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Phase space master equations for quantum Brownian motion in a periodic potential: comparison of various kinetic models

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Abstract

The dynamics of quantum Brownian particles in a cosine periodic potential are studied using the phase space formalism associated with the Wigner representation of quantum mechanics. Various kinetic phase space master equation models describing quantum Brownian motion in a potential are compared by evaluating the dynamic structure factor and escape rate from the differential recurrence relations generated by the models. The numerical solution is accomplished via matrix continued fractions in the manner customarily used for the classical Fokker–Planck equation. The results of numerical calculations of the escape rate from a well of the cosine potential are compared with those given analytically by the quantum-mechanical reaction rate theory solution of the Kramers turnover problem for a periodic potential, given by Georgievskii and Pollak (1994 *Phys. Rev. E* **49** 5098), enabling one to appraise each model.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Quantum dissipation, in particular quantum Brownian motion, poses one of the most interesting and topical problems in the quantum mechanics of open systems, especially in the study of the passage to the classical limit, prompting *inter alia* the development of diverse methods for the theoretical treatment of the dynamics of quantum dissipative processes. These

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include representations in terms of the reduced density matrix [1–5], path integrals [2] and master equations in phase space [6, 7]. Now, in the phase space or Wigner representation (also known as the Moyal quantization [8]), the translational quantum Brownian motion can be formulated in terms of a *quasi-probability* density $W(x, p, t)$ in the phase space of the positions and momenta (x, p). This representation, originally devised by Wigner [9] for closed systems in order to obtain quantum corrections to the Maxwell–Boltzmann distribution, contains only such features that are common to both quantum and classical statistical mechanics and formally represents (as emphasized by Moyal) quantum mechanics as a statistical theory on the classical phase space [8]. Therefore, it is especially suited to semiclassical methods of solution, providing a natural quantum–classical correspondence, since in the classical limit $\hbar \to 0$ ($\hbar$ is Planck's reduced constant), the Wigner function becomes the classical phase space distribution function.

As far as the description of the *closed* system is concerned, the quantum master equation for the distribution function $W(x, p, t)$ has the form

$$\frac{\partial}{\partial t}W + \hat{M}_W W = 0. \tag{1}$$

Here, the operator $\hat{M}_W$ is the evolution operator for the closed system (which is the quantum analog of the classical Liouville operator) defined by

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

Equation (1) is known as the Wigner–Moyal equation and applies to the non-dissipative closed system dynamics of both pure and mixed states. Clearly, quantum effects arise from the terms containing $\hbar$. The stationary solution of equation (1) is the equilibrium Wigner distribution $W_0(x, p)$, which satisfies $\hat{M}_W W_0 = 0$.

Now, in order to treat the dynamics of quantum dissipative processes, i.e. open systems, in particular quantum effects in the Brownian motion, Caldeira and Leggett [2] used the influence functional (or real-time path integral) method of Feynman and Vernon [10] to obtain an evolution equation for the relevant reduced density matrix ρ. The model for the dissipative interaction of a particle with its surroundings consists of a continuum of harmonic oscillators, comprising a boson bath, where a specific form (namely one ensuring Markov behavior so that a master equation description is possible) for the product of the density of bath modes and the square of the coupling coefficient is assumed. The resulting evolution equation for ρ is valid in the weak-coupling and high-temperature limit and is obtained by tracing over the bath variables. Furthermore, it may be transformed to the phase space representation via the overlap integral definition of the Wigner function $W(x, p, t)$, resulting in the phase space evolution equation

$$\frac{\partial W}{\partial t} + \hat{M}_W W = \gamma \frac{\partial}{\partial p}\left[pW + \frac{m}{\beta}\frac{\partial W}{\partial p}\right]. \tag{3}$$

Here $\beta = 1/(k_B T)$, where $k_B T$ is the thermal energy and γ is a damping parameter (measure of the strength of the coupling to the bath). Equation (3) is simply the master equation for the closed system augmented by the classical collision kernel of Brownian motion. We remark that if only the lowest order quantum term in $\hat{M}_W$ is considered, equation (3) is often referred to as the semiclassical version of the Klein–Kramers equation. The Wigner function approach has resulted in a large body of work [11–20], where the main objective has been to study semiclassical corrections to the theory of the Brownian motion by forming the master equation

$$\frac{\partial}{\partial t}W + \hat{M}_W W = \hat{M}_D W. \tag{4}$$

Here, the operator $\hat{M}_D$ accounts for effects due to the coupling to the environment (dissipation and fluctuations) and, as one would expect for an almost classical system [21, 22], has the form of a Kramers–Moyal expansion truncated at the second term:

$$\hat{M}_D W = \frac{\partial}{\partial p}\left[D_p pW + D_{pp}\frac{\partial W}{\partial p} + D_{px}\frac{\partial W}{\partial x}\right] + \frac{\partial}{\partial x}\left[D_{xx}\frac{\partial W}{\partial x}\right]. \tag{5}$$

The coefficients D_p, D_{pp}, D_{px} and D_{xx} are coordinate, momentum and time-dependent parameters which are to be determined. In the classical limit $\hbar \to 0$, equation (4) reduces to the Klein–Kramers (Fokker–Planck) equation [23, 24] for the joint distribution function, which now becomes a *true* probability distribution of positions and momenta of point particles with separable and additive Hamiltonians, so that the Kramers–Moyal coefficients are

$$D_p = \gamma, \qquad D_{pp} = \gamma m/\beta, \qquad D_{px} = 0, \qquad D_{xx} = 0.$$

The main advantage of the phase space approach now becomes apparent, namely it provides a master equation that may be solved using the methods [18, 23, 24] associated with the classical theory of the Brownian motion in a potential, allowing one [14, 16] to study the quantum–classical correspondence for dissipative systems.

Now, an essential requirement for a density matrix ρ is that it must be *positive definitive*. Thus, when the density operator is represented in a Hilbert space basis set and brought into diagonal form, its eigenvalues must be positive [11]. In other words, when the operator is transformed to the position representation, it must represent the correct quantum-mechanical probability for the displacements. However, as is well known [6], solutions of the reduced density operator version of the Caldeira–Leggett equation (3) are not guaranteed to preserve this property during time evolution, even if they commence in this way. Such behavior is in contrast to that of quantum master equations for the density matrix evolution, which can be expressed in the so-called Lindblad form [25]. These have time-dependent solutions which always remain positive. Thus, in order to ensure positivity of the solutions of the reduced density operator evolution equation at all times, Diósi [3, 4] included two additional smoothing terms in the Caldeira–Leggett equation (see equation (9) below). A particular simplification of Diósi's equation leads to the density matrix evolution equation of Vacchini [5], and Vacchini and Hornberger [26]. In particular, in [26] it has been shown how Vacchini's equation may be obtained as the diffusion limit of a quantum linear Boltzmann equation, while other questions concerning the derivation of the various master equations and their complete positivity have been discussed in detail in [26].

Yet another form of the master equation for the quantum Brownian motion of a particle in a potential $V(x)$ has been proposed by Coffey *et al* [14–16]. In order to determine the explicit form of the coefficients $D_p, D_{pp}, D_{px}, D_{xx}$ in equation (5), they used Wigner's equilibrium distribution $W_0(x, p)$. The distribution $W_0(x, p)$ satisfies Wigner's equation (1). On the other hand, $W_0(x, p)$ must also be the equilibrium solution of the generic master equation (5), i.e. it must also satisfy $\hat{M}_D W_0 = 0$. The imposition of the (canonical) Wigner phase space distribution $W_0(x, p)$ as the equilibrium solution of the master equation (5) by them appears to be the exact analog of the *ansatz* of a Maxwell–Boltzmann stationary distribution in order to calculate diffusion coefficients in the Fokker–Planck equation of the classical theory of the Brownian motion [24]. In other words, the condition $\hat{M}_D W_0 = 0$ is entirely equivalent to the condition $St(W_0) = 0$ of classical kinetic theory, where $St(W)$ is the collision kernel and $W_0(x, p) \sim \exp[-\beta(p^2/2m + V(x))]$ is the equilibrium distribution function. Here, $W(x, p, t)$ is the phase space distribution obeying the kinetic equation

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial W}{\partial p} = St(W).$$

In particular, this condition is satisfied for the Klein–Kramers equation, where $St(W) = \gamma\partial_p\left[pW + (m/\beta)\partial_p W\right]$. In the quantum case, this idea has been used before, e.g. by Gross and Lebowitz [27] in their formulation of quantum kinetic models of impulsive collisions. According to [27], for a system with a time-dependent Hamiltonian H, the equation governing the time behavior of the density matrix ρ is

$$\frac{\partial\rho}{\partial t} + \frac{i}{\hbar}[H, \rho] = St(\rho), \tag{6}$$

where $St(\rho)$ is the collision kernel operator satisfying the condition $St(\rho_0) = 0$, $\rho_0 = \mathrm{e}^{-\beta H_0}/\mathrm{Tr}(\mathrm{e}^{-\beta H_0})$ is the equilibrium density matrix and H_0 is the time-independent Hamiltonian. The distribution $W_0(x, p)$ corresponds to the canonical density matrix ρ_0.

Recalling that the phase space evolution equation is simply the Fourier transform of the density matrix evolution equation written in overlap form as given by Wigner [9], it is then possible to compare the predictions of each particular evolution equation. As far as such a comparison is concerned, one should also refer to another class of kinetic models, namely *extended diffusion models,* long familiar in the kinetic theory of gases and fluids [27–29]. In contrast to models based on a Brownian motion *Stosszahlansatz,* it is assumed in extended diffusion that a particle moves freely in space until interrupted by *instantaneous* collisions. In other words, the duration of a collision is assumed to be much smaller than the average time between collisions. The impact approximation (i.e. the infinitesimal duration of collisions) and free motion of particles between collisions are features common to all extended diffusion models. The collisions take place at random times governed by a Poisson distribution and they randomize both the position and momentum of a particle. Extended diffusion models have been successfully used to interpret experimental spectra of both classical and quantum systems [30]. However, a drawback associated with them is the *ad hoc* introduction of a phenomenological parameter, namely the time between collisions. Nevertheless, if this parameter is known or can be calculated from an independent approach, such simple kinetic models may yield a reasonable description of the quantum dissipative process in the semiclassical limit.

Here, in order to appraise the various models, we compare the dynamical structure factor and escape rate evaluated from the modified Caldeira–Leggett equations proposed by Diósi [3, 4], Vacchini [5], Coffey *et al* [14–17] and the Lorentz model (a particular case of the extended diffusion models) [27–30]. The comparisons will be made in the Wigner–Moyal phase space representation by considering a particle moving in the periodic potential [15, 16]

$$V(x) = -V_0\cos(x/x_0), \tag{7}$$

where x is the position of the particle and x_0 is a characteristic length. Both the classical and the quantum Brownian motion in this potential have been used, for example, to model the diffusion in solids, pre-melting materials, films and surfaces [31–33]. Here, we shall compare the results for the escape rate for the various models (as adapted to periodic potentials) with those yielded by generalizing the classical solution of the Kramers turnover problem, i.e. the calculation of the escape rate for all values of the dissipation to include quantum effects as accomplished by Mel'nikov [34, 35], Pollak *et al* [36] and Rips and Pollak [37]. Regarding escape from a cosine periodic potential, Georgievskii and Pollak [38] have obtained the quantum escape rate above the crossover temperature between tunneling and thermal activation. The escape rate from a single well of a periodic potential like equation (7), where the period of the potential coincides with the domain of a well, is qualitatively different from the escape rate from a metastable well because the periodic potential is *multistable*. Thus a particle, once it has escaped a particular well, may again be trapped due to thermal fluctuations in another well. Moreover, jumps of either a single lattice spacing or of *many* lattice spacings are possible. Thus from a mathematical point of view one has to take into account the *nonperiodic* solution of the various master equations.

2. Quantum master equation in phase space

Wigner's representation of quantum mechanics can be formally defined [8, 39] as a means of associating a c-number (or classically meaningful) function in the classical phase space of positions x and momenta p with every operator that is a function of position and momentum operators $(\hat{x}, \hat{p})$ in a Hilbert space. It is in effect the inverse of Weyl's rule [8, 39], which is used to interpret quantum-mechanical operators in terms of their classical equivalents. The Wigner phase space distribution $W(x, p, t)$, which is real but not everywhere positive (i.e. it may exhibit [11] negative basins) so that it must be regarded as a joint quasi-probability distribution, allows one to calculate quantum-mechanical expectation values using the concepts of classical statistical mechanics. Moreover, notwithstanding that it is a quasi-probability distribution, it yields the correct marginal distributions for position and momentum. Wigner [9, 11, 39–41], by first introducing a density matrix for a pure state $\rho(x_2, x_1) = \psi^*(x_1)\psi(x_2)$ and the overlap coordinates $x = (x_1 + x_2)/2$ and $y = x_2 - x_1$, inferred that the Wigner function can be written as

$$W(x, p, t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \rho\left(x + \frac{1}{2}y, x - \frac{1}{2}y\right) \mathrm{e}^{-\mathrm{i}py/\hbar}\,\mathrm{d}y. \tag{8}$$

Equation (8) is simply the Fourier transform or overlap integral (we note that at $y = 0$, the overlap is just the familiar quantum-mechanical probability density function) of the spatial correlation function $\psi^*(x - y/2)\psi(x + y/2)$. It is also valid for a mixed state where the density operator can be written in terms of a linear combination of density operators. Thus, if either the density operator evolution equation (independent of representation) or that equation in the coordinate representation is known, the Wigner distribution can be found by Fourier transformation and vice versa, as illustrated by equations (5.10)–(5.14) of Caldeira and Leggett [2].

As far as the Caldeira–Leggett model is concerned, the Wigner phase space representation of their density operator evolution equation, namely equation (3), is simply the master equation for the closed system equation (1), augmented by the classical collision kernel of Brownian motion. Now, according to Caldeira and Leggett, equation (3) is valid at relatively high temperatures and for Markovian coupling to the heat bath. However, the corresponding density operator evolution equation is not of the Lindblad form so that positivity of the density operator is not preserved. One should remark that positivity of the density operator does not in itself imply that the underlying physics is realistic. Moreover, a positive density operator does not necessarily lead to phase space quasi-distributions that lack negative basins, as demonstrated by Wyatt [11]. Prompted by these considerations, Diósi [3, 4] in a more refined derivation (cf equation (29) of [3]) of the density operator form of the Caldeira–Leggett equation found two additional smoothing terms, rendering the time-dependent solution of the evolution equation for the density operator $\rho(t)$, namely

$$\dot{\rho} = -\frac{\mathrm{i}}{\hbar}[H, \rho] - \frac{\mathrm{i}}{\hbar}\gamma[x, \{p, \rho\}] - \gamma\frac{2m}{\hbar^2\beta}[x, [x, \rho]] - \gamma\frac{\beta}{6m}[p, [p, \rho]] - \gamma\frac{\Omega\beta}{3\pi}[x, [p, \rho]]$$

completely positive [6, 7], where Ω is regarded as a cutoff frequency for the harmonic bath. Later, Vacchini [5] derived yet another equation which reads as

$$\dot{\rho} = -\frac{\mathrm{i}}{\hbar}[H, \rho] - \frac{\mathrm{i}}{\hbar}\gamma[x, \{p, \rho\}] - \gamma\frac{2m}{\hbar^2\beta}[x, [x, \rho]] - \gamma\frac{\beta}{8m}[p, [p, \rho]].$$

The corresponding phase space forms [6, 11] of these modified Caldeira–Leggett equations are

$$\frac{\partial}{\partial t}W + \hat{M}_W W = \gamma\frac{\partial}{\partial p}\left[pW + \frac{m}{\beta}\frac{\partial W}{\partial p}\right] + \frac{\gamma\hbar^2\beta}{12m}\frac{\partial^2 W}{\partial x^2} + \frac{\gamma\Omega\hbar^2\beta}{6\pi}\frac{\partial^2 W}{\partial p\partial x}, \tag{9}$$

(for the Diósi model) and

$$\frac{\partial}{\partial t}W + \hat{M}_W W = \gamma \frac{\partial}{\partial p}\left[pW + \frac{m}{\beta}\frac{\partial W}{\partial p}\right] + \frac{\gamma\hbar^2\beta}{16m}\frac{\partial^2 W}{\partial x^2} \tag{10}$$

(for the Vacchini model). As briefly mentioned above, by postulating the Wigner equilibrium distribution $W_0(x, p)$ as the stationary solution, Coffey *et al* [14–16] obtained the phase space master equation

$$\frac{\partial W}{\partial t} + \hat{M}_W W = \gamma \frac{\partial}{\partial p}\left[pW + \frac{m}{\beta}\frac{\partial W}{\partial p}\right] + \frac{\gamma\beta\hbar^2}{12}V''(x)\frac{\partial^2 W}{\partial p^2}. \tag{11}$$

Here, only terms of order $\hbar^2$ are included, although the method may be carried on to any order in $\hbar^2$ [14–16]. A systematic method for calculating higher order corrections to equation (11) has been given in [14]. Such corrections may be calculated, in principle, to any desired order in $\hbar^2$. This perturbation procedure is directly analogous to that used by Wigner [47] to calculate quantum corrections to the distribution function of the closed system. Here, the distribution function is expanded in Hermite polynomials in the momentum where the coefficients involve the derivatives of the potential.

Equation (11) has been derived [14–16] in the high-temperature limit and in the approximation of Ohmic damping, where D_p, D_{pp}, D_{xp} in equation (5) are time independent. The evolution equation for the density matrix ρ corresponding to equation (11) is (again to order $\hbar^2$)

$$\dot{\rho} = -\frac{\mathrm{i}}{\hbar}[H, \rho] - \frac{\mathrm{i}}{\hbar}\gamma\left(\frac{1}{2}[x, \{p, \rho\}] - \frac{\mathrm{i}m}{\hbar\beta}[x, [x, \rho]] - \frac{\mathrm{i}\hbar\beta}{6}\left[x, \left[\frac{\mathrm{d}V}{\mathrm{d}x}, \rho\right]\right]\right).$$

Equation (11) and equations (9) and (10) obviously reduce to the Caldeira–Leggett equation in the high-temperature limit ($\beta \to 0$). However, for finite β, differences between the results predicted by the various models exist and it is the understanding of these deviations that is the subject of this paper.

For comparison, we shall also treat a particular extended diffusion model, namely the Lorentz or τ-approximation [27–30]. This model assumes that collisions change the state of a particle in such a way that the probability of finding the particle in a new state is proportional to the equilibrium density operator $\rho_0 = \mathrm{e}^{-\beta H_0}/\mathrm{Tr}\left(\mathrm{e}^{-\beta H_0}\right)$. Thus, a collision integral of the Lorentz model in the single relaxation time approximation can be written as

$$St(\rho) = -\frac{\rho - \rho_0}{\tau}, \tag{12}$$

where τ is the phenomenological parameter, characterizing relaxation processes. Consequently, the phase space evolution equation for the Lorentz model is

$$\frac{\partial}{\partial t}W + \hat{M}_W W = -\frac{W - W_0}{\tau}, \tag{13}$$

where W_0 is the corresponding Wigner stationary (i.e. the canonical) distribution function satisfying $\hat{M}_W W_0 = 0$. Equation (12) describes relaxation of the density operator ρ to ρ_0 with relaxation time τ, which is the mean time between collisions.

Now in each of the master equations, we make the following rescaling to the normalized variables [16]:

$$x/x_0 \to x, \qquad p\eta/mx_0 \to p, \qquad t/\eta \to t, \qquad \eta\gamma \to \gamma, \qquad \eta\Omega/\pi \to \Omega,$$
$$\beta V(x) \to V(x), \qquad \eta = \sqrt{\beta m x_0^2/2}, \qquad g = \beta V_0, \qquad \Lambda = \beta^2\hbar^2/(48\eta^2).$$

We then have from equations (9) to (11)

$$\frac{\partial W}{\partial t} = -p\frac{\partial W}{\partial x} + \frac{1}{2}\frac{\partial V}{\partial x}\frac{\partial W}{\partial p} + \frac{\gamma}{2}\frac{\partial}{\partial p}\left[2pW + \frac{\partial W}{\partial p}\right] + DW, \tag{14}$$

where the potential is now $V(x) = -g\cos x$. Equation (14) represents the classical Klein–Kramers equation written in terms of normalized variables plus a quantum correction term DW, which for the Diósi, Vacchini and Coffey *et al* kinetic models is, respectively,

$$DW = \Lambda\left(-\frac{1}{4}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3} + 2\gamma\frac{\partial^2 W}{\partial x^2} + 4\gamma\Omega\frac{\partial^2 W}{\partial p\partial x}\right), \tag{15}$$

$$DW = \Lambda\left(-\frac{1}{4}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3} + \frac{3\gamma}{2}\frac{\partial^2 W}{\partial x^2}\right), \tag{16}$$

$$DW = \Lambda\left(-\frac{1}{4}\frac{\partial^3 V}{\partial x^3}\frac{\partial^3 W}{\partial p^3} + \gamma\frac{\partial^2 V}{\partial x^2}\frac{\partial^2 W}{\partial p^2}\right). \tag{17}$$

First, we discuss the stationary solutions of the master equation (14).

3. Stationary distributions

The stationary solution of equation (14) with the correction given by equation (17) is the Wigner distribution function [14–17]

$$W_0(x, p) = Z^{-1}\,\mathrm{e}^{-p^2-V}\{1 + \Lambda[(V')^2 - 3V'' + 2p^2V'']\}, \tag{18}$$

where the partition function Z is

$$Z = \sqrt{\pi}\int_0^{2\pi}[1 + \Lambda(V'(x))^2 - 2\Lambda V''(x)]\,\mathrm{e}^{-V(x)}\,\mathrm{d}x = Z_{\mathrm{cl}}[1 - \Lambda g I_1(g)/I_0(g)], \tag{19}$$

where $Z_{\mathrm{cl}} = 2\pi^{3/2}I_0(g)$ is the classical partition function and $I_v(z)$ is the modified Bessel function of the first kind of integer order. This solution is of course *independent* of the dissipation. Clearly, the distribution W_0 is also a stationary solution of the Lorentz model equation (13).

In contrast, the stationary solution $W_D(x, p)$ of the Diósi model (equation (14) with the quantum correction term given by equation (15)) *depends* on the damping parameter γ and is given by

$$W_D(x, p) = Z_D^{-1}\,\mathrm{e}^{-p^2-V}\{1 + \Lambda[(V')^2 - 3V'' + 2p^2V'' + 4\gamma(\gamma + 2\Omega)V - 4p\gamma V']\}, \tag{20}$$

where

$$\begin{aligned} Z_D^{-1} &= \left(\sqrt{\pi}\int_0^{2\pi}\{1 + \Lambda[(V'(x))^2 - 2V''(x) + 4\gamma(\gamma + 2\Omega)V(x)]\}\,\mathrm{e}^{-V(x)}\,\mathrm{d}x\right)^{-1} \\ &= Z_{\mathrm{cl}}^{-1}\{1 + \Lambda[1 + 4\gamma(\gamma + 2\Omega)]gI_1(g)/I_0(g)\}. \end{aligned} \tag{21}$$

In the zero dissipation limit, $\gamma \to 0$, $W_D(x, p)$ becomes the Wigner distribution $W_0(x, p)$. Obviously, equation (21) holds only at relatively low damping

$$\Lambda\,[1 + 4\gamma(\gamma + 2\Omega)]\,gI_1(g)/I_0(g) \ll 1 \tag{22}$$

to ensure the validity of the perturbation expansion.

Now, the stationary solutions for the Caldeira–Leggett and Vacchini models cannot be presented in the analytic form of a series of powers of Λ. Nevertheless, they can be calculated numerically using matrix continued fractions [14, 15]. However, because for $\Omega = 0$ the only difference between the Diósi and Vacchini models lies in the coefficients 2 and 3/2, respectively (cf equations (15) and (16)), so that their solutions then have similar behavior, we may consider the Diósi model with $\Omega = 0$ as a simplified version of the Vacchini model.

4. Solution of the time-dependent master equation

The foregoing discussion refers purely to the time-independent solutions of the master equations. We now consider time-dependent solutions. To investigate the process whereby the particle traverses the periodic potential, we must obtain as explained above the nonperiodic solution [16, 23] of equation (14). Thus, we make the *ansatz*

$$W(x,p,t) = \int_{-1/2}^{1/2} w(k,x,p,t)\,\mathrm{e}^{-\mathrm{i}kx}\,\mathrm{d}k, \tag{23}$$

where w is periodic in x with period 2π and it is assumed [23] that the wave vector k is restricted to the first Brillouin zone, $-1/2 \leqslant k \leqslant 1/2$. The periodic function w can then be expanded in a Fourier series in the position x and in orthogonal Hermite functions $H_n(p)$ in the momentum p, viz, [16, 23, 32]

$$w(k,x,p,t) = \frac{\mathrm{e}^{-p^2+(g/2)\cos x}}{2\pi^{3/2}} \sum_{n=0}^{\infty}\sum_{q=-\infty}^{\infty} \frac{c_{n,q}(k,t)}{\sqrt{2^n n!}} H_n(p)\,\mathrm{e}^{-\mathrm{i}qx}. \tag{24}$$

By substituting equations (23) and (24) into equations (14)–(17), we find by orthogonality, after some algebra involving the recurrence relations of the Hermite polynomials, that the Fourier coefficients $c_{n,q}(k,t)$ for the various kinetic models satisfy the following differential recurrence relations: we have for the Diósi ($B = 2$) and Vacchini ($B = 3/2$ and $\Omega = 0$) master equations,

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}c_{n,q} + \gamma\left[n + B\left((q+k)^2 - \frac{g^2}{8}\right)\Lambda\right]c_{n,q} \\
&\quad = \mathrm{i}\sqrt{\frac{n}{2}}\left[(q+k)\,(1+8\Omega\gamma\Lambda)\,c_{n-1,q} + \frac{g}{4}\,(1-8\Omega\gamma\Lambda)\left(c_{n-1,q+1} - c_{n-1,q-1}\right)\right] \\
&\quad + \mathrm{i}\sqrt{\frac{n+1}{2}}\left[(q+k)c_{n+1,q} - \frac{g}{4}\left(c_{n+1,q+1} - c_{n+1,q-1}\right)\right] \\
&\quad + \mathrm{i}\Lambda g\sqrt{\frac{n(n-1)(n-2)}{8}}\left(c_{n-3,q+1} - c_{n-3,q-1}\right) \\
&\quad + \gamma\Lambda g\frac{B}{2}\left[\left(q+k+\frac{1}{2}\right)c_{n,q+1} - \left(q+k-\frac{1}{2}\right)c_{n,q-1} - \frac{g}{8}\left(c_{n,q+2} + c_{n,q-2}\right)\right],
\end{aligned} \tag{25}$$

while for the master equation (11) given by Coffey *et al*

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}c_{n,q} + \gamma[nc_{n,q} - \Lambda g\sqrt{n(n-1)}(c_{n-2,q+1} + c_{n-2,q-1})] \\
&\quad = \mathrm{i}\sqrt{n/2}[(q+k)c_{n-1,q} + g(c_{n-1,q+1} - c_{n-1,q-1})/4] \\
&\quad + \mathrm{i}\sqrt{(n+1)/2}[(q+k)c_{n+1,q} - g(c_{n+1,q+1} - c_{n+1,q-1})/4] \\
&\quad + \mathrm{i}\Lambda g\sqrt{n(n-1)(n-2)/8}(c_{n-3,q+1} - c_{n-3,q-1}).
\end{aligned} \tag{26}$$

Finally, for the Lorentz master equation (13), the Fourier coefficients $c_{n,q}(k,t)$ satisfy the differential recurrence relation

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}c_{n,q} &= -\tau^{-1}(c_{n,q} - c_{n,q}(0)) + \mathrm{i}\sqrt{n/2}[(q+k)c_{n-1,q} + g(c_{n-1,q+1} - c_{n-1,q-1})/4] \\
&\quad + \mathrm{i}\sqrt{(n+1)/2}[(q+k)c_{n+1,q} - g(c_{n+1,q+1} - c_{n+1,q-1})/4] \\
&\quad + \mathrm{i}\Lambda g\sqrt{n(n-1)(n-2)/8}(c_{n-3,q+1} - c_{n-3,q-1}).
\end{aligned} \tag{27}$$

All the foregoing differential recurrence relations, each involving two indices, may now be arranged (details are given in the appendix) as matrix three-term recurrence relations. These

recurrence relations can be solved in terms of matrix continued fractions [15–17, 32]. Thus, one may evaluate any desired observable such as the dynamic structure factor, etc.

5. Dynamic structure factor

We can evaluate the intermediate scattering function $S(k,t)$, i.e. the characteristic function of the displacement of the particle as it wanders through the wells, as a linear combination of the Fourier coefficients $c_{0,q}(k,t)$ [16]:

$$S(k,t) = \langle \mathrm{e}^{\mathrm{i}k[x(t)-x(0)]}\rangle_0 = \sum\nolimits_{q=0}^{\infty} a_q c_{0,q}(k,t) \tag{28}$$

The a_q are the Fourier coefficients of the expansion of $\mathrm{e}^{-V(x)/2}$ where for convenience we have written $\mathrm{e}^{\mathrm{i}kx(t)} = \mathrm{e}^{V(x(t))/2}\sum_{q=0}^{\infty} a_q\,\mathrm{e}^{\mathrm{i}(q+k)x(t)}$ and the angular brackets denote equilibrium ensemble averages. By using the orthogonality properties of the circular functions $\left\{\mathrm{e}^{\mathrm{i}qx}\right\}$, we have from equation (28) the Fourier coefficients in terms of the modified Bessel functions

$$a_q = \frac{1}{2\pi}\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}qx - V(x)/2}\,\mathrm{d}x = I_{|q|}(g/2). \tag{29}$$

Thus we ultimately have for the structure factor, which is simply the one-sided Fourier transform of the intermediate scattering function,

$$\tilde{S}(k,\omega) = \sum\nolimits_{q=0}^{\infty} I_{|q|}(g/2)\tilde{c}_{0,q}(k,\omega). \tag{30}$$

Hence, one can calculate the decay rate $\Gamma \approx \tau^{-1}$ as the inverse of the average longest relaxation time, which is defined as follows [16]. The intermediate scattering function $S(k,t)$ can be approximately represented at long times as the single exponential $S(k,t) = h(k)\,\mathrm{e}^{-t/\tau(k)}$ or in the frequency domain as the Lorentzian structure factor:

$$\tilde{S}(k,\omega) = \frac{h(k)}{\mathrm{i}\omega + \tau^{-1}(k)}. \tag{31}$$

Thus, τ^{-1} as a function of the wave number can be extracted as

$$\tau(k) = \lim_{\omega\to 0}\frac{\tilde{S}(k,0) - \tilde{S}(k,\omega)}{\mathrm{i}\omega\,\tilde{S}(k,\omega)}. \tag{32}$$

Hence, we have for the average decay rate

$$\tau^{-1} = 2\int_0^{1/2} \tau^{-1}(k)\,\mathrm{d}k. \tag{33}$$

The average jump rate accounts for the possibility mentioned above that, in a periodic potential (which is of course multistable), the particle having escaped a particular well may again be trapped due to thermal fluctuations in another well. Moreover, jumps of either a single lattice spacing or of many lattice spacings are possible. Thus, the escape rate in a periodic potential is called the jump rate [32]. The foregoing result pertains to the Caldeira–Leggett, Diósi, Vacchini and Coffey *et al* kinetic models allowing us to estimate the average greatest relaxation time for these. In contrast, for the Lorentz kinetic model, which has nothing to do with Brownian motion *per se*, the intermediate scattering function $\tilde{S}(k,\omega)$ can also be approximately presented as

$$\tilde{S}_L(k,\omega) \approx \frac{h(k)}{\mathrm{i}\omega + \tau^{-1}}, \tag{34}$$

where the quantity τ in this instance is regarded as a phenomenological parameter and in order to determine it, we use Mel'nikov's estimate [34–38] of the greatest relaxation time τ_M.

6. Mel'nikov equation for the greatest relaxation time

We saw that Mel'nikov [34, 35] has extended his solution of the classical Kramers turnover problem, which is of course based on the theory of classical Brownian motion, to include quantum effects in a semiclassical way. He effected the generalization by simply inserting [34] 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, where the energy dissipated per cycle of the almost periodic motion of a particle on a noisy trajectory corresponding to the barrier energy is of the order of the thermal energy. In the approximation of Ohmic damping, he was then able to write a universal formula for the quantum rate $\Gamma^M = \tau_M^{-1}$ valid for all values of damping at temperatures above the crossover temperature between tunneling and thermal activation

$$\Gamma^M = \Gamma_{\mathrm{IHD}}\Upsilon. \tag{35}$$

Here, Γ_{IHD} is the quantum escape rate from an isolated well in the intermediate to high damping (IHD) region ($\gamma \geqslant 1$) and Υ is the quantum depopulation factor. Later Rips and Pollak [37], following earlier work of Pollak *et al* [36], gave a consistent solution of the quantum Kramers turnover problem, demonstrating how the Mel'nikov equation (35) can be obtained without his *ad hoc* interpolation between the weak and strong damping regimes. Finally, in the context of our problem, Georgievskii and Pollak [38] treated the escape rate problem in a periodic cosine potential, which is qualitatively different from that for a metastable well because the periodic potential is multistable, showing that the quantum depopulation factor Υ in equation (35) is given by the integral

$$\Upsilon = 4\int_0^1 \sin^2(\pi k)F(k)\,\mathrm{d}k. \tag{36}$$

The function $F(k)$, which takes into account both the multistable nature of the potential and the Kramers turnover between the very low damping and IHD regimes, is (in our notation)

$$F(k) = \exp\left\{\frac{a\sin a}{\pi}\int_{-\infty}^{\infty}\ln\left[\frac{1-\mathrm{e}^{-2R(x)}}{1+\mathrm{e}^{-2R(x)}-2\,\mathrm{e}^{-R(x)}\cos(2\pi k)}\right]\frac{\mathrm{d}x}{\cosh(2ax)-\cos a}\right\},$$

$$R(x) = \frac{\pi\gamma}{\sqrt{3\Lambda}}\int_{-\infty}^{\infty}\frac{\cosh(\sqrt{\Lambda}y)-\cos(2\sqrt{\Lambda}xy)}{y\sinh(\sqrt{\Lambda}y)\cosh^2[\pi y/(2\sqrt{6g})]}\,\mathrm{d}y.$$

Here, $a = \sqrt{3\Lambda}(\sqrt{\gamma^2+2g}-\gamma)$ and $\delta = 8\gamma\sqrt{2g}$ is the dimensionless classical action associated with the path of a particle librating in a well of the cosine potential with energy equal to the barrier energy, i.e. the critical energy trajectory on which escape may take place by dint of a thermal fluctuation [42]. In the classical limit [34] $R(x) \to \delta(x^2+1/4)$, we have $F_M(k) = \mathrm{e}^{\sigma(k,\delta)-\sigma(0,2\delta)/2}$, where

$$\sigma(k,\delta) = 2\sum_{n=1}^{\infty} n^{-1}\mathrm{erfc}(\sqrt{n\delta}/2)\cos(2\pi nk).$$

In calculating the escape rate in the IHD limit only for the cosine potential given by equation (1) it is sufficient [16] to consider the escape rate from an isolated well. The IHD quantum escape rate Γ_{IHD} from such a well is [14, 16]

$$\Gamma_{\mathrm{IHD}} = \frac{\Xi}{2\pi\eta}(\sqrt{\gamma^2+2g}-\gamma)\,\mathrm{e}^{-2g}, \tag{37}$$

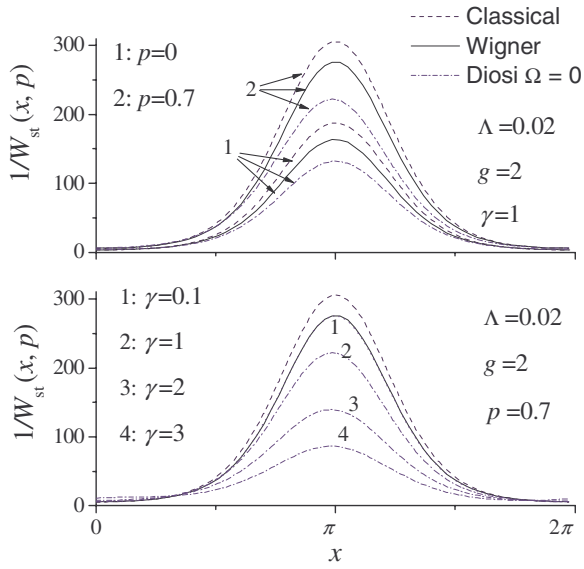

Figure 1 Inverse stationary distributions of the Diósi (dash-dotted lines) kinetic model (equation (20) with $\Omega = 0$) versus the coordinate x for various values of the momentum $p = 0$, $p = 0.7$ and $\gamma = 1$ and various values of the damping parameter $\gamma = 0.1$, $\gamma = 1$, $\gamma = 2$, and $\gamma = 3$ and $p = 0.7$, with $g = 2$ and $\Lambda = 0.02$. The inverses of the Wigner stationary distribution $1/W_0(x, p)$ (solid lines) and of the classical Maxwell–Boltzmann distribution (dashed lines, $\Lambda = 0$) are also shown.

where

$$\Xi = \prod_{n=1}^{\infty} \frac{{\omega_a}^2 + (2\pi n/\hbar\beta)^2 + 2\pi n\gamma/\hbar\beta}{-{\omega_c}^2 + (2\pi n/\hbar\beta)^2 + 2\pi n\gamma/\hbar\beta} \tag{38}$$

is the quantum correction factor [1, 43] and $\omega_c = \sqrt{|V''(x_c)|/m} = \omega_a = \sqrt{V''(x_a)/m}$ are the saddle and well angular frequencies. If the conditions $\hbar\gamma\beta \ll 2\pi$ and $g\Lambda \ll 1$ are fulfilled and if only leading quantum correction terms (of order $\hbar^2$) are taken into account, equation (38) reduces to the well-known result $\Xi = 1 + \beta^2\hbar^2\left(\omega_c^2 + \omega_a^2\right)/24 + \cdots$ [1]. Equation (35), combined with equations (36)–(38), now yields an estimate for the inverse of the greatest relaxation time. Comprehensive reviews of applications and developments of Kramers' escape rate theory have been given by Mel'nikov [34], Hänggi *et al* [44], Coffey *et al* [45] and Pollak and Talkner [46].

7. Results and discussion

The inverse stationary distributions for the various kinetic models versus the position x for different values of the momentum p are shown in figure 1. Clearly, the Diósi stationary distribution function agrees with the Wigner function $W_0(x, p)$ only for small damping $\gamma < 0.1$. For large γ, the deviation of the Diósi and by inference the Vacchini distribution from $W_0(x, p)$ is significant. In the classical limit $\Lambda \to 0$, all semiclassical stationary distributions reduce to the classical Maxwell–Boltzmann distribution.

The real and imaginary parts of the normalized dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$ versus the dimensionless frequency $\eta\omega$ for damping $\gamma = 0.5$, 5 and 20 are presented in figure 2 for the various kinetic models. The results for the Lorentz model, with the relaxation

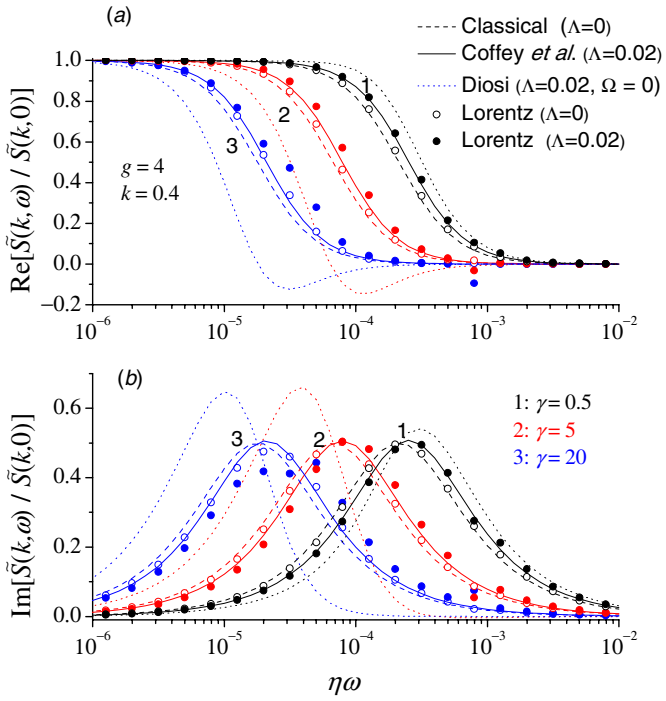

Figure 2 The real and imaginary parts of the normalized dynamic structure factor $\tilde{S}(k,\omega)/\tilde{S}(k,0)$ versus $\eta\omega$ for various values of damping parameter $\gamma = 0.5, 5, 20$ and the barrier parameter $g = 4$ and the wave number $k = 0.4$. Solid and dashed lines: the matrix continued fraction solution with $\Lambda = 0.02$ and $\Lambda = 0$ (classical case), respectively. Closed and open circles: the Lorentz model. Dotted lines: the Diósi model with $\Lambda = 0.02$ and $\Omega = 0$.

time calculated from Mel'nikov's equation (35), as applied to the cosine potential, are shown alongside the classical results ($\Lambda = 0$) for comparison. Clearly, both the Coffey *et al* and the Lorentz models for *all damping* and the Diósi model for low damping ($\gamma \ll 1$) differ only slightly from the classical theory based on the Klein–Kramers equation. This is of course consistent with an almost classical treatment of the problem [22]. However, in the IHD range, $\gamma > 1$, the Diósi model predicts a pronounced deviation from the classical results. In particular, in figure 2(a) the negative excursions in the real part of the dynamic structure factor are reminiscent of a resonance absorption, which becomes more and more pronounced as the dissipative coupling to the bath is increased. The same behavior is reflected in the imaginary part, where for large dissipation the behavior is symptomatic of a resonant peak, rather than the Lorentzian behavior associated with the other models. This behavior in IHD arises because the perturbation solution for $\tilde{S}(k,\omega)$ for the Diósi model is no longer valid for $\gamma > 1$. (Recall that the first-order quantum correction term increases as $\Lambda\gamma^2$ for $\gamma \gg 1$, see, e.g., equation (21).)

Turning now to the greatest relaxation time τ, shown in figure 3 as a function of the damping parameter γ, it is apparent that the numerical solution of the master equation (11) is closely followed by the quantum reaction rate theory solution embodied in equations (35) and (36). Moreover, that solution is consistent with the expected lowering of the potential barrier due to quantum effects anticipated by Wigner [47] on the basis of his generalization of classical transition state theory to quantum mechanics. The Diósi model (for $\Omega \ll 1$) also agrees with the quantum reaction rate theory results for weak coupling $\gamma < 0.1$. This is so

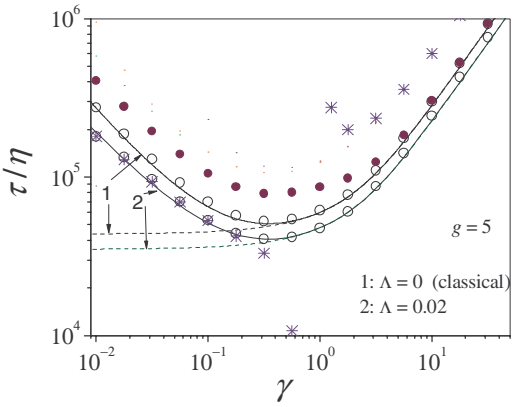

Figure 3 Greatest relaxation time τ/η versus dimensionless damping parameter γ for the barrier parameter $g = 5$. Solid lines: the turnover equation (35) for $\Lambda = 0$ (classical case; curve 1) and $\Lambda = 0.02$ (curve 2). Dashed lines: the IHD equation (37) for $\Lambda = 0$ (curve 1) and $\Lambda = 0.02$ (curve 2). Open circles: master equation (11). Filled circles: the Caldeira–Leggett master equation (3). Asterisks: the Diósi master equation (9) with $\Omega = 0$ (fittings for other values of $\Omega \neq 0$ yield substantial deviations from the predictions of the escape rate theory).

because the stationary distribution function for the Diósi model for $\gamma < 0.1$ is very close in this range of damping to the Wigner function $W_0(x, p)$ (see figure 1). However, the Diósi model yields τ at variance with escape rate theory in regions of damping higher than those characterizing the Kramers turnover region. These deviations appearing in figure 3 at IHD arise because the perturbation solutions for $\tilde{S}(k, \omega)$ used in the calculation of the escape rate are simply not applicable there. However, in contrast to all the other models which yield results more or less in accord with reaction rate theory, the Caldeira–Leggett model in the form of the semiclassical Klein–Kramers equation (3) yields classical results for high damping and predicts *decrease* of the escape rate for low damping, apparently, because the first-order correction in the quantum parameter is retained in the conservative term, while it is assumed [11] that the collision term is still given by the classical Fokker–Planck operator. However, it is quite evident in the first place from the discussion given by Caldeira and Leggett that retention of the quantum term in the conservative part of their equation (5.14) is inconsistent with retaining the classical Fokker–Planck operator on the right-hand side of that equation. 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., regarding the diffusion coefficient as a constant (cf [21]), the characteristic lowering of the barrier produced by the quantum tunneling near the top of the barrier cannot be reproduced, neither can one regain the results of quantum reaction rate theory [36–38 , 47].

To conclude, using the master equation in the phase space representation, we have evaluated quantum effects in the Brownian motion in a cosine periodic potential for various kinetic models grounded in different physical assumptions. Our method uses the techniques previously developed for the classical Fokker–Planck equation [23, 24] facilitating a simple treatment which allows one to study the interplay of tunneling, thermal fluctuations and dissipation in the quantum Brownian motion. In particular, we have been able to evaluate, in semiclassical fashion, quantum effects in the relevant quantities (stationary distribution, dynamic structure factor and escape rate) and the influence of quantum tunneling on their high-temperature behavior. We have shown that the model master equations (9) for $\Omega \ll 1$

(Diósi model), (10) (and by inference the Vacchini model) and (11) (Coffey *et al* model) yield similar results for low damping ($\gamma < 0.1$). Furthermore, the master equations (11) and (13) (Lorentz model) provide a reasonable description of the quantum dissipative process for intermediate damping, unlike the master equations (9) and (10), which are not applicable in the IHD region (because the perturbation solutions depend on the damping, e.g., equation (21), and so are no longer valid for $\gamma > 1$). We remark that we have illustrated our results using a periodic cosine potential. However, this is purely for the sake of convenience as similar behavior may be expected for other potentials, e.g., for a 2–4 double well potential (cf the calculation of the greatest relaxation time for this potential carried out in [17]), tilted periodic potential etc.

Finally, we emphasize that in the derivation of the master equation (11), the equilibrium Wigner function $W_0(x, p)$ for vanishing damping ($\gamma \to 0$) has been used to determine the explicit form of the coefficients D_p, D_{pp}, D_{px} in equation (5). However, it is known from the theory of quantum open systems [48] that the equilibrium state in general may deviate from the canonical distribution ρ_0; the latter describes the thermal equilibrium of the system in the weak coupling and high-temperature limits only. Hence, the stationary distribution may also differ from the canonical distribution ρ_0; in particular, it may depend on the damping [48]. For a periodic potential, the damping dependence of the stationary distribution is unknown. Thus, the conditions under which the stationary distribution may be approximated by the Wigner distribution $W_0(x, p)$ are important in establishing a possible range of validity for the kinetic model embodied in equation (11). Certainly, the model may be used in the high-temperature limit because the stationary distribution then always reduces to $W_0(x, p)$. Moreover, one would expect that the master equation (11) is a reasonable approximation for the kinetics of a quantum Brownian particle in a periodic potential $V(x)$, when $\beta\hbar\gamma \ll 1$. Finally, the extension of our approach [49, 50] to spin dynamics governed by the $SU(2)$ rotation group (rather than the Heisenberg–Weyl group of translations), which contains the same assumption concerning the canonical distribution as the equilibrium distribution, can also be used to calculate the integral relaxation time of the magnetization etc. The ensuing results are in agreement with those predicted by alternative methods such as the quantum Hubbard operator representation of the evolution equation for the spin density matrix [51, 52].

Acknowledgments

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Appendix. The matrix continued fraction solution of equations (25)–(27)

We seek perturbation solutions of equations (25) (for $B = 2$) and (26) in the form $c_{n,q} = c^0_{n,q}(k, t) + \Lambda c^1_{n,q}(k, t)$. Thus, we introduce the column vectors $\mathbf{C}^0_n(t)$ and $\mathbf{C}^1_n(t)$:

$$\mathbf{C}^0_n(t) = \begin{pmatrix} \vdots \\ c^0_{n-1,-1}(k,t) \\ c^0_{n-1,0}(k,t) \\ c^0_{n-1,1}(k,t) \\ \vdots \end{pmatrix} \quad \text{and} \quad \mathbf{C}^1_n(t) = \begin{pmatrix} \vdots \\ c^1_{n-1,-1}(k,t) \\ c^1_{n-1,0}(k,t) \\ c^1_{n-1,1}(k,t) \\ \vdots \end{pmatrix}.$$

Now, by seeking a perturbation solution as $\mathbf{C}_n(t) = \mathbf{C}_n^0(t) + \Lambda \mathbf{C}_n^1(t)$, equations (25) and (26) can be rearranged in the zero order and first order of perturbation theory as the set of matrix *three-term* recurrence equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{C}_n^0(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}^0(t) - \gamma(n-1)\mathbf{C}_n^0(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^0(t). \tag{A.1}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{C}_n^1(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}^1(t) - \gamma(n-1)\mathbf{C}_n^1(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^1(t) + \mathbf{R}_n^0(t), \tag{A.2}$$

where

$$\mathbf{Q}_n^{\pm} = i\sqrt{\frac{n}{2} - \frac{1 \mp 1}{4}} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & k-1 & \mp g/4 & 0 & \cdots \\ \cdots & \pm g/4 & k & \mp g/4 & \cdots \\ \cdots & 0 & \pm g/4 & k+1 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

The vector $\mathbf{R}_n^0(t)$ for the Diósi kinetic model is then

$$\mathbf{R}_n^0(t) = \mathbf{s}_n \mathbf{C}_{n-1}^0(t) + \mathbf{p}_n \mathbf{C}_n^0(t) + \mathbf{r}_n \mathbf{C}_{n-3}^0(t)$$

and for that of Coffey *et al*

$$\mathbf{R}_n^0(t) = \mathbf{q}_n \mathbf{C}_{n-2}^0(t) + \mathbf{r}_n \mathbf{C}_{n-3}^0(t),$$

where $\mathbf{s}_n = 8\Omega\gamma\sqrt{1 - 1/n}\mathbf{Q}_n^+$,

$$\mathbf{q}_n = \gamma g\sqrt{(n-1)(n-2)} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & 1 & 0 & 1 & \cdots \\ \cdots & 0 & 1 & 0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{r}_n = \mathrm{i}g\sqrt{\frac{(n-1)(n-2)(n-3)}{8}} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & -1 & 0 & 1 & \cdots \\ \cdots & 0 & -1 & 0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

$$\mathbf{p}_n = \gamma \begin{pmatrix} \ddots & \ddots & \ddots & 0 & \iddots \\ \ddots & -(2(k-1)^2 - g^2/4) & g(k-1/2) & -g^2/8 & 0 \\ \ddots & -g(k-1/2) & -(2k^2 - g^2/4) & g(k+1/2) & \ddots \\ 0 & -g^2/8 & -g(k+1/2) & -(2(k+1)^2 - g^2/4) & \ddots \\ \iddots & 0 & \ddots & \ddots & \ddots \end{pmatrix}.$$

The initial conditions follow from the stationary distribution in the phase space. The initial conditions $c_{n,q}(0) = c_{n,q}^0(0) + \Lambda c_{n,q}^1(0)$ are evaluated as

$$c_{n,q}(0) = \frac{1}{\sqrt{2^n n!}} \int_{-\infty}^{\infty} \int_0^{2\pi} H_n(p)\, \mathrm{e}^{\mathrm{i}qx + V(x)/2} W_0(x, p)\, \mathrm{d}x\, \mathrm{d}p.$$

For the classical Boltzmann distribution, $c^0_{n,q}(0) = 0$ $(n > 0)$ and

$$c^0_{0,q}(0) = \sqrt{\pi} Z^{-1}_{cl} \int_0^{2\pi} \mathrm{e}^{\mathrm{i}qx - V(x)/2}\,\mathrm{d}x = 2\pi^{3/2} Z^{-1}_{\mathrm{cl}} I_{|q|}(g/2).$$

Thus, $\mathbf{C}^0_1(0) \neq \mathbf{0}$ and $\mathbf{C}^0_n(0) = \mathbf{0}$, $n \geqslant 2$. The first-order perturbation initial conditions $c^1_{n,q}(0)$ differ from model to model. For that of Coffey *et al*, they are

$$\begin{aligned} c^1_{0,q}(0) &= \sqrt{\pi} Z^{-1} \int_0^{2\pi} [(V'(x))^2 - 2V''(x)]\,\mathrm{e}^{\mathrm{i}qx - V(x)/2}\,\mathrm{d}x \\ &= -2\pi^{3/2} Z^{-1}_{\mathrm{cl}} [(2q)^2 - gI_1(g)/I_0(g)] I_q(g/2), \end{aligned}$$

$$c^1_{2,q}(0) = \sqrt{2\pi} Z^{-1}_{\mathrm{cl}} \int_0^{2\pi} V''(x)\,\mathrm{e}^{\mathrm{i}qx - V(x)/2}\,\mathrm{d}x = \frac{g}{\sqrt{2}} \big(c^0_{0,q+1}(0) + c^0_{0,q-1}(0)\big),$$

so that the vector initial conditions are $\mathbf{C}^1_1(0) \neq \mathbf{0}$, $\mathbf{C}^1_2(0) = \mathbf{0}$, $\mathbf{C}^1_3(0) \neq \mathbf{0}$. For the Diósi model, they are

$$\begin{aligned} c^1_{0,q}(0) &= \frac{\sqrt{\pi}}{Z_{cl}} \int_0^{2\pi} \mathrm{e}^{\mathrm{i}qx - V/2} \left[V'^2 - 2V'' + 4\gamma(\gamma + 2\Omega)V + (1 + 4\gamma(\gamma + 2\Omega)) g \frac{I_1(g)}{I_0(g)} \right] \mathrm{d}x \\ &= -\frac{2\pi^{3/2}}{Z_{\mathrm{cl}}} \left\{ \left[4q^2 - (1 + 4\gamma(\gamma + 2\Omega)) g \frac{I_1(g)}{I_0(g)} \right] I_q(g/2) \right. \\ &\quad \left. + 2\gamma(\gamma + 2\Omega) g [I_{q+1}(g/2) + I_{q-1}(g/2)] \right\}, \end{aligned}$$

$$c^1_{1,q}(0) = -2\sqrt{2\pi} Z^{-1}_{\mathrm{cl}} \gamma \int_0^{2\pi} V'(x)\,\mathrm{e}^{\mathrm{i}qx - V(x)/2}\,\mathrm{d}x = -\mathrm{i}4(2\pi)^{3/2} Z^{-1}_{\mathrm{cl}} q\gamma I_q(g/2),$$

$$c^1_{2,q}(0) = \sqrt{2\pi} Z^{-1}_{\mathrm{cl}} \int_0^{2\pi} V''(x)\,\mathrm{e}^{\mathrm{i}qx - V(x)/2}\,\mathrm{d}x = \frac{g}{\sqrt{2}} \big(c^0_{0,q+1}(0) + c^0_{0,q-1}(0)\big),$$

and the vector initial conditions are $\mathbf{C}^1_1(0) \neq \mathbf{0}$, $\mathbf{C}^1_2(0) \neq \mathbf{0}$, $\mathbf{C}^1_3(0) \neq \mathbf{0}$. All other vectors are zero $\mathbf{C}^1_n(0) = \mathbf{0}$, $n \geqslant 4$.

Taking the Laplace transform of equation (A.1), namely $\tilde{\mathbf{C}}^0_n(s) = \int_0^\infty \mathbf{C}^0_n(t)\,\mathrm{e}^{-st}\mathrm{d}t$ and applying the general matrix method of solution of three-term recurrence equations [16, 23, 24], we have the zero- and first-order vectors

$$\tilde{\mathbf{C}}^0_1(s) = \mathbf{\Delta}_1(s)\mathbf{C}^0_1(0),$$

$$\tilde{\mathbf{C}}^0_n(s) = \mathbf{S}^-_n \tilde{\mathbf{C}}^0_{n-1}(s) = \mathbf{S}^-_n \mathbf{S}^-_{n-1} \ldots \mathbf{S}^-_2 \mathbf{\Delta}_1(s) \mathbf{C}^0_1(0), \qquad n \geqslant 2,$$

$$\tilde{\mathbf{C}}^1_1(s) = \mathbf{\Delta}_1(s) \left[\big(\mathbf{C}^1_1(0) + \tilde{\mathbf{R}}^0_1(s)\big) + \sum_{j=1}^{\infty} \left[\prod_{k=1}^{j} \mathbf{Q}^+_k \mathbf{\Delta}_{k+1}(s) \right] \big(\mathbf{C}^1_{j+1}(0) + \tilde{\mathbf{R}}^0_{j+1}(s)\big) \right],$$

$$\begin{aligned} \tilde{\mathbf{C}}^1_n(s) &= \mathbf{\Delta}_n(s) \mathbf{Q}^-_n \tilde{\mathbf{C}}^1_{n-1}(s) + \mathbf{\Delta}_n(s) \left[\big(\mathbf{C}^1_n(0) + \tilde{\mathbf{R}}^0_n(s)\big) + \sum_{j=1}^{\infty} \left[\prod_{k=1}^{j} \mathbf{Q}^+_{n+k-1} \mathbf{\Delta}_{n+k}(s) \right] \right. \\ &\quad \left. \times \big(\mathbf{C}^1_{n+j}(0) + \tilde{\mathbf{R}}^0_{n+j}(s)\big) \right], \end{aligned}$$

where $\mathbf{S}_n^- = \mathbf{\Delta}_n(s)\mathbf{Q}_n^-$, $\mathbf{S}_n^+ = \mathbf{Q}_{n-1}^+\mathbf{\Delta}_n(s)$, and the matrix continued fraction $\mathbf{\Delta}_n(s)$ is defined by the recurrence equation

$$\mathbf{\Delta}_n(s) = \left\{[s + \gamma(n-1)]\mathbf{I} - \mathbf{Q}_n^+\mathbf{\Delta}_{n+1}(s)\mathbf{Q}_{n+1}^-\right\}^{-1}.$$

Taking into account the initial conditions, the expression for $\tilde{\mathbf{C}}_1^1(s)$ simplifies to

$$\tilde{\mathbf{C}}_1^1(s) = \mathbf{\Delta}_1(s)\left[\mathbf{C}_1^1(0) + \tilde{\mathbf{R}}_1^0(s)\right] + \mathbf{\Delta}_1(s)\mathbf{S}_2^+\left[\mathbf{C}_2^1(0) + \tilde{\mathbf{R}}_2^0(s)\right] + \mathbf{\Delta}_1(s)\mathbf{S}_2^+\mathbf{S}_3^+[\mathbf{C}_3^1(0) + \mathbf{F}],$$

where

$$\mathbf{F} = \tilde{\mathbf{R}}_3^0(s) + \mathbf{S}_4^+\left[\tilde{\mathbf{R}}_4^0(s) + \mathbf{S}_5^+\left[\tilde{\mathbf{R}}_5^0(s) + \cdots\right]\right].$$

For the Lorentz model, equation (27) can be rearranged as

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{C}_n^0(t) = \mathbf{Q}_n^-\mathbf{C}_{n-1}^0(t) - \tau^{-1}\mathbf{C}_n^0(t) + \tau^{-1}\mathbf{C}_1^0(0)\delta_{n,1} + \mathbf{Q}_n^+\mathbf{C}_{n+1}^0(t),$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{C}_n^1(t) = \mathbf{Q}_n^-\mathbf{C}_{n-1}^1(t) - \tau^{-1}\mathbf{C}_n^1(t) + \mathbf{Q}_n^+\mathbf{C}_{n+1}^1(t) + \tau^{-1}\mathbf{C}_1^1(0)\delta_{n,1} + \tau^{-1}\mathbf{C}_3^1(0)\delta_{n,3} + \mathbf{R}_n^0(t),$$

where $\mathbf{R}_n^0(t) = \mathbf{r}_n\mathbf{C}_{n-3}^0(t)$. The above equations have the following solution for zero- and first-order vectors

$$\tilde{\mathbf{C}}_1^0(s) = \left[1 + (s\tau)^{-1}\right]\mathbf{\Delta}'_1(s)\mathbf{C}_1^0(0),$$

$$\tilde{\mathbf{C}}_n^0(s) = \mathbf{S}'^-_n\tilde{\mathbf{C}}_{n-1}^0(s) = \left[1 + (s\tau)^{-1}\right]\mathbf{S}'^-_n\mathbf{S}'^-_{n-1}\ldots\mathbf{S}'^-_2\mathbf{\Delta}'_1(s)\mathbf{C}_1^0(0), \qquad n \geqslant 2,$$

$$\tilde{\mathbf{C}}_1^1(s) = \left[1 + (s\tau)^{-1}\right]\mathbf{\Delta}'_1(s)\mathbf{C}_1^1(0) + \mathbf{\Delta}'_1(s)\mathbf{S}'^+_2\mathbf{S}'^+_3[\left[1 + (s\tau)^{-1}\right]\mathbf{C}_3^1(0) + \mathbf{F}],$$

where $\mathbf{S}'^-_n = \mathbf{\Delta}'_n(s)\mathbf{Q}_n^-$, $\mathbf{S}'^+_n = \mathbf{Q}_{n-1}^+\mathbf{\Delta}'_n(s)$, $\mathbf{F} = \mathbf{S}'^+_4\left[\tilde{\mathbf{R}}_4^0(s) + \mathbf{S}'^+_5\left[\tilde{\mathbf{R}}_5^0(s) + \cdots\right]\right]$, and the matrix continued fraction $\mathbf{\Delta}'_n(s)$ is defined by the recurrence equation

$$\mathbf{\Delta}'_n(s) = \left\{\left[s + \tau^{-1}\right]\mathbf{I} - \mathbf{Q}_n^+\mathbf{\Delta}_{n+1}(s)\mathbf{Q}_{n+1}^-\right\}^{-1}.$$

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