter VIII we have shown how the calculations may be extended to the fourth order. Essentially nothing new is involved. However it is obvious from Chapter VIII that the mathematical manipulations become considerably more complicated. It is planned to carry out a comprehensive numerical analysis in the manner outlined for the squared term in Chapter VII in the future. This will provide both a useful check on the convergence of the perturbation procedure in the quantum parameter and will provide a more accurate description of the quantum effects

when these are not automatically assumed small. We remark that Wigner [18] originally included the fourth order effects in his 1932 discussion of the quantum corrections to the Maxwell-Boltzmann distribution, i.e. classical thermodynamic equilibrium.

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