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Abstract. Chandrasekhar's phenomenological theory of brownian motion is transcribed to the quantum regime. The statistics used is that of Boltzmann but the free particle was treated, in addition, with Fermi–Dirac statistics followed by some discussion relating to the measurements of low temperatures. Difficulties arising from the dissipative processes involved are by-passed with the aid of a new methodology enabling one to obtain a propagator in configuration space, which embraces single-particle dissipative forces. This sort of propagator is in turn used for the construction of a type of a nonequilibrium density matrix for the quantum brownian particle. Exact nonequilibrium density matrices for the free and the harmonically bound brownian particles under the influence of external time dependent forces are obtained. Finally, a quantum Fokker–Planck type equation for the general brownian particle is derived. The analysis proceeds via functional integration.

1. Introduction

It was Einstein's idea (1956) that the phenomenon of brownian motion, exhibited by particles of colloidal size in a liquid environment, results from collisions by the molecules of the surrounding medium, due to the thermal agitation of the latter. Langevin (1908) was able to dress the idea, mathematically, with his equations for the brownian particle. Further, the theory of brownian motion with classical dynamics was developed by Uhlenbeck and Ornstein (1930) and Chandrasekhar (1943).

As is well known, brownian motion is not restricted to particles of colloidal size, but may be equally well exhibited by particles of atomic or even electronic dimensions. In such cases, particularly in the latter, one can no longer employ classical dynamics, but has to have recourse to the quantum regime. Furthermore, in the case of electrons at low temperature, it would be necessary to couple Fermi–Dirac statistics with quantum dynamics.

The classical theory of brownian motion, apart from explaining a fundamental phenomenon, also deals with mathematically tractable problems of nonequilibrium statistical physics. The theory is based on the Langevin model which simulates the many-particle medium interaction experienced by the brownian particle by two single-particle forces; a dissipative, and a random force. The model displays a great attraction ih that it reduces an essentially many-particle problem to a single-particle one. Now, due to the fact that dissipative forces are not in general hamiltonian-derivable, it would seem that a quantum-mechanical construction of a density matrix for the brownian particle, based on the Langevin model, would inevitably entail difficulties. A circumstantial discussion of the difficulties involved has been given by Kubo (1969). However, the simplicity of the model is such that it would be worth while attempting to develop a quantum-mechanical counterpart. The transcription to the quantum regime requires

knowledge of the random force autocorrelation, which, unlike the classical state of affairs, varies from case to case. The evaluation of this autocorrelation is easily accomplished within the framework of the Heisenberg picture by comparing the mean energy of the brownian particle in a state of thermodynamic equilibrium, obtained by equilibrium statistical mechanics, with that obtained from an appropriate nonequilibrium method.

In § 2 we evaluate the various autocorrelation functions for the random force in the cases of free and harmonically bound particles using Boltzmann statistics. In addition the free electron case is treated with Fermi–Dirac statistics, resulting in an expression markedly different from the one corresponding to Boltzmann statistics.

In § 3 we work out a type of nonequilibrium density matrix for the brownian quantum oscillator within the framework of the Schrödinger picture. In this connection we present a methodology capable of handling single-particle dissipative forces. However, the approach is not free of defects, and these are pointed out in the text. Finally, § 4 deals with an equation of motion for the density matrix of a general brownian particle.

2. The random force autocorrelations

In the case of classical dynamics the Langevin equation of motion, for the brownian particle in a potential field $U(x)$ and under the influence of a time prescribed force $F(t)$, is:

$$m\frac{d^2x}{dt^2}+\frac{\partial}{\partial x}U(x)-F(t) = -\frac{m}{t_0}\frac{dx}{dt}+f(t). \tag{2.1}$$

The forces on the right-hand side of (2.1) simulate the many-body medium interaction experienced by the brownian particle. As is well known, the particle constantly loses energy through the dissipative force $-(m/t_0)\dot{x}$, while through the force $f(t)$, taken to be a random force, its energy is restored on average. t_0 is the particle relaxation time.

Chandrasekhar (1943) assumed the distribution of the random force within a short time interval to be gaussian, and the random forces at two distinct times to be uncorrelated. Now, the high collision rate (10^{20} collisions/s) enables the use of a functional probability for the random force,

$$W_0^t[f(\tau)] \prod_{0\leqslant\tau<t} df(\tau) = \exp\left(-\int_0^t \frac{1}{2C}f^2(\tau)\,d\tau\right) \prod_{0\leqslant\tau<t} \left(\frac{d\tau}{2\pi C}\right)^{3/2} df(\tau), \tag{2.2}$$

embodying the above assumptions.

The distribution given by (2.2) implies the averages:

$$\langle f(\tau)\rangle = 0, \qquad \langle f_j(\tau_1)f_k(\tau_2)\rangle = C\delta_{jk}\delta(\tau_1-\tau_2). \tag{2.3}$$

The coefficient C in the random force autocorrelation given in (2.3) and appearing in the distribution (2.2) in the classical case is the same irrespective of the potential $U(x)$, and is given by:

$$C = 2\frac{m}{t_0}\kappa T \tag{2.4}$$

where T is the medium temperature and κ Boltzmann's constant. However, in the case of quantum dynamics the uncertainty principle correlates the kinetic and potential

energies, and the situation in which C is independent of the potential energy is no longer valid.

For the evaluation of the random force autocorrelation we shall rely on two different procedures for obtaining the average energy in a state of thermodynamic equilibrium; an equilibrium and a nonequilibrium procedure. Our system will consist of brownian particles considered independent of each other. The state of thermodynamic equilibrium is brought about by environmental and very slight interparticle interactions, which are simulated by the frictional and the random force. Although these interactions are responsible for bringing about the state of equilibrium they do not finally appear in the equilibrium distribution of the system. Actually the distribution is fully determined by the system hamiltonian $H(p, x)$ alone. Since the medium interactions are mainly responsible for the eventual establishment of equilibrium, it should be possible to obtain the average energy per particle of the system of interest determined by its own forces and the environmental interactions. The necessary averages are to be taken over distributions pertaining to the system plus the environment.

More specifically, let $X(t)$ and $P(t)$ be the position and momentum operators of a brownian particle, at time t, obtained from its (operator) equation of motion, which involves the medium interactions. In the case of the Langevin model they will be functions of the initial values of the position and momentum operators and functionals of the random force.

In short they will look like:

$$X(t) = X(x', p'; {}_0^t[f(\tau)])$$
$$P(t) = P(x', p'; {}_0^t[f(\tau)])$$

(2.5)

where x' and p' $(= -i\hbar\partial/\partial x')$ are the initial operator conditions of the particle.

Introducing the expressions (2.5) into the hamiltonian for the brownian particle, we may interpret the result as the 'instantaneous energy operator' of a particular brownian particle. Now, in order to obtain the mean energy per particle we have to average both against the density matrix of the initial conditions, ρ_{in}, and the distribution of the random force. The result will be the double average:

$$\langle\!\langle H(P(t), X(t))\rangle\!\rangle$$
$$= \int \left(\int \{H(P(t), X(t))\rho_{in}(x'|x)\}_{x=x'} \, dx \right) W_0^t[f(\tau)] \prod_{0 \leqslant \tau < t} df(\tau).$$

(2.6)

In the absence of external forces, equilibrium statistical mechanics tells us that the average energy per particle is obtained via the equilibrium density matrix ρ_{eq} as follows:

$$\langle H(p, x)\rangle = \int \{H(p, x)\rho_{eq}(x|x')\}_{x'=x} \, dx.$$

(2.7)

When the initial conditions in (2.6) relate to the state of equilibrium, described by the density matrix ρ_{eq} of (2.7), then the average energies obtained through the nonequilibrium procedure described by (2.6) and the equilibrium way of (2.7) should coincide. Equating (2.6) (with $\rho_{in} = \rho_{eq}$) to (2.7) we are led to an equation involving the coefficient C appearing in the random force autocorrelation (2.3), from which it can be evaluated.

The equation is:

$$\langle\!\langle H(P(t), X(t))\rangle\!\rangle = \langle H(p, x)\rangle; \qquad \rho_{in} = \rho_{eq}.$$

(2.8)

We now ask the question, what happens when external forces are switched on our system of interest? Are they likely to engender changes in the random force autocorrelation? Certainly, if they are capable of creating, eventually, a new state of equilibrium affairs, they are bound to modify the random force autocorrelation accordingly. However, in the case of a time prescribed external force, in the cases of free and harmonically bound particles, such a force superimposes itself upon the fluctuating force, and under these circumstances its characteristics remain unaltered.

In what follows we shall exemplify the above procedure in the case of the free and harmonically bound brownian particles. Furthermore, we shall build up a body of expressions necessary for the construction of the corresponding density matrices of the next section.

For the free particle the Langevin operator equation is:

$$\frac{d\boldsymbol{p}}{dt} = -\frac{1}{t_0}\boldsymbol{p} + f(t). \tag{2.9}$$

The solution which satisfies the initial condition

$$\boldsymbol{P}(0) = \boldsymbol{p}' = \frac{\hbar}{i}\frac{\partial}{\partial x'}$$

is:

$$\boldsymbol{P}(t) = \exp\left(-\frac{t}{t_0}\right)\boldsymbol{p}' + \int_0^t d\tau \exp\left(\frac{\tau - t}{t_0}\right)f(\tau). \tag{2.10}$$

The hamiltonian is $H = p^2/2m$. Therefore (2.6) becomes:

$$\left\langle\!\left\langle \frac{1}{2m}\boldsymbol{P}^2(t) \right\rangle\!\right\rangle = \exp\left(-2\frac{t}{t_0}\right)\frac{1}{2m}\langle p'^2\rangle + \frac{Ct_0}{2m}\left\{1 - \exp\left(-2\frac{t}{t_0}\right)\right\} \tag{2.11}$$

where for the derivation of (2.11) we have made use of the random force autocorrelation, given in (2.3)

Since the system of our brownian particles remains in the same macroscopic equilibrium state, the average initial energy $\langle p'^2/2m\rangle$, and the mean energy, $\langle p^2/2m\rangle$, at any time t should be the same. This energy is obtained via the density matrix pertaining to the statistics of the system.

Making use of (2.8) we find C, in the case of free particles, to be given by:

$$C = 2\frac{m}{t_0}\frac{2}{3}\left\langle \frac{1}{2m}p^2 \right\rangle. \tag{2.12}$$

In the case of Boltzmann statistics the equilibrium density matrix is

$$\rho_{eq}^{B}(x|x') = \frac{1}{V}\exp\left(-\frac{m}{2\hbar^2\beta}(x - x')^2\right) \tag{2.13a}$$

while the corresponding distribution for Fermi–Dirac statistics is:

$$\rho_{eq}^{FD}(x|x') = \frac{1}{N}\int \frac{d\boldsymbol{k}}{(2\pi)^3}\frac{2}{\exp\{\beta(\epsilon_k - \zeta)\} + 1}\exp\{i\boldsymbol{k}\cdot(x - x')\}. \tag{2.13b}$$

In (2.13b) N is the number of brownian particles in the system, $\epsilon_k\,(=\hbar^2k^2/2m)$ is the free particle energy associated with the wavevector $\boldsymbol{k}$, and ζ is the chemical potential of the system.

Evaluating now the mean equilibrium energy per particle in the two regimes of statistics, we obtain, utilizing (2.12), the values of the random force autocorrelation coefficient, C_B and C_F, for Boltzmann and Fermi–Dirac statistics as:

$$C_B = 2\frac{m}{t_0}\kappa T \qquad (2.14a)$$

(in agreement with Chandrasekhar's result) and

$$C_F = 2\frac{m}{t_0}\kappa T\left(\frac{\kappa T}{\epsilon_F}\right)^{3/2}\int_0^\infty du\frac{u^{3/2}}{\exp(u-\beta\zeta)+1} \qquad (2.14b)$$

where ϵ_F is the Fermi energy given by

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3N\pi^2}{V}\right)^{2/3}$$

and u is a dimensionless variable ($u = \hbar^2 k^2/2m\kappa T$) introduced in (2.13b) to facilitate the derivation of (2.14b).

The expression for C associated with Boltzmann statistics, in spite of the quantum dynamics used for its derivation, does not involve Planck's constant $\hbar$ and therefore coincides with the corresponding classical result. This is so, since with Boltzmann statistics, in the limit of large volume, the free-particle classical and quantal statistical treatments converge to each other. However, with Fermi–Dirac statistics the quantum effects persist irrespective of the system size. As is well known, for large temperatures the quantum statistical result tends to the classical one. At low temperatures the difference becomes more pronounced. Thus, the low temperature asymptotic expression for C_F, obtained from the corresponding mean energy of free fermions, through (2.12), is given by:

$$C_F = \frac{4}{3}\frac{m}{t_0}\left(\frac{3}{5}\epsilon_F + \frac{\pi^2}{4}\frac{(\kappa T)^2}{\epsilon_F}\right). \qquad (2.14c)$$

From this we see that at absolute zero $C_F = 4m\epsilon_F/5t_0$, while its corresponding value with Boltzmann statistics is $C_B = 0$.

As a simple application let us now evaluate the voltage autocorrelation $\langle\!\langle \mathscr{V}(t)\mathscr{V}(t+\tau)\rangle\!\rangle$ of a resistor due to the brownian motion of its conduction electrons. The voltage operator for such a resistor of length l, resistance R, with N conduction electrons, and which is taken along the x direction, will be:

$$\mathscr{V}(t) = \frac{e}{l}R\sum_{j=1}^N \frac{P_x^{(j)}(t)}{m} \qquad (2.15a)$$

where $P_x^{(j)}(t)$ is the x component of the momentum operator of the jth conduction electron at time t. Utilizing (2.15a) we write the thermal voltage autocorrelation as:

$$\langle\!\langle \mathscr{V}(t)\mathscr{V}(t+\tau)\rangle\!\rangle = \frac{e^2}{m^2l^2}\sum_{j,s=1}^N \langle\!\langle P_x^{(j)}(t)P_x^{(s)}(t+\tau)\rangle\!\rangle \qquad (2.15b)$$

where the double averaging refers to the averages taken against the density matrix of the initial conditions and the distribution of the random force.

Essentially the evaluation of (2.15b) requires a two-body density matrix for the initial conditions, but here we are dealing with nearly independent particles and the momentum correlations relating to two particles will be approximately zero. We are

then left with the evaluation of a single-particle momentum autocorrelation. The result is:

$$\langle\!\langle \mathscr{V}(t)\mathscr{V}(t+\tau) \rangle\!\rangle = \frac{e^2}{m^2 l^2} RN \langle\!\langle P_x(t)P_x(t+\tau) \rangle\!\rangle$$

$$= R\frac{C_{\mathrm{F}}}{2m} \exp\left(-\frac{|\tau|}{t_0}\right) \tag{2.15c}$$

where for the derivation of (2.15c) we have combined (2.10), (2.3) and (2.13b). Furthermore we have made use of the formula, $R = l^2 m/e^2 N t_0$, expressing the resistance in terms of the electron relaxation time. C_{F} is given by (2.14b).

Fourier transforming the voltage fluctuation formula (2.15c) with respect to τ and specializing to the case of near absolute zero temperatures, using (2.14c), we have:

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} \langle\!\langle \mathscr{V}(t)\mathscr{V}(t+\tau)\rangle\!\rangle \exp(\mathrm{i}\omega\tau)\,\mathrm{d}\tau$$

$$= \frac{2}{\pi}R\left(\frac{1}{5}\epsilon_{\mathrm{F}}+\frac{3}{4}\pi^2\frac{(\kappa T)^2}{\epsilon_{\mathrm{F}}}\right)\frac{1}{1+(\omega t_0)^2}; \qquad T \simeq 0\ \mathrm{K}. \tag{2.15d}$$

The result (2.15d), taking account of the proper electron statistics, may indicate a more appropriate scale for the calibration of the low temperature quantum flux thermometers (Kamper 1967, Kamper and Zimmerman 1971, Giffard *et al* 1972) as compared with the linear scale in use.

Let us now work out the case when an externally applied time dependent force $F(t)$ acts on the free brownian particle. We shall be interested in obtaining the averages for the momentum, position, and energy, which will be used in the derivations of the next section.

In this case the operator equation is:

$$\dot{p} = -\frac{1}{t_0}p + F(t) + f(t). \tag{2.16}$$

The solution, for the momentum and position, satisfying the initial conditions,

$$P(0) = p' = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x'}, \qquad X(0) = x'$$

is given by:

$$P(t) = \exp\left(-\frac{t}{t_0}\right)p' + \int_0^t \mathrm{d}\tau \exp\left(\frac{\tau-t}{t_0}\right)(F(\tau)+f(\tau)) \tag{2.17a}$$

$$X(t) = x' + mt_0\left\{1-\exp\left(-\frac{t}{t_0}\right)\right\}p' + mt_0\int_0^t \mathrm{d}\tau\left\{1-\exp\left(\frac{\tau-t}{t_0}\right)\right\}(F(\tau)+f(\tau)). \tag{2.17b}$$

The above expressions for the momentum and position involve as random elements the thermal force $f(t)$ and the initial conditions (x', p'). The average value of any quantity which is a function of $P(t)$ or $X(t)$ is to be taken against the thermal force distribution (2.2), and the density matrix ρ_{eq} which, depending on the statistics, will be (2.13a) in the case of Boltzmann statistics or (2.13b) in the case of Fermi–Dirac statistics.

Proceeding in this way we obtain the average values of the momentum and position, the momentum autocorrelation and the kinetic energy:

$$\langle\!\langle P(t)\rangle\!\rangle = \int_0^t \mathrm{d}\tau \exp\left(\frac{\tau - t}{t_0}\right) F(\tau) \tag{2.18a}$$

$$\langle\!\langle X(t)\rangle\!\rangle = mt_0 \int_0^t \mathrm{d}\tau \left\{1 - \exp\left(\frac{\tau - t}{t_0}\right)\right\} F(\tau) \tag{2.18b}$$

$$\langle\!\langle P_\alpha(t)P_\beta(0)\rangle\!\rangle = \langle p_\alpha^2\rangle_{\mathrm{eq}}\delta_{\alpha\beta}\exp\left(-\frac{t}{t_0}\right) \tag{2.18c}$$

$$\left\langle\!\!\left\langle \frac{1}{2m}P^2(t)\right\rangle\!\!\right\rangle = \left(\begin{array}{l} \frac{3}{2}\kappa T \\[2mm] \frac{3}{2}kT\left(\dfrac{kT}{\epsilon_{\mathrm{F}}}\right)^{3/2}\displaystyle\int_0^\infty \mathrm{d}u\,\dfrac{u^{3/2}}{\exp(u - \beta\zeta) + 1} \end{array}\right.\begin{array}{l}\text{Boltzmann statistics}\\[4mm]\text{Fermi–Dirac statistics}\end{array}$$

$$+\frac{1}{2m}\left\{\int_0^t \mathrm{d}\tau \exp\left(\frac{\tau - t}{t_0}\right) F(\tau)\right\}^2. \tag{2.18d}$$

The double averages emphasize the two averaging procedures relating to the thermal force on one hand and the initial conditions on the other. Single averages with the suffix 'eq' indicate that the averaging is performed against the equilibrium density matrix.

The first two averages (2.18*a, b*) express the response of the system of brownian particles, in terms of momentum and displacement, to the external force $F(t)$. The momentum autocorrelation, given in (2.18*c*), shows the decay pattern of this quantity.

The final relation gives the average energy of our particle at time t in terms of the mean equilibrium energy and an additional energy picked up from the external field.

Let us now turn our attention to the brownian motion of the quantum oscillator. The Langevin equation of motion, when a time prescribed external force is operating, is given by:

$$\dot{p} = -\frac{1}{t_0}p - m\Omega^2 x + F(t) + f(t); \qquad p = m\dot{x}. \tag{2.19}$$

The equilibrium density matrix, appropriate for the situation prevailing before the introduction of the external force, is:

$$\rho_{\mathrm{eq}}(x|x') = \left(\frac{m\Omega}{\pi\hbar}\tanh(\tfrac{1}{2}\beta\hbar\Omega)\right)^{3/2}$$

$$\times \exp\left(-\frac{m\Omega}{2\hbar\sinh(\beta\hbar\Omega)}\{(x^2 + x'^2)\cosh(\beta\hbar\Omega) - 2x\cdot x'\}\right). \tag{2.20}$$

This is in conformity with Boltzmann statistics which we shall assume for the remainder of this section.

We shall require the solution for the momentum and position of the operator equation (2.19) satisfying the initial conditions:

$$P(0) = p', \qquad X(0) = x'.$$

We have:

$$P(t) = \left\{ \left(\cos \Omega' t - \frac{1}{2t_0\Omega'} \sin \Omega' t \right) p' - m\frac{\Omega^2}{\Omega'} \sin \Omega' t\, x' \right\} \exp\left(-\frac{t}{2t_0} \right)$$

$$+ \int_0^t d\tau \left(\cos \Omega'(t-\tau) - \frac{1}{2t_0\Omega'} \sin \Omega'(t-\tau) \right) \exp\left(\frac{\tau-t}{2t_0} \right) (F(\tau)+f(\tau)) \qquad (2.21a)$$

$$X(t) = \left\{ \frac{1}{m\Omega'} \sin \Omega' t\, p' + \left(\cos \Omega' t + \frac{1}{2t_0\Omega'} \sin \Omega' t \right) x' \right\} \exp\left(-\frac{t}{2t_0} \right)$$

$$+ \frac{1}{m\Omega'} \int_0^t d\tau \sin \Omega'(t-\tau) \exp\left(\frac{\tau-t}{2t_0} \right) (F(\tau)+f(\tau)) \qquad (2.21b)$$

where $\Omega' = \{\Omega^2 - (1/2t_0)^2\}^{1/2}$. The above expressions hold equally well in the case where the restoring force prevails over the medium resistance $(\Omega > 1/2t_0)$ and vice versa, but in the latter case we have to take account of the imaginary sign of the square root giving Ω'.

The hamiltonian characterizing the state of equilibrium for the quantum oscillator is:

$$H(p, x) = \frac{1}{2m}p^2 + \frac{m}{2}\Omega^2 x^2. \qquad (2.22)$$

We wish now to evaluate the random force autocorrelation coefficient for the quantum oscillator. For this purpose we shall make use of the expressions for the momentum $P(t)$ and the position $X(t)$ given by (2.21a, b) with zero external force. Inserting these expressions into the hamiltonian (2.22) and making use of formula (2.8) relating the nonequilibrium and equilibrium procedures for evaluating the thermal energy, we have:

$$\left\langle\!\!\left\langle \frac{1}{2m}P^2(t) + \frac{m}{2}\Omega^2 X^2(t) \right\rangle\!\!\right\rangle = \left\langle \frac{1}{2m}p^2 + \frac{m}{2}\Omega^2 x^2 \right\rangle_{eq}$$

$$= \tfrac{1}{2}\hbar\Omega \coth(\tfrac{1}{2}\beta\hbar\Omega). \qquad (2.23)$$

The autocorrelation coefficient C appears on the left-hand side of (2.23). Its value thus obtained is given by:

$$C = \frac{m}{t_0}\hbar\Omega \coth\left(\frac{\hbar\Omega}{2\kappa T} \right). \qquad (2.24)$$

It should be noted here, that as a result of the quantum dynamics the value of the random force autocorrelation coefficient depends greatly on the potential energy in question, whereas in the case of classical dynamics C has the same value irrespective of the potential. The difference is due to the uncertainty principle interrelating the kinetic and potential energies. Incidentally, (2.24) could be obtained from kinetic energy considerations but even so the involvement of the potential energy would have been inescapable. In the case of free particles (Boltzmann statistics) both classical and quantal treatments yield the same value for C, a result of the correspondence principle.

Let us now work with the external force $F(t)$ switched on the brownian particles. The mean values of the momentum and displacement, obtained by averaging (2.21a, b)

over the distribution of the thermal force (2.2) and that of the initial conditions (2.20), are given by:

$$\langle\!\langle P(t)\rangle\!\rangle = \int_0^t d\tau\left(\cos\Omega'(t-\tau)-\frac{1}{2t_0\Omega'}\sin\Omega'(t-\tau)\right)\exp\left(\frac{\tau-t}{2t_0}\right)F(\tau) \qquad (2.25a)$$

$$\langle\!\langle X(t)\rangle\!\rangle = \int_0^t d\tau\frac{1}{m\Omega'}\sin\Omega'(t-\tau)\exp\left(\frac{\tau-t}{2t_0}\right)F(\tau). \qquad (2.25b)$$

Finally it is a matter of routine exercise to establish the following relation for the brownian oscillator:

$$\left\langle\!\!\left\langle\frac{1}{2m}P^2(t)+\frac{m}{2}\Omega^2X^2(t)-F(t)\,.\,X(t)\right\rangle\!\!\right\rangle$$

$$= \left\langle\frac{1}{2m}p^2+\frac{m}{2}\Omega^2x^2\right\rangle_{\mathrm{eq}}+\frac{1}{2m}\langle\!\langle P(t)\rangle\!\rangle^2+\frac{m}{2}\Omega^2\langle\!\langle X(t)\rangle\!\rangle^2-F(t)\,.\,\langle\!\langle X(t)\rangle\!\rangle. \qquad (2.26)$$

A more telling way of putting this result for the nonequilibrium mean energy given by (2.26) is:

$$\langle\!\langle H(P(t),X(t))\rangle\!\rangle = \langle H(p,x)\rangle_{\mathrm{eq}}+H(\langle\!\langle P(t)\rangle\!\rangle,\langle\!\langle X(t)\rangle\!\rangle).$$

The above relation states that the equilibrium mean energy is a sort of zero point for the average nonequilibrium energy, and that the additional mean energy, acquired by the system, upon switching on external forces is simply obtained from the system hamiltonian ($H = p^2/2m+m\Omega^2x^2/2$) by replacing the momentum and position operators by their average instantaneous values. However, the general validity of such a statement, even in the regime of brownian motion, should be considered as one of a good approximation.

In the next section we shall proceed to the derivation of an appropriate nonequilibrium density matrix.

3. Nonequilibrium density matrix for the quantum oscillator

Distribution functions for the brownian motion of the quantum oscillator have been devised by a number of authors (Montroll and Shuler 1957, Schwinger 1961, Phillipson 1971, Agarwal 1971 and others). A somewhat troublesome situation likely to arise in such a derivation stems from the difficulty of including dissipative terms in the hamiltonian of the brownian particle. The various authors circumvented this difficulty by building in the density matrices or their equations of motion, at some stage or another, a dissipative mechanism. Thus, Montroll and Shuler in their equation, governing the rate of change of the fraction of oscillators in the nth state of excitation, model the energy losses, through radiation and collisions, by a de-excitation transition probability. Phillipson, essentially, replaces each oscillator eigenfunction by a modulated plane wave carrying momentum equal to the mean momentum of the classical brownian particle and having an amplitude obtained from the corresponding eigenfunction referred to a moving system following the average motion. Agarwal employs Wigner's phase-space distribution functions and in this way enables himself to obtain a quantum

version of the Fokker–Planck equation for the oscillator. Schwinger uses his quantum action in which he embodies random forces and in addition manipulates the necessary dissipative process. In our approach we transcribe the classical theory of brownian motion to the quantum regime working solely within the configuration space. Inevitably we are also faced with the problem of how to include a type of Stokes resistance in a single-particle lagrangian. This is done with the aid of a multiplier analogous to the Euler integrating factor (Havas 1957). This procedure, in a strict quantum-mechanical sense, presents certain disadvantages (Marcuse 1970). However, this should not deter us from manipulating with such a formalism, for this can be made to yield correct information.

We begin with the classical Langevin equation (2.1) which in the case of a harmonically bound charged brownian particle under the influence of a time prescribed electric field $\mathscr{E}(t)$ is:

$$m\ddot{x} = -\frac{m}{t_0}\dot{x} - m\Omega^2 x + e\mathscr{E}(t) + f(t). \tag{3.1}$$

In the previous section, basically we employed the Heisenberg picture and thus enabled ourselves to quantize the equation of motion (3.1). However, in order to develop a density matrix (in the Schrödinger picture) we require the propagator associated with the equation of motion (3.1). This in turn presupposes a lagrangian capable of generating the classical equation of motion. At this point our troubles begin to emerge, for there is no genuine lagrangian function capable of yielding the dissipative force $-(m/t_0)\dot{x}$ appearing on the right-hand side of (3.1). Nevertheless, the function:

$$L_0 = \exp\left(\frac{t}{t_0}\right)(\tfrac{1}{2}m\dot{x}^2 - \tfrac{1}{2}m\Omega^2 x^2 + e\mathscr{E}(t).x + f(t).x) \tag{3.2}$$

while not a proper lagrangian, will serve as such, for when fed into the Euler–Lagrange equations it engenders the equation of motion (3.1).

In what follows we shall use (3.2) as our lagrangian. From it we shall construct the associated hamiltonian, action, and operators in accordance with the usual rules. Our generalized momentum will be:

$$\not{p} = \frac{\partial L_0}{\partial \dot{x}} = \exp\left(\frac{t}{t_0}\right)m\dot{x}. \tag{3.3}$$

The hamiltonian will be:

$$\begin{aligned}
\mathscr{H}_0 &= \not{p}.x - L_0 \\
&= \exp\left(-\frac{t}{t_0}\right)\frac{1}{2m}\not{p}^2 - \exp\left(\frac{t}{t_0}\right)\left(\frac{m}{2}\Omega^2 x^2 - e\mathscr{E}(t)x - f(t).x\right).
\end{aligned} \tag{3.4}$$

Needless to say the hamiltonian $\mathscr{H}_0$, constructed in the above manner, can no longer be interpreted as energy. The difficulty lies with the terms that rise exponentially with time, but this is precisely the price we have to pay for replacing many-particle interactions with just a couple of terms and so eventually dealing with a single-particle lagrangian.

Since our lagrangian (3.2) is quadratic in $\dot{x}, x$ we can obtain the associated propagator exactly from the classical action, using the Van Vleck–Pauli formula (Jones and Papadopoulos 1971). To obtain the classical path $X(t)$ from the equation of motion (3.1),

which at zero time starts from x' and reaches x at time t, we utilize expression (2.21b) with $F(t) = e\mathscr{E}(t)$ and interpret the operators p', x' as scalars. We then evaluate p' so that the condition $X(t) = x$ is satisfied. Next we feed the expression for the classical path, thus derived, into the action formula, and so we obtain the following result for the action along the classical path:

$$
\begin{aligned}
S(xt|x'0\,; [f(\tau)]) &= \int_0^t d\tau L_0[X(\tau)] \\
&= \frac{m}{4t_0}\left\{ x'^2 - x^2 \exp\!\left(\frac{t}{t_0}\right)\right\} \\
&\quad + \frac{m\Omega'}{2\sin\Omega't}\left[\cos\Omega't\left\{ x'^2 + x^2 \exp\!\left(\frac{t}{t_0}\right)\right\} - 2x'\,.\,x\exp\!\left(\frac{t}{2t_0}\right)\right] \\
&\quad + \frac{1}{\sin\Omega't}\int_0^t d\tau\left\{ x'\sin\Omega'(t-\tau) + x\exp\!\left(\frac{t}{2t_0}\right)\sin\Omega'\tau\right\} \\
&\quad \times \exp\!\left(\frac{\tau}{2t_0}\right)\,.\,(e\mathscr{E}(\tau) + f(\tau)) - \frac{1}{m\Omega'\sin\Omega't} \\
&\quad \times \int_0^t d\tau\int_0^\tau d\tau'\sin\Omega'(t-\tau)\sin\Omega'\tau'\exp\!\left(\frac{\tau+\tau'}{2t_0}\right) \\
&\quad \times (e\mathscr{E}(\tau) + f(\tau))\,.\,(e\mathscr{E}(\tau') + f(\tau')).
\end{aligned}
\tag{3.5}
$$

For the sake of emphasis we have indicated, on the left-hand side of (3.5), that the action is a functional of the random force.

With the aid of Van Vleck–Pauli formula, our propagator readily takes the form:

$$
K(xt|x'0\,; [f]) = \left\{\frac{m\Omega'}{2\pi i\hbar\sin\Omega't}\exp\!\left(\frac{t}{2t_0}\right)\right\}^{3/2}\exp\!\left(\frac{i}{\hbar}S(xt|x'0\,; [f])\right).
\tag{3.6}
$$

Clearly the propagator, through the action, becomes a functional of the random force. It is a quadratic exponential in the random force. Although, sometimes, we average propagators involving random elements we shall not be doing so, for such a procedure would only yield averaged wavefunctions, a thing which is not quite what we are aiming at in the quantum mechanics of nonequilibrium processes. What we are actually interested in, in this case, is the mean value of operators, and therefore the quantity to be averaged is a sort of probability amplitude rather than the wavefunction itself. In terms of propagators we require the following averaged product:

$$
\langle K(xt|x_1 0\,; [f])K^*(x't|x_2 0\,; [f])\rangle_{\text{fnl}}
$$

$$
= \int KK^* \exp\!\left(-\int_0^t \frac{1}{2C}f^2(\tau)\,d\tau\right)\prod_{0\leqslant\tau<t}\left(\frac{2\pi C}{d\tau}\right)^{-3/2} df(\tau)
\tag{3.7}
$$

taken against the functional distribution of the random force. This propagates quantities of the form $\Psi(x_1, 0)\Psi^*(x_2, 0)$; Ψ being the wavefunction of the system at zero time. Therefore, the quantity $\langle KK^*\rangle_{\text{fnl}}$ defined in (3.7) is the propagator for the density matrix. Feynman employs quantities like KK^* in the form of a double path integral, from which he obtains an influence functional (see Feynman and Vernon 1963). Edwards (1962), also, in dealing with the averaging of quantities of interest, established that the

desired averages can be obtained from the appropriate averaged propagator (see also Brittin and Chappell 1969).

Fortunately, by having to form KK^*, for our averaging purposes, we arrive at a linear exponential functional which is much easier to average than the quadratic functional we would have had to deal with if we had to average the propagator K alone. The functional average $\langle KK^* \rangle_{\rm fnl}$ is to be considered as an ensemble-averaged density matrix propagator; the ensemble being represented by the functional distribution of the thermal force (2.2). Inserting in formula (3.7) the expression for the propagator K associated with the randomly driven damped oscillator, given in (3.6), and utilizing for the random force autocorrelation C the appropriate value for the oscillator, given by (2.24), we obtain the following expression for the ensemble average density matrix propagator:

$$
\langle K(xt|x_1 0; [f]) K^*(x't|x_2 0; [f]) \rangle_{\rm fnl}
$$

$$
= \left\{ \frac{m\Omega'}{2\pi i\hbar \sin \Omega't} \exp\left(\frac{t}{2t_0}\right) \right\}^3 \exp\left(\frac{im}{4\hbar t_0} \left\{ (x_1^2 - x_2^2) - (x^2 - x'^2) \exp\left(\frac{t}{t_0}\right) \right\} \right.
$$

$$
+ \frac{i}{\hbar} \frac{m\Omega'}{2\sin \Omega't} \left[\cos \Omega't \left\{ (x_1^2 - x_2^2) + (x^2 - x'^2) \exp\left(\frac{t}{t_0}\right) \right\} \right.
$$

$$
\left. - 2(x_1 . x - x_2 . x') \exp\left(\frac{t}{2t_0}\right) \right] + \frac{i}{\hbar \sin \Omega't}
$$

$$
\times \int_0^t d\tau \left\{ (x_1 - x_2) \sin \Omega'(t - \tau) + (x - x') \exp\left(\frac{t}{2t_0}\right) \sin \Omega'\tau \right\} \exp\left(\frac{\tau}{2t_0}\right) e\mathscr{E}(\tau)
$$

$$
- \frac{C}{2\hbar^2 \sin^2\Omega't}
$$

$$
\times \int_0^t d\tau \left. \left\{ (x_1 - x_2) \sin \Omega'(t - \tau) + (x - x') \exp\left(\frac{t}{2t_0}\right) \sin \Omega'\tau \right\}^2 \exp\left(\frac{\tau}{t_0}\right) \right) \quad (3.8)
$$

where for the derivation of (3.8) we have made use of the functional integration formula appearing in the appendix of Papadopoulos (1967) in connection with functional integrals in brownian motion.

The ensemble-average density matrix propagator (3.8) will be used to propagate the density matrix (2.20), pertaining to a system of (charged) harmonic oscillators in a state of thermodynamic equilibrium, which from zero time onwards are disturbed by an externally applied electric field $\mathscr{E}(t)$. The density matrix at time t is given by:

$$
\rho(x|x'; t) = \int dx_1 \, dx_2 \langle KK^* \rangle_{\rm fnl} \rho_{\rm eq}(x_1|x_2) = \langle\!\langle KK^* \rangle\!\rangle. \quad (3.9)
$$

The first average on the right-hand side of (3.9) refers to the ensemble average, effected via functional integration, while the other refers to that of the initial conditions, taken against their equilibrium distribution. Therefore, we may interpret the nonequilibrium density matrix, given by (3.9), as a further average of the nonequilibrium density matrix propagator $\langle KK^* \rangle_{\rm fnl}$ taken in relation to the ensemble of the initial conditions. Needless to stress that this mode of description, essentially, has to do with the Langevin model.

The evaluation of (3.9) with the aid of (2.20), the equilibrium distribution for the oscillator, involves only gaussian integrations. The result is:

$$\rho(x|x';t) = \left(\frac{m\Omega}{\pi\hbar} \tanh(\tfrac{1}{2}\beta\hbar\Omega) \right)^{3/2} \exp\left[\frac{m\Omega}{4\hbar} \coth(\tfrac{1}{2}\beta\hbar\Omega)(x-x')^2 \left\{ 1 - \exp\left(\frac{2t}{t_0} \right) \right\} \right.$$

$$- \frac{m\Omega}{2\hbar \sinh(\beta\hbar\Omega)} \left[\cosh(\beta\hbar\Omega) \{ (x - \langle\!\langle X \rangle\!\rangle)^2 + (x' - \langle\!\langle X \rangle\!\rangle)^2 \} \right.$$

$$\left. \left. - 2(x - \langle\!\langle X \rangle\!\rangle) \cdot (x' - \langle\!\langle X \rangle\!\rangle) \right] \right] \exp\left\{ \frac{i}{\hbar} \exp\left(\frac{t}{t_0} \right) \langle\!\langle P \rangle\!\rangle \cdot (x - x') \right\} \tag{3.10}$$

where $\langle\!\langle X \rangle\!\rangle = \langle\!\langle X(t) \rangle\!\rangle$ and $\langle\!\langle P \rangle\!\rangle = \langle\!\langle P(t) \rangle\!\rangle$ are the doubly-averaged values of the displacement and momentum of the oscillator, given by (2.25a, b), with the external force $F(t)$ replaced by $e\mathscr{E}(t)$.

Looking at the distribution (3.10) we observe, even in the absence of the external force, the rather extraordinary indefinite evolution in time. The situation should not be disturbing for our quantities of interest are obtained by averaging operators modified in such a way so that they suppress in full the undesired features bound to come from the distribution if the operators were used without due adjustment. This is done in a manner, perfectly systematic, according to rules dictated by generalized dynamics. The procedure will become quite clear in the evaluations that follow.

We begin with the kinematic momentum $m\dot{x}(t)$ the momentum denoted by p in the previous section. According to (3.3), the kinematic momentum is given, in terms of the generalized momentum $\not{p}$ by:

$$m\dot{x}(t) = \exp\left(-\frac{t}{t_0} \right) \not{p}. \tag{3.11}$$

The associated operator identity is obtained, in the usual manner, by replacing the generalized operator $\not{p}$ by the operator $(\hbar/i)\partial/\partial x$, and thus we have:

$$m\dot{x}_{\text{op}} = \exp\left(-\frac{t}{t_0} \right) \frac{\hbar}{i} \frac{\partial}{\partial x}. \tag{3.11a}$$

The averaging of this operator, and in fact any operator A, is effected, as per usual, according to the formula:

$$\langle A \rangle = \int \{ A\rho(x|x';t) \}_{x'=x} \, dx. \tag{3.12}$$

The position operator x_{op} is just x.

Utilizing (3.12) with $A = m\dot{x}_{\text{op}}$, given by (3.11a) and ρ taken from (3.10) for the oscillator, we obtain for the average value of the kinematic momentum the result:

$$\langle m\dot{x}_{\text{op}} \rangle = \langle\!\langle P(t) \rangle\!\rangle \tag{3.13a}$$

where $\langle\!\langle P(t) \rangle\!\rangle$ is the expression given in (2.25a), which is precisely the result obtained,

earlier on, in the framework of the Heisenberg picture. This does not involve $\hbar$, and it is, therefore, the same result obtained by use of classical dynamics.

For the average position we have:

$$\langle x_{\mathrm{op}} \rangle = \langle x \rangle = \langle\!\langle X(t) \rangle\!\rangle \qquad (3.13b)$$

where $\langle\!\langle X(t) \rangle\!\rangle$ is given by (2.25b) of the previous section.

The mean kinetic energy of a forced harmonically bound particle is obtained by averaging the kinetic energy operator:

$$\frac{m}{2}\dot{x}_{\mathrm{op}}^2 = -\exp\!\left(-\frac{2t}{t_0}\right)\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad (3.14a)$$

which leads to the result:

$$\langle \tfrac{1}{2}m\dot{x}_{\mathrm{op}}^2 \rangle = \tfrac{3}{4}\hbar\Omega \coth(\tfrac{1}{2}\beta\hbar\Omega) + \tfrac{1}{2}m\langle \dot{x}_{\mathrm{op}} \rangle^2 \qquad (3.14b)$$

where the first term on the right-hand side of (3.14b) is the mean kinetic energy under equilibrium conditions.

The mean potential energy of the quantum oscillator, under the influence of a time dependent force, is given by:

$$\langle \tfrac{1}{2}m\Omega^2 x^2 - e\mathscr{E}(t) \cdot x \rangle = \tfrac{3}{4}\hbar\Omega \coth(\tfrac{1}{2}\beta\hbar\Omega) + \tfrac{1}{2}m\Omega^2\langle x \rangle^2 - e\mathscr{E}(t) \cdot \langle x \rangle. \qquad (3.15)$$

Again it is worthwhile to comment on the pattern according to which the mean non-equilibrium quantity decomposes into its equilibrium part and the part obtained by replacing the momentum and position operators with their mean values. The mean value of the total energy is easily obtained by adding (3.14b) and (3.15).

We would now like to derive the free brownian particle density matrix as a limiting case of the oscillator density matrix. As a matter of fact we did work out such a density matrix, directly, by propagating the equilibrium free-particle distribution, given by (2.13a), but to our amazement the propagated distribution was unable to yield any average value for the displacement other than zero, even when the particles were acted upon by an external force. The case for the velocity was alright. Such a deficiency should be attributed to the fact that the eigenfunctions in the equilibrium matrix (2.13a) satisfy periodic boundary conditions (and not the conditions associated with bounding walls). Now, periodic boundary conditions imply that any point in space can be taken as origin and in this way the displacement averages are lost. One way for remedying the situation is by employing a more accurate density matrix, relating to the conditions of the bounding walls. Such a density matrix can be obtained from Pauli (1952), but here we shall adopt an alternative procedure, that of replacing the confining effect of a vessel by a three-dimensional oscillator well of an appropriate strength. Such a device was originally employed by Darwin (1930) in connection with what, in those days, used to be a thorny problem, the magnetization of free electrons confined in a finite region.

For the transition from the oscillator to the free particle an appropriate parameter is required. It is obtained by comparing (2.20), the oscillator equilibrium distribution, with the corresponding free-particle distribution (2.13a) when the oscillator frequency Ω approaches zero. With Ω in the vicinity of zero we can replace the hyperbolic functions in the oscillator equilibrium distribution by their expansions up to first order in Ω and in this way we enable ourselves to recover the equilibrium free-particle density matrix by

taking

$$\Omega^2 = \frac{2\pi}{m\beta V^{2/3}}. \tag{3.16}$$

This is precisely the value of Ω^2 used in Derrick's work (1969) in connection with statistical mechanics of interacting particles contained by a potential well instead of a box. In the derivation of (3.16) we had in mind that the volume V is very large, and so Ω is sufficiently small. Let us now use the Ω from (3.16) in the nonequilibrium density matrix (3.10) for the harmonic oscillator. We may then argue that because of the smallness of Ω we can expand the hyperbolic functions up to first order in Ω (if any) and take Ω in the dynamic parts of the distribution tending to zero. But, precisely this procedure will lead us to the deficient density matrix, which could be obtained by propagating the free-particle distribution (2.13a). To avoid this situation we should take account of the quantum effects of the oscillator well confinement, which in the end of the averaging processes will be dropped out. To this end we require the expansions to be taken a step further. The dimensionless parameter naturally arising is

$$\eta = (\beta\hbar\Omega)^2 = \frac{2\pi\beta\hbar^2}{mV^{2/3}} \tag{3.17}$$

which is a combination of the microscopic quantities $\hbar$, κ and the macroscopic quantities T, V. It is a measure of the quantum effects due to vessel confinement. For a volume of 1 cm^3 and ordinary temperature its magnitude is of the order of 10^{-40}.

Even with such an inconceivably small value for η it is necessary that it should be kept in the expression arising from the term

$$-\frac{m\Omega}{2\hbar\sin(\beta\hbar\Omega)}[\cosh(\beta\hbar\Omega)\{(x-\langle x\rangle)^2+(x'-\langle x\rangle)^2\}-2(x-\langle x\rangle).(x'-\langle x\rangle)] \tag{3.18}$$

in the exponential argument of the distribution (3.10) if we wish to extract the correct displacement averages. (3.18) is associated with the potential energy and, as such, incorporates the confinement effects. We retain η to first order in this term, and proceed elsewhere to the limit of Ω tending to zero apart from the normalization factor for which the asymptotic value $1/V$ was established earlier on. The above expression may be interpreted as the exponential argument of the distribution for harmonically bound particles in a state of equilibrium with reference to a moving frame following the average motion. The term preceding this relates to the kinetic energy, while the last term is the phase of a plane wave which, apart from the exponentially increasing factor, carries momentum equal to the average particle momentum.

With the above replacements and limiting procedures on the oscillator distribution (3.10) we obtain the following nonequilibrium density matrix for the brownian particle acted upon by a time dependent external force:

$$\rho^{\text{free}}(x|x';t) = \frac{1}{V}\exp\left[\frac{m}{2\hbar^2\beta}(x-x')^2\left\{1-\exp\left(\frac{2t}{t_0}\right)\right\}\right.$$

$$\left.-\frac{m}{2\hbar^2\beta}[(1+\tfrac{1}{3}\eta)\{(x-\langle x\rangle)^2+(x'-\langle x\rangle)^2\}-2(1-\tfrac{1}{6}\eta)(x-\langle x\rangle).(x'-\langle x\rangle)]\right]$$

$$\times\exp\left\{\frac{i}{\hbar}\exp\left(\frac{t}{t_0}\right)\langle m\dot{x}_{\text{op}}\rangle.(x-x')\right\}. \tag{3.19}$$

It can be easily verified that the expression for η given by (3.17) is such that (3.19) is correctly normalized.

The averages $\langle x \rangle$ and $\langle m\dot{x}_{op} \rangle$ appearing in (3.19) are given by the expressions for $\langle\!\langle X(t) \rangle\!\rangle$ and $\langle\!\langle P(t) \rangle\!\rangle$ for the free particle given by (2.18a, b) taken with $F(\tau) = e\mathscr{E}(\tau)$.

The above distribution yields the velocity, displacement and rest averages correctly. As pointed out, earlier on, the parameter η which may appear in the averaged expressions is to be put equal to zero. Re-evaluation of averages, relating to the forced brownian particles by means of the above density matrix, leads to the expressions obtained in the previous section.

By way of observation the following variant of the expression (3.19) for the free particle density matrix can yield the quantities of interest by averaging the usual (unmodified) operators:

$$\rho'^{\text{free}}(x|x';t) = \frac{1}{V}\exp\left(-\frac{m}{2\hbar^2\beta}\left[(1+\tfrac{1}{3}\eta)\{(x-\langle x\rangle)^2+(x'-\langle x\rangle)^2\}\right.\right.$$
$$\left.\left.-2(1-\tfrac{1}{6}\eta)(x-\langle x\rangle)\cdot(x'-\langle x\rangle)]\right)\exp\left(\frac{i}{\hbar}\langle m\dot{x}_{op}\rangle\cdot(x-x')\right). \tag{3.20}$$

Next, we shall obtain an equation of motion for the nonequilibrium density matrix for the general brownian particle.

4. Equation of motion for the density matrix propagator

Edwards (1965), in his paper on the density of states and the Boltzmann equation for electrons in disordered systems, works out a quantum equation suitable for brownian motion. He begins with the (deterministic) functional probability of finding, at time t, a particular wavefunction and its complex conjugate. Such a probability is the propagator of a Liouville equation, pertaining to the circumstances, which he obtains from the rate of change of his functional probability. Further, from the Liouville equation by suitable averaging he is led to a Fokker–Planck equation. His formalism is quite general, revealing a number of interesting features, and particularly making visible in a natural fashion the dependence of the collision time on the particle velocity.

However, our aim below is to provide a more restricted equation for the non-equilibrium distribution for the brownian particle within the framework of the Langevin model. We begin with the density matrix propagator constructed according to (3.7) and associated with the Langevin equation (2.1). This satisfies a Smoluchowski–Kolmogorov–Chapman type equation, that is,

$$\langle K(xt+\Delta t|x_1 0;[f])K^*(x't+\Delta t|x_2 0;[f])\rangle_{\text{fnl}}$$

$$= \int dy_1\, dy_2 \langle K(xt+\Delta t|y_1 t;[f])K^*(x't+\Delta t|y_2 t;[f])\rangle_{\text{fnl}}$$

$$\times \langle K(y_1 t|x_1 0;[f])K^*(y_2 t|x_2 0;[f])\rangle_{\text{fnl}}. \tag{4.1}$$

The procedure for the derivation of (4.1) is analogous to the one used for obtaining the corresponding classical case devised in Papadopoulos (1968). It should be noted here

that no restriction is imposed on the magnitude of the time interval Δt. However, for the purpose of deriving a differential equation for our density matrix propagator Δt will be taken small.

To facilitate the integrations we put:

$$y_1 = x - \xi, \qquad y_2 = x' - \xi'.$$

Then the short-time (deterministic) propagator, from t to $t + \Delta t$, takes the form:

$K(xt + \Delta t | x - \xi t; [f])$

$$\simeq \left\{ \frac{m}{2\pi i\hbar\Delta t} \exp\left(\frac{t}{t_0}\right) \right\}^{3/2} \exp\left\{ \frac{i}{\hbar} \exp\left(\frac{t}{t_0}\right) \left(\frac{m}{2\Delta t}\xi^2 - U(x - \xi, t)\Delta t \right) \right.$$

$$\left. + \frac{i}{\hbar} \int_t^{t+\Delta t} \exp\left(\frac{\tau}{t_0}\right) x(\tau) . f(\tau) d\tau \right\} \tag{4.2}$$

where by $U(x, t)$ we have denoted $U(x) - \boldsymbol{F} . \boldsymbol{x}$.

A similar expression can be written for the complex conjugate form of this propagator with dashed coordinates.

The ensemble average of the corresponding transition amplitude is:

$$\mathcal{T}(\xi; \xi') = \langle K(xt + \Delta t | x - \xi t; [f]) K^*(x't + \Delta t x' - \xi' t; [f]) \rangle_{\text{fnl}}$$

$$= \left\{ \frac{m}{2\pi\hbar\Delta t} \exp\left(\frac{t}{t_0}\right) \right\}^3$$

$$\times \exp\left\{ \frac{i}{\hbar} \exp\left(\frac{t}{t_0}\right) \left(\frac{m}{2\Delta t}(\xi^2 - \xi'^2) - (U(x - \xi, t) - U(x' - \xi', t))\Delta t \right) \right\}$$

$$\times \exp\left\{ -\frac{\Delta t}{2C\hbar^2} \exp\left(\frac{2t}{t_0}\right) \{(x - x')^2 - (\xi - \xi')^2\} \right\}. \tag{4.3}$$

The transition amplitude $\mathcal{T}(\xi; \xi')$ is the analogue of the short-time transition probability of the classical case. The last exponential in (4.3) is the outcome of the averaging against the thermal force distribution and embodies the statistical content of the transition amplitude.

Let us now proceed in the usual way of expanding the left-hand side of the integral equation (4.1) in powers of Δt and the right-hand side, except for the transition amplitude, in powers of ξ, ξ'. We keep terms up to first order in Δt, for higher-order terms will, in the end, vanish as Δt goes to zero.

Thus, from (4.1) we arrive at:

$$\langle KK^* \rangle + \Delta t \frac{\partial}{\partial t} \langle KK^* \rangle + \dots$$

$$= \int d\xi \, d\xi' \mathcal{T}(\xi; \xi') \left(1 - \xi . \frac{\partial}{\partial x} - \xi' . \frac{\partial}{\partial x'} + \frac{1}{2}\xi^2 \frac{\partial^2}{\partial x^2} \right.$$

$$\left. + \frac{1}{2}\xi'^2 \frac{\partial^2}{\partial x'^2} + \xi\xi' \frac{\partial^2}{\partial x \partial x'} + \dots \right) \langle KK^* \rangle \tag{4.4}$$

where $\langle KK^* \rangle$ is a shortened version of the density matrix propagator

$$\langle K(xt | x_1 0; [f]) K^*(x't | x_2 0; [f]) \rangle_{\text{fnl}}$$

which does not involve ξ or ξ'. It remains now to integrate the right-hand side of (4.4) over ξ and ξ'. Of the resulting expressions we need only retain terms up to first order in Δt. To this effect it is sufficient to employ the following approximate form for the transition amplitude:

$$\mathcal{T}(\xi;\xi') \simeq \left\{ \frac{m}{2\pi\hbar\Delta t} \exp\left(\frac{t}{t_0}\right) \right\}^3 \exp\left\{ \frac{im}{2\hbar\Delta t} \exp\left(\frac{t}{t_0}\right)(\xi^2 - \xi'^2) \right\}$$

$$\times \left\{ 1 - \frac{i}{\hbar} \exp\left(\frac{t}{t_0}\right)(U(x,t) - U(x',t))\Delta t - \frac{1}{2C\hbar^2} \exp\left(\frac{t}{t_0}\right)(x-x')^2\Delta t \right\} \qquad (4.5)$$

where on the right-hand side of (4.5) we have omitted terms involving ξ or ξ' which are already of order Δt, since upon integration the order of Δt would further increase. The following results will be used:

$$\int d\xi\, d\xi'\, \mathcal{T}(\xi;\xi') = 1 - \frac{i}{\hbar} \exp\left(\frac{t}{t_0}\right)(U(x,t) - U(x',t))\Delta t + O\{(\Delta t)^2\}$$

$$\int d\xi\, d\xi'\, \mathcal{T}(\xi;\xi')(\xi^2,\xi'^2) = \frac{\hbar}{i} \exp\left(-\frac{t}{t_0}\right)\frac{\Delta t}{m}(1,-1) + O\{(\Delta t)^2\}$$

$$\int d\xi\, d\xi'\, \mathcal{T}(\xi;\xi')(\xi,\xi',\xi\xi') = (0,0,0) + O\{(\Delta t)^2\}. \qquad (4.6)$$

Inserting the results (4.6) into (4.5) we can cancel out the $\langle KK^* \rangle$ on the left-hand side of (4.5) with the $\langle KK^* \rangle$ created on the right-hand side. Further, dividing by Δt on both sides and passing to the limit as Δt goes to zero we are left with the desired equation for our nonequilibrium density matrix:

$$i\hbar\frac{\partial}{\partial t}\langle KK^* \rangle = \mathcal{H}\langle KK^* \rangle - \mathcal{H}'\langle KK^* \rangle - \frac{i}{2C\hbar} \exp\left(2\frac{t}{t_0}\right)(x-x')^2\langle KK^* \rangle \qquad (4.7)$$

where $\mathcal{H}$ in (4.7) stands for the hamiltonian operator, corresponding to the lagrangian of our problem, that is,

$$\mathcal{H} = -\exp\left(-\frac{t}{t_0}\right)\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \exp\left(\frac{t}{t_0}\right)U(x,t). \qquad (4.8)$$

The dashed $\mathcal{H}$ in (4.7) is just the operator (4.8) with x replaced by x', and is acting on the dashed x's of the density matrix $\langle KK^* \rangle$.

The last term in the equation (4.7) for the nonequilibrium density matrix represents the effect of the collisions. With the exception of this term it is formally the usual density matrix equation. The equation as a whole can be considered as a quantum analogue of the Fokker–Planck equation for brownian motion in the single-particle configuration space.

Acknowledgments

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