Semiclassical Klein–Kramers and Smoluchowski equations for the Brownian motion of a particle in an external potential

2007 J. Phys. A: Math. Theor. 40 F91

(http://iopscience.iop.org/1751-8121/40/3/F02)

IOP FTC
INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND THEORETICAL

J. Phys. A: Math. Theor. **40** (2007) F91–F98 doi:10.1088/1751-8113/40/3/F02

FAST TRACK COMMUNICATION

Semiclassical Klein–Kramers and Smoluchowski equations for the Brownian motion of a particle in an external potential

W T Coffey[1], Yu P Kalmykov[2], S V Titov[1,3] and B P Mulligan[3]

[1] Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Ireland
[2] Laboratoire de Mathématiques et Physique des Systèmes, Université de Perpignan, 52, Avenue de Paul Alduy, 66860 Perpignan Cedex, France
[3] Institute of Radio Engineering and Electronics of the Russian Academy of Sciences, Vvedenskii Square 1, Fryazino, 141190, Russian Federation

Received 17 October 2006, in final form 9 November 2006
Published 20 December 2006
Online at stacks.iop.org/JPhysA/40/F91

Abstract

The quantum Brownian motion of a particle in an external potential $V(x)$ is treated using the master equation for the Wigner distribution function $W(x, p, t)$ in phase space (x, p). A heuristic method of determination of diffusion coefficients in the master equation is proposed. The time evolution equation so obtained contains explicit quantum correction terms up to $o(\hbar^4)$ and in the classical limit, $\hbar \to 0$, reduces to the Klein–Kramers equation. For a quantum oscillator, the method yields an evolution equation for $W(x, p, t)$ coinciding with that of Agarwal (1971 *Phys. Rev.* A **4** 739). In the non-inertial regime, by applying the Brinkman expansion of the momentum distribution in Weber functions (Brinkman 1956 *Physica* **22** 29), the corresponding semiclassical Smoluchowski equation is derived.

PACS numbers: 03.65.Yz, 05.40.−a

In the last two decades there has been a revival of interest in the Wigner phase-space formalism [1] in quantum mechanics and its manifold applications (e.g., [2, 3]). Wigner [1] showed that quantum mechanics can be reformulated in terms of a phase space (x, p) quasiprobability distribution

$$W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \rho\left(x + \frac{1}{2}y, x - \frac{1}{2}y\right) \mathrm{e}^{-\mathrm{i}py/\hbar}\, \mathrm{d}y,$$

where $\hbar$ is Planck's constant and $\rho(x, x') = \langle x|\widehat{\rho}|x'\rangle$ is the density matrix. The Wigner function $W(x, p, t)$ exhibits most of the properties of a classical phase-space distribution.

The expectation value of a quantum operator $\widehat{Q}$ may then be calculated using the Wigner function from the corresponding classical variable $Q(x, p)$ as

$$\langle Q\rangle(t) = \int W(x, p, t)\, Q(x, p)\, \mathrm{d}x\, \mathrm{d}p.$$

For *closed* quantum systems, the time behaviour of the Wigner function is governed by an evolution equation equivalent to the Schrödinger equation. The Wigner formalism may also be applied to *open* quantum systems [3]. In particular, it provides a useful tool for introducing quantum corrections to classical models of dissipation such as many-body collisions or Brownian motion [4–10]. In this context 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 [7–10]. The oscillators represent the normal modes of the bath. Quantization of the bath of oscillators then yields the semiclassical master equation [7–10]

$$\frac{\partial W}{\partial t} + \widehat{M}_W W = \widehat{M}_D W, \tag{1}$$

where the operators $\widehat{M}_W$ and $\widehat{M}_D$ are defined as

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

$$\widehat{M}_D W = \frac{\partial}{\partial p}\left[D_p p W + D_{pp}\frac{\partial W}{\partial p} + D_{xp}\frac{\partial W}{\partial x}\right]. \tag{3}$$

Here D_p, D_{pp}, D_{xp} are coordinate, momentum and time-dependent parameters to be determined. The left-hand side of equation (1) is the quantum analogue of the Liouville equation, while $\widehat{M}_D W$ characterizes the interaction of the Brownian particle with the thermal bath at temperature T; the term $\widehat{M}_D W$ being the analogue of the collision kernel (*stosszahlansatz*) in the classical kinetic theory. Conditions for the validity of the master equation (1) are discussed elsewhere (e.g., [9] and [10]). We remark that in general the kernel $\widehat{M}_D W$ contains additional quantum correction terms [10]. Most of these terms can be incorporated in the present treatment, e.g. the term $\partial_p D_{xp}\partial_x$ in equation (3) absent in the original Caldeira–Leggett equation [7] is included in $\widehat{M}_D W$ explicitly as in [10] (this term describes quantum mechanical coupled p–x diffusion).

Being in possession of the functional form of the master equation (1) for the Brownian particle, the crucial step is to determine the coefficients D_p, D_{pp}, D_{xp}. In the classical limit, $\hbar \to 0$, equation (1) reduces [7, 11] to the Klein–Kramers (Fokker–Planck) equation and D_p, D_{pp}, D_{xp} become

$$D_p = \gamma, \qquad D_{pp} = \gamma m/\beta, \qquad D_{xp} = 0, \tag{4}$$

where $\beta = (kT)^{-1}$, k is the Boltzmann constant, $\gamma = \zeta/m$ is a dissipation parameter and ζ is the friction coefficient. The classical Klein–Kramers equation has been extensively applied to the Brownian motion in a potential [12, 13]. For example, as shown by Brinkman [14] on expansion of W in an orthonormal basis of Weber functions $\{D_n\}$, namely,

$$W(x, p, t) = \mathrm{e}^{-\beta p^2/4m} \sum_{n=0}^{\infty} D_n(p\sqrt{\beta/m})\varphi_n(x, t), \tag{5}$$

where $D_n(y) = 2^{-n/2}\,\mathrm{e}^{-y^2/4} H_n(y/\sqrt{2})$ and $H_n(z)$ is the Hermite polynomial of order n, equation (1) becomes a partial three-term differential recurrence relation in the distribution

functions $\varphi_n(x,t)$, $n \geqslant 0$. In particular, $\varphi_0(x,t)$ yields the configuration space distribution function $P(x,t) = \int W(x,p,t)\,\mathrm{d}p \equiv \varphi_0(x,t)$. The solution of the recurrence relations of the φ_n postulating an appropriate spatial basis may be further expressed as infinite matrix continued fractions which are easily computed as pioneered by Risken [12]. For a Maxwellian initial distribution of velocities, the solution for the configuration space distribution $P(x,t)$ is equivalent [12, 13] on expansion of the relevant continued fraction in series to the solution rendered in powers of current operators in configuration space originally given by Brinkman [14]. The Smoluchowski equation for $P(x,t)$, valid in the high friction or small mass limit of the dissipation dynamics, may be rigorously obtained from Brinkman's solution corroborating the earlier work of Kramers [15]. Kramers heuristically derived the Smoluchowski equation from the Klein–Kramers equation. He proceeded by splitting that equation into two parts, consisting of the Smoluchowski operator acting on the phase-space distribution and a remainder; assuming that the dissipation coefficient is very large he shows that the contribution of the remainder to the configuration space distribution is approximately zero while the first part reduces to the Smoluchowski equation. Recently, García–Palacios and Zueco [10] have shown how classical (Brinkman's and matrix continued fraction) methods of solution of the classical Klein–Kramers equation could be extended to analyse the master equation (1).

Hitherto calculations of D_p, D_{pp}, D_{xp} in the quantum case have usually been undertaken for a Brownian harmonic oscillator, see, e.g., [9, 16–19]. As far as semiclassical treatments of the Brownian motion in an anharmonic potential are concerned little in the way of solution of equation (1) apart from the pioneering work of Wigner (on quantum corrections to the classical distribution function in the closed system) 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 a Brownian particle moving in an *arbitrary* potential $V(x)$ and interacting with a reservoir at temperature T. For simplicity, we evaluate D_p, D_{pp}, D_{xp} in the approximation of frequency independent or Ohmic damping, where D_p, D_{pp}, D_{xp} in equation (1) are *independent* of the time [9, 17]. We have chosen the Ohmic damping since that is used most extensively indeed almost universally in the discussion of dissipative systems. Moreover, it is the damping underlying the classical Brownian motion and so is appropriate here since our objective is to understand how quantum effects treated in semiclassical fashion alter the classical Brownian motion in a potential. A detailed discussion of various damping mechanisms in the context of quantum effects is given in [17]. Continuing our analysis we show starting from Wigner's (semiclassical) method of perturbation in $\hbar$ and applying it to equation (1) in combination with the *ansatz* that the Wigner phase-space equilibrium distribution must satisfy that equation, how (a) the coefficients D_p, D_{pp}, D_{xp} can be evaluated, how (b) Brinkman's method may be transparently extended to the quantum case and how (c) a quantum Smoluchowski equation (having the Wigner configuration space distribution as equilibrium solution) follows directly from the quantum Brinkman recurrence relations.

In order to determine the explicit form of D_p, D_{pp}, D_{xp} in equation (1), we first recall Wigner's results [1] for the unnormalized equilibrium distribution $W_0(x,p)$. The equilibrium distribution $W_0(x,p)$ (being a stationary solution of the equation $\dot{W}_0 + \widehat{M}_W W_0 = 0$) can be developed in a power series in $\hbar^2$ as [1]

$$W_0(x,p) = \mathrm{e}^{-\beta\varepsilon(x,p)} + \hbar^2 w_2(x,p) + \hbar^4 w_4(x,p) + \cdots,$$

where $\varepsilon(x,p) = p^2/2m + V(x)$ is the energy. The term in w_2 yields the quantum correction to the classical distribution function [1] to first order in $\hbar^2$ and is (cf Wigner's equation (25))

$$W_0(x,p) = \mathrm{e}^{-\beta\varepsilon(x,p)}\{1 + \Lambda[\beta(V'(x))^2 - 3V''(x) + (\beta p^2/m)V''(x)] + \cdots\}, \tag{6}$$

where $\Lambda = \hbar^2\beta^2/(24m)$ is the characteristic quantum parameter (for simplicity we consider only the leading quantum correction terms). The corresponding equilibrium distribution function in configuration space $P_{st}(x) \sim \int W_0(x, p)\,\mathrm{d}p$ is [cf Wigner's equation (28) in [1]]

$$P_{st}(x) = \mathrm{e}^{-\beta V(x)}\{1 + \Lambda[\beta(V'(x))^2 - 2V''(x)] + \cdots\}. \tag{7}$$

Equation (7) demonstrates how the probability of a configuration given by the Boltzmann factor $\mathrm{e}^{-\beta V(x)}$ in classical theory (and holding in quantum theory for high temperatures) is modified for lower temperatures. Furthermore, the equilibrium Wigner distribution $W_0(x, p)$ must be the equilibrium solution of the generic master equation (1), i.e., it must satisfy $\partial_t W_0 + \widehat{M}_W W_0 = \widehat{M}_D W_0$. However, the function $W_0(x, p)$ satisfies the equation $\partial_t W_0 + \widehat{M}_W W_0 = 0$ [1]. Thus $W_0(x, p)$ must satisfy $\widehat{M}_D W_0 = 0$. Seeking D_p, D_{xp}, D_{pp} as

$$D_p = \gamma + \hbar^2 d_2^p(x, p) + \cdots, \qquad D_{pp} = \frac{\gamma m}{\beta} + \hbar^2 d_2^{pp}(x, p) + \cdots,$$

$$D_{xp} = \hbar^2 d_2^{xp}(x, p) + \cdots$$

and substituting equation (6) into equation (1), one then finds if $W_0(x, p)$ is a solution of $\widehat{M}_D W_0 = 0$ that D_p and D_{xp} remain as in equation (4) and only D_{pp} must be altered to read

$$D_{pp} = (\gamma m/\beta)[1 + 2\Lambda V''(x) + \cdots].$$

Thus the explicit form of $\widehat{M}_D W$ to $o(\hbar^2)$ is from equation (3)

$$\widehat{M}_D W = \gamma \frac{\partial}{\partial p}\left[pW + \frac{m}{\beta}\left(1 + 2\Lambda\frac{\partial^2 V}{\partial x^2}\right)\frac{\partial W}{\partial p}\right] + \cdots. \tag{8}$$

The imposition of the Wigner phase-space distribution $W_0(x, p)$ as the equilibrium solution of equation (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 and Kramers [12, 13] to calculate diffusion coefficients in the classical theory of the Brownian motion. Furthermore, the condition $\widehat{M}_D W_0 = 0$ is completely 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 $St(f_0) = 0$ ($f(x, p, t)$ is the phase-space distribution function obeying the kinetic equation $\mathrm{d}f/\mathrm{d}t = St(f)$). In particular, this is so for the classical Klein–Kramers equation.

Equation (8) is obtained for arbitrary $V(x)$. For illustration, we consider a harmonic potential $V(x) = m\omega_0^2 x^2/2$, which is of the utmost importance as the quantum Brownian oscillator model is ubiquitous in physics [2]. Here the calculation is simplified because the normalized equilibrium Wigner function can be presented in the simple exact form [18, 19]

$$W_0(x, p) = \frac{\tanh(\beta\hbar\omega_0/2)}{\pi\hbar}\exp\left(-\frac{x^2}{2\langle x^2\rangle} - \frac{p^2}{2\langle p^2\rangle}\right), \tag{9}$$

where $\langle x^2\rangle = \frac{\hbar}{2m\omega_0}\coth\frac{\beta\hbar\omega_0}{2}$ and $\langle p^2\rangle = \frac{m\hbar\omega_0}{2}\coth\frac{\beta\hbar\omega_0}{2}$. Noting equation (9), we may evaluate $\widehat{M}_D W$ for a quantum oscillator in closed form. Our heuristic procedure yields

$$\widehat{M}_D W = \gamma \frac{\partial}{\partial p}\left[pW + \langle p^2\rangle\frac{\partial W}{\partial p}\right]. \tag{10}$$

The master equation (1) with the collision kernel as in equation (10) coincides in all respects with that of Agarwal [18], who first developed a detailed theory of Brownian motion of a quantum oscillator (see his equation (2.11) with $\lambda = 0$). It is known, however, for a quantum Brownian oscillator, that the equilibrium distribution as well as the equilibrium averages $\langle x^2\rangle$ and $\langle p^2\rangle$ *depend on the damping* (appropriate equations are given in chapter 6 of [2]). However, according to [2], these equations reduce to equation (9) 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 $\gamma/\omega_0 < 0.1$ for all $\beta\hbar\omega_0$ [2] (see also figure 3 of [19]). Hence for $\beta\hbar\gamma \leqslant 1$, the Agarwal model may be used as a good approximation describing the kinetics of a quantum oscillator.

Equation (8) constitutes the first novel result of our communication. One may regard equation (8) as a generalization of the Agarwal quantum kinetic model for an oscillator [18] to the Brownian motion of a particle in a potential $V(x)$. Our second task is to show how the master equation (1) with $\widehat{M}_D W$ given by equation (8) may be written in general as a set of differential recurrence relations for the functions φ_n and how the quantum Smoluchowski equation for the configuration space distribution function φ_0 can be obtained from these by using Brinkman's method [14]. Thus one assumes [10] (just as the classical case) that the Wigner function W may be expanded in the Weber functions D_n as equation (5). By substituting equation (5) into equation (1), we have via the orthogonality and recurrence properties of D_n the quantum Brinkman equations for $\varphi_n(x,t)$

$$\frac{\partial\varphi_n}{\partial t} + n\gamma\varphi_n + \frac{1}{\sqrt{\beta m}}\left[\frac{\partial\varphi_{n-1}}{\partial x} + (n+1)\frac{\partial\varphi_{n+1}}{\partial x}\right] + \sqrt{\frac{\beta}{m}}\frac{\partial V}{\partial x}\varphi_{n-1} = \Lambda\left(2\gamma\frac{\partial^2 V}{\partial x^2}\varphi_{n-2} + \frac{1}{\sqrt{\beta m}}\frac{\partial^3 V}{\partial x^3}\varphi_{n-3}\right). \tag{11}$$

In the classical limit ($\Lambda = 0$), Brinkman's recurrence equation (11) has been solved for many potentials using matrix continued fraction methods as described in [12, 13]. As the semiclassical equation (11) constitutes a partial differential recurrence relation essentially similar to the classical one, Brinkman's solution may also be applied here. Equation (11) then yields to first order in $\hbar^2$, quantum corrections to the non-equilibrium configuration space functions $\varphi_n(x,t)$.

Now one of our objectives is simply to show (guided everywhere by Brinkman's classical calculation [14]) how equation (11) yields a quantum Smoluchowski equation. In order to accomplish this we note that in the non-inertial or high damping limit ($m \to 0$ or $\gamma = \zeta/m \gg 1$), the ratio $\dot{\varphi}_n/\gamma \approx 0, \quad n \geqslant 1$, thus we have from equation (11) the following hierarchy:

$$\frac{\partial\varphi_0}{\partial t} = -\frac{1}{\sqrt{\beta m}}\frac{\partial\varphi_1}{\partial x}, \tag{12}$$

$$\varphi_1 = -\frac{1}{\gamma\sqrt{\beta m}}\left(\frac{\partial\varphi_0}{\partial x} + 2\frac{\partial\varphi_2}{\partial x} + \beta V'\varphi_0\right), \tag{13}$$

$$\varphi_2 = -\frac{1}{2\gamma\sqrt{\beta m}}\left(\frac{\partial\varphi_1}{\partial x} + 3\frac{\partial\varphi_3}{\partial x} + \beta V'\varphi_1\right) + \Lambda V''\varphi_0, \tag{14}$$

etc. If we now close the set by supposing $\varphi_3 = 0$ then the first two terms on the right-hand side of equation (14) vanish when $m \to 0$ so that $\varphi_2 = \varphi_0\Lambda V''(x)$. The system of equations (12)–(14) is now closed and can be rearranged as an equation for the configuration space distribution function $P(x,t) = \varphi_0(x,t)$, namely,

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left\{\frac{P}{\zeta}\frac{\partial V}{\partial x} + \frac{\partial}{\partial x}(DP)\right\}, \tag{15}$$

where $\zeta = \gamma m$ and $D = [1 + 2\Lambda V''(x)]/(\zeta\beta) + O(\hbar^4)$ have the meaning of friction and diffusion coefficients, respectively. For a quantum oscillator, the diffusion coefficient D is independent of x and is given by $D = \frac{\hbar\omega_0}{2\zeta}\coth\frac{\beta\hbar\omega_0}{2}$. Furthermore equation (15) reduces to the classical Smoluchowski equation if $\Lambda = 0$. The semiclassical Smoluchowski equation (15)

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 [12, 13] reads

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

Here the dot denotes the time derivative and $\lambda(t)$ is a random force with Gaussian white noise properties, namely, $\overline{\lambda(t)} = 0$, $\overline{\lambda(t)\lambda(t')} = (2\zeta/\beta)\delta(t-t')$ (the overbar means statistical averaging). Just as in the classical case, the semiclassical Smoluchowski equation (15) may be applied to the study of the long time (or low frequency) relaxational behaviour of a system [13].

We emphasize that it is often preferable to write D in the equivalent form

$$D = \{\zeta\beta[1 - 2\Lambda V''(x)]\}^{-1} + o(\hbar^2) \tag{16}$$

so ensuring that equation (15) does not violate the second law of thermodynamics irrespective of the form of the potential [20]. 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 just $o(\hbar^2)$) as evidenced by Machura *et al* [20] in their discussion of a quantum Smoluchowski equation deduced by Ankerhold *et al* [21] (via the path integral formulation of quantum dissipative systems). That equation is *very similar* but not *identical* to equation (15) and reads in our notation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left\{ \frac{P}{\zeta}\frac{\partial}{\partial x} V_{ef} + \frac{\partial}{\partial x}\,[D_A P] \right\}, \tag{17}$$

where

$$V_{ef} = V(x) + \lambda V''(x)/2, \qquad D_A = \{\zeta\beta[1 - \beta\lambda V''(x)]\}^{-1},$$

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 a quantum parameter [21] (in our notation). 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 ($\hbar\gamma\beta \ll 2\pi$); we see that equation (17) differs from equation (15) only via $(\lambda/2)V''$ in V_{ef}. Nevertheless, this difference is important, because the stationary solution of equation (17) is $P_A(x) \sim \mathrm{e}^{-\beta V}[1 + \Lambda(\beta V'^2 - 3V'') + \cdots]$ [21], which is similar to the coordinate-dependent part of the Wigner phase-space distribution $W_0(x, p)$ (resulting from the omission of the p^2 term in equation (6)). Thus, $P_A(x)$ does not coincide with the true Wigner equilibrium distribution in configuration space $P_{st}(x)$ from equation (7) [1] (which includes by integration with respect to p the contribution of the p^2 term). Obviously, $P_{st}(x)$ *does not satisfy* equation (17) in the high temperature limit as one would expect.

The explicit form of the semiclassical kernel $\widehat{M}_D W$, equation (8), and the time evolution equation (15) in the non-inertial (overdamped) limit for the Brownian motion of a particle in a potential $V(x)$ are our main results. They contain the leading order quantum correction to the collision kernel of the classical Klein–Kramers and Smoluchowski equations. These equations are written explicitly to $o(\hbar^2)$. In like manner higher order quantum correction terms to the master equation (1) may be calculated. Thus that equation can be given, in principle to any desired degree r of $\hbar^{2r}$. However, the correction terms become more complicated with increasing r; see, e.g., [1], where the explicit equation for the equilibrium Wigner distribution

$W_0(x, p)$ is presented to $o(\hbar^4)$. By using the explicit form for $W_0(x, p)$ from [1], we have the next term in the perturbation expansion of D_{pp} and D in equations (1) and (15), namely,

$$D_{pp} = \frac{m\gamma}{\beta}\left\{1 + 2\Lambda V'' - \frac{2\Lambda^2}{5}\left[6V'''V' + 2V''^2 + 3V^{(4)}\left(\frac{p^2}{m} - \frac{5}{\beta}\right)\right]\right\} + \cdots,$$

$$D = \frac{1}{\zeta\beta}\left[1 - 2\Lambda V'' + \frac{12\Lambda^2}{5}(V'''V' + 2V''^2 - \beta^{-1}V^{(4)})\right]^{-1} + \cdots.$$

(the coefficients D_p and D_{xp} remain as in equation (4)). We emphasize that in our heuristic method of calculation of D_{pp}, D, etc, the equilibrium Wigner function $W_0(x, p)$ for vanishing damping ($\gamma \to 0$) was used. In quantum dissipative systems, however, the equilibrium distribution $W_\gamma(x, p)$ in general depends on the damping [2]. For an arbitrary potential $V(x)$, the damping dependence of $W_\gamma(x, p)$ is unknown. Nevertheless, the conditions already mentioned, under which $W_\gamma(x, p)$ for the harmonic oscillator may be approximated by the Wigner distribution $W_0(x, p)$, may be useful in establishing a possible range of validity for our *ansatz*. In particular, $W_\gamma(x, p)$ always reduces to $W_0(x, p)$ in the high temperature limit. Moreover, the difference between $W_\gamma(x, p)$ and $W_0(x, p)$ may be negligible for a large range of variation of the model parameters (ζ, β, m) as we have indicated for a quantum oscillator. For example, analysis of figure 3 of [19] (reproduced in figure 6.2 of [2]) shows that even if $\beta\hbar\omega_0 \sim 1$ (i.e., the limiting value below which one would expect slow convergence of the Taylor series) although $\gamma/\omega_0 < 0.1$, the difference between the damping-dependent stationary distribution $W_\gamma(x, p)$ and the Wigner distribution $W_0(x, p)$ is negligible. Thus one would expect that the kernel $\widehat{M}_D W$ from equation (8) is a reasonable approximation for the kinetics of a quantum Brownian particle in a potential $V(x)$ when $\beta\hbar\zeta/m \ll 1$. In this context, we remark that proceeding (in the manner of the Kramers intermediate-to-high damping calculation [15] of the escape rate from a potential well) from equation (1) with $\widehat{M}_D W$ from equation (10), and assuming that the equilibrium solution is the Wigner function $W_0(x, p)$ yields the escape rate Γ_{IHD} as [22]

$$\Gamma_{IHD} = \Xi\frac{\omega_a}{2\pi\omega_c}\left(\sqrt{\gamma^2/4 + \omega_c^2} - \gamma/2\right)\mathrm{e}^{-\beta\Delta V}.$$

Here $\Xi = (\omega_c/\omega_a)\sinh(\hbar\beta\omega_a/2)/\sin(\hbar\beta\omega_c/2)$ is the quantum correction factor as yielded by equation (10) (in full agreement with quantum transition state theory [2, 23, 24]), ω_a and ω_c denote the well and barrier (saddle) angular frequencies, and ΔV is the barrier height. On the other hand, the corresponding correction factor incorporating the damping dependence of the equilibrium distribution is [2]

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

Now Ξ_W reduces to Ξ when $\hbar\gamma\beta \ll 2\pi$ [2]. Here the damping independent Ξ is a fair approximation to Ξ_W, lending support to our argument that the approximation of the equilibrium distribution $W_\gamma(x, p)$ by the Wigner distribution $W_0(x, p)$ may ultimately yield a reasonable description of the dynamics of quantum dissipative systems.

In conclusion, we have suggested a heuristic procedure for obtaining the diffusion coefficients in semiclassical evolution equations for arbitrary potentials by demonstrating how classical tools can be transferred to the quantum domain via the phase-space formalism. The explicit form of our evolution equations (kinetic models) we have given implies how existing powerful methods of solution of the classical Klein–Kramers equation for Brownian motion in a potential may be generalized to quantum systems (see [10] for details). Thus

quantum effects on diffusive transport properties and parameters characterizing the quantum Brownian motion (such as correlation functions, dynamic susceptibilities, etc) can be estimated for arbitrary potentials hence allowing one some insight into the very complicated dynamics of quantum dissipative systems.

Acknowledgment

This publication has emanated from research conducted with the financial support of Science Foundation Ireland (Project 05/RFP/PHY/0070).

References

[1] Wigner E P 1932 *Phys. Rev.* **40** 749
[2] Weiss U 1999 *Quantum Dissipative Systems* 2nd edn (Singapore: World Scientific)
[3] Gardiner C W and Zoller P 2000 *Quantum Noise* 2nd edn (Berlin: Springer)
[4] Ploszajczak M and Rhoades-Brown M J 1985 *Phys. Rev. Lett.* **55** 147
[5] Cohen D 1997 *Phys. Rev. Lett.* **78** 2878
[6] Johansen L M 1998 *Phys. Rev. Lett.* **80** 5461
[7] Caldeira A O and Leggett A J 1983 *Physica* A **121** 587
[8] Tanimura Y and Wolynes P G 1991 *Phys. Rev.* A **43** 4131
[9] Halliwell J J and Yu T 1996 *Phys. Rev.* D **53** 2012
[10] García-Palacios J L and Zueco D 2004 *J. Phys. A: Math. Gen.* **37** 10735
García-Palacios J L 2004 *Europhys. Lett.* **65** 735
[11] Dekker H 1977 *Phys. Rev.* A **16** 2116
[12] Risken H 1989 *The Fokker–Planck Equation* 2nd edn (Berlin: Springer)
[13] Coffey W T, Kalmykov Yu P and Waldron J T 2004 *The Langevin Equation* 2nd edn (Singapore: World Scientific)
[14] Brinkman H C 1956 *Physica* **22** 29
[15] Kramers H A 1940 *Physica (Amsterdam)* **7** 284
[16] Karrlein R and Grabert H 1997 *Phys. Rev.* E **55** 153
[17] Ford G W and O'Connell R F 2001 *Phys. Rev.* D **64** 105020
[18] Agarwal G S 1971 *Phys. Rev.* A **4** 739
[19] Grabert H, Schramm P and Ingold G L 1988 *Phys. Rep.* **168** 115
[20] Machura L, Kostur M, Hänggi P, Talkner P and Luczka J 2004 *Phys. Rev.* E **70** 031107
[21] Ankerhold J, Pechukas P and Grabert H 2001 *Phys. Rev. Lett.* **87** 086802
Ankerhold J, Pechukas P and Grabert H 2005 *Chaos* **15** 026106
[22] Coffey W T, Kalmykov Yu P, Titov S V and Mulligan B P *Phys. Chem. Chen. Phys.* at press
[23] Wigner E P 1932 *Z. Phys. Chem.* B **19** 203
[24] Hänggi P, Grabert H, Ingold G L and Weiss U 1985 *Phys. Rev. Lett.* **55** 761