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Relaxation Properties of Weakly Coupled Classical Systems

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The relaxation properties of a small classical system weakly coupled to a large classical system which acts as a heat bath are described using a generalized Fokker–Planck equation. The Fokker–Planck equation is derived in general using a modification of the elimination of fast variables techniques previously described. The specific example in which the small system is a harmonic oscillator linearly coupled to the heat bath is treated in detail and it is demonstrated that there is a dynamic frequency shift as well as a statistical shift of the oscillator frequency.

KEY WORDS: Relaxation; weak coupling; Fokker–Planck equation.

1. INTRODUCTION

The theoretical description of the relaxation properties of systems in the weak coupling limit has a long history. Both classical and quantum systems have been studied using a variety of techniques, such as projection operators, kinetic theory, stochastic theory, and Feynman path integrals. The results of these studies have yielded master or generalized Fokker–Planck equations for the system distribution function or generalized Langevin equations for the dynamical variables of the system. Interest in this subject has been revived due to the spate of work on quantum tunneling phenomena in condensed systems stimulated by the seminal studies of Leggett and co-workers (see ref. 1 for a review). The number of papers written on this subject in the past few years is extremely large and a variety of different results have been obtained.

It is a great personal and professional pleasure to dedicate this article to Nico van Kampen, whose influence permeates this work.

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It is difficult to overestimate the importance of the study of weakly coupled systems, since all modern treatments of time-dependent phenomena depend on either (1) the weak coupling of some variables of the system to other variables within the system, or (2) the weak coupling between the system and an external bath. Examples of category 1 are the hydrodynamic variables which are weakly coupled to the molecular variables of the system. Examples which may fall into either category 1 or 2 depending on one's point of view are spin variables which are weakly coupled to lattice variables. An example of category 2 is Brownian motion, where the weak coupling between the Brownian particle and the bath is due to the ratio of the masses of a bath particle to that of the Brownian particle. In all of these examples, the time dependence of the pertinent system variables is on a slow time scale compared to the time dependence of the molecular variables in the system or in the bath. There have been many successful treatments of these phenomena.

A much more difficult problem to treat is the case in which a system is weakly coupled to a bath but in which the time scales of the system variables are comparable to the time scales of the bath variables. We propose to study this problem using techniques previously developed.[2]

The modern treatment of weakly coupled systems is based on the seminal work by van Hove,[3] Zwanzig,[4] Montroll,[5] and Prigogine and his collaborators.[6] This work is based on splitting the system Hamiltonian H into two parts H_0 and λV and discussing the decay of the system to equilibrium with respect to the Hamiltonian H_0 due to the perturbation λV, using the weak coupling approximation. The results of these studies are master equations for the diagonal elements of the density matrix of the system. All of these treatments use the assumption that at $t=0$ there are random phases in the system. Unfortunately, there is no reason to believe that this initial condition is appropriate for the treatment of these systems. Indeed, it is the form of the distribution function or density matrix for times longer than a molecular time $\tau_m \approx 10^{-12}$ sec, but shorter than $\lambda^{-2}\tau_m$, that is important for deriving the relaxation equations of interest.

In the more recent developments, interest has been focused on the properties of a small system—molecular or mesoscopic—in weak interaction with a large, macroscopic system or heat bath.[7-20] The properties of interest are the mode of decay of the small system to equilibrium and the form of its equilibrium distribution. In almost all cases, special forms for the small system, the large system, and the weak coupling between the small and large systems have been chosen. The small system has been considered to be a two-level system or a harmonic oscillator; the large system has been considered to be a collection of uncoupled harmonic oscillators; and the coupling has been considered to be a product of linear functions of the bath and small-system coordinates. There has been no general scheme developed which ensures that the distribution function of the small system relaxes to the appropriate form when corrections higher order in λ are considered.

In this paper, we study the properties of a small system in weak interaction with a large system, using extensions of the techniques previously developed for treating classical and quantum Brownian motion.[2] We insist that the treatment yield relaxation equations such that the equilibrium distribution function for the system be of the proper form for the system in weak interaction with the bath to the appropriate order in the weak coupling parameter λ. Further, we insist that when the equilibrium solution is substituted into the relaxation equation the streaming and dissipative terms become zero separately. This is the only way of ensuring that the distinction between streaming and dissipative terms be properly maintained.

In Section 2, we describe the system under consideration, the projection operator used in this investigation, and its essential properties, and derive exact equations for the projected distribution function. In Section 3, we obtain a generalized Fokker–Planck equation. In Section 4, we apply these considerations to the special case in which the system is a harmonic oscillator weakly coupled to the bath by a potential linear in the system coordinates. All of these results are for classical systems but can be extended to quantum systems as well. Finally, in Section 5 we present a summary and conclusions.

2. THE PROJECTION OPERATOR AND EXACT DYNAMIC EQUATIONS

In this section we introduce a projection operator that allows us to separate the Liouville equation unambiguously into Euler (streaming) and dissipative parts.

We consider a classical overall system consisting of a system with a small number of degrees of freedom interacting with its environment. The latter, denoted the bath, has a large number of degrees of freedom. The Hamiltonian of the overall system, i.e., system plus bath, is

$$H = H_s(\mathbf{R}, \mathbf{P}) + H_b(\mathbf{r}, \mathbf{p}) + \lambda\Phi(\mathbf{R}, \mathbf{r}) \tag{2.1}$$

Here, $\mathbf{R}$ and $\mathbf{P}$ denote the small number of system coordinates and momenta, $\mathbf{r}$ and $\mathbf{p}$ denote the very large number of bath coordinates and momenta,

$$H_s = \mathbf{P}^2/2M + V(\mathbf{R}) \tag{2.2}$$

is the Hamiltonian of the system,

$$H_b = \mathbf{p}^2/2m + U(\mathbf{r}) \tag{2.3}$$

is the Hamiltonian of the N particles of the bath interacting via the potential $U(\mathbf{r})$, $\Phi(\mathbf{R}, \mathbf{r})$ is the interaction potential between the system and the bath, and λ is the strength of the interaction. The phase point of the bath is denoted by $X = (\mathbf{r}, \mathbf{p})$.

In the absence of interaction between the system and bath ($\lambda = 0$), the bath will relax toward equilibrium due to its large number of degrees of freedom, with characteristic time τ_b; the system, however, will not relax to equilibrium, because of its small number of degrees of freedom. The characteristic time of the system motion is τ_s. When the interaction is turned on ($\lambda \neq 0$) the overall system will relax to equilibrium. If the interaction is sufficiently weak, the relaxation time τ_R will be much longer than τ_b or τ_s. The relaxation to equilibrium for the overall system ($\lambda \neq 0$) and for the isolated bath ($\lambda = 0$) has to be understood in the sense that reduced quantities, depending on a small number of degrees of freedom, will relax toward their equilibrium values.

Before proceeding with the analysis of the time dependence of the distribution functions of the system, we present the equilibrium forms for these functions. The equilibrium distribution function for the overall system is

$$\rho_e(\mathbf{R}, \mathbf{P}, \mathbf{X}) = e^{-\beta H} \Big/ \int e^{-\beta H} \, d\mathbf{R} \, d\mathbf{P} \, dX \tag{2.4}$$

The reduced equilibrium function for the system is

$$W_e(\mathbf{R}, \mathbf{P}) \equiv \int \rho_e(\mathbf{R}, \mathbf{P}, X) \, dX = \frac{e^{-\beta H_s} \int e^{-\beta(H_b + \lambda\Phi)} \, dX}{\int e^{-\beta H_s} \, d\mathbf{R} \, d\mathbf{P} \int e^{-\beta(H_b + \lambda\Phi)} dX} \tag{2.5}$$

We define the quantity $\omega(R, \lambda)$ by

$$\begin{aligned} e^{-\beta\lambda\omega(\mathbf{R}, \lambda)} &\equiv \int e^{-\beta H_b} e^{-\beta\lambda\Phi} \, dX \Big/ \int e^{-\beta H_b} \, dX \\ &= \int \rho_b^{(0)}(X) e^{-\beta\lambda\Phi} \, dX \equiv \langle e^{-\beta\lambda\Phi} \rangle_0 \end{aligned} \tag{2.6}$$

where $\lambda\omega(\mathbf{R}, \lambda)$ is the potential of mean force due to the interaction of the system with the bath and

$$\rho_b^{(0)} = e^{-\beta H_b} \Big/ \int e^{-\beta H_b} \, dX \tag{2.7}$$

is the equilibrium distribution function for the isolated bath. Equations (2.4) and (2.5) can be rewritten

$$\rho_e(\mathbf{R}, \mathbf{P}, X) = \rho_b^{(0)} e^{-\beta(H_s + \lambda\Phi)} \Big/ \int e^{-\beta(H_s + \lambda\omega)} \, d\mathbf{R} \, d\mathbf{P} \tag{2.8}$$

and

$$W_e(\mathbf{R}, \mathbf{P}) = e^{-\beta(H_s + \lambda\omega)} \Big/ \int e^{-\beta(H_s + \lambda\omega)} \, d\mathbf{R} \, d\mathbf{P} \tag{2.9}$$

Finally, the conditional equilibrium function for the bath for fixed **R** and **P** is given by

$$\tilde{\rho}_e(R, X) \equiv \rho_e / W_e = \rho_b^{(0)} e^{-\beta\lambda\Phi} e^{\beta\lambda\omega} \tag{2.10}$$

where

$$\int \tilde{\rho}_e \, dX = 1 \tag{2.11}$$

and

$$\rho_e = \tilde{\rho}_e W_e \tag{2.12}$$

exactly.

The time evolution of the probability distribution function of the overall system is given by the Liouville equation

$$\partial\rho(\mathbf{R}, \mathbf{P}, \mathbf{X}, t)/\partial t = L\rho(\mathbf{R}, \mathbf{P}, \mathbf{X}, t) \tag{2.13}$$

where L is the total Liouvillian

$$L = L_s + L_b + \lambda L_I \equiv L_0 + \lambda L_I \tag{2.14}$$

The isolated system Liouvillian is

$$L_s = -\mathbf{P}/M \cdot \nabla_R + \nabla_R V(\mathbf{R}) \cdot \nabla_P \tag{2.15a}$$

the isolated bath Liouvillian is

$$L_b = -\mathbf{p}/m \cdot \nabla_r + \nabla_r U(\mathbf{r}) \cdot \nabla_p \tag{2.15b}$$

and the interaction Liouvillian is

$$L_I = \nabla_R \Phi \cdot \nabla_P + \nabla_r \Phi \cdot \nabla_p \tag{2.15c}$$

We wish to obtain an equation for the time dependence of the reduced probability density of the system

$$W(\mathbf{R}, \mathbf{P}, t) = \int \rho(\mathbf{R}, \mathbf{P}, X, t)\, dX \tag{2.16}$$

using projection operator techniques. The projection operator with the most felicitous properties is defined by

$$\mathsf{P}B = \tilde{\rho}_e \int B\, dX \tag{2.17}$$

where B is an arbitrary dynamical variable and $\tilde{\rho}_e$ is given in Eq. (2.10).

We introduce the quantities

$$y(t) \equiv \mathsf{P}\rho(t) = \tilde{\rho}_e W(\mathbf{R}, \mathbf{P}, t) \tag{2.18}$$

and

$$z(t) \equiv (1 - \mathsf{P})\, \rho(t) \equiv Q\rho(t) \tag{2.19}$$

The time derivatives of these quantities obey the equations

$$\dot{y}(t) = \tilde{\rho}_e \dot{W}(t) = \tilde{\rho}_e \left[L_s W(t) + \lambda \int \nabla_R \Phi \tilde{\rho}_e\, dX \cdot \nabla_P W(t) \right.$$
$$\left. + \lambda \nabla_P \cdot \int \nabla_R \Phi z(t)\, dX \right] \tag{2.20a}$$

and

$$\dot{z}(t) = QLQz(t) + QLy(t) \tag{2.20b}$$

which follow from Eq. (2.13) and the facts that

$$\mathsf{P}L_b B = 0, \qquad \mathsf{P}L_s B = \tilde{\rho}_e L_s \int B\, dX, \qquad \mathsf{P}L_I B = \tilde{\rho}_e \int \nabla_R \Phi \cdot \nabla_P B\, dX$$
$$\int y(t)\, dX = W(t), \qquad \int z(t)\, dX = 0 \tag{2.21}$$

It follows from the definition of $\tilde{\rho}_e$, Eq. (2.10), that

$$\nabla_R \int \tilde{\rho}_e\, dX = 0 = -\beta \int \tilde{\rho}_e (\lambda \nabla_R \Phi - \lambda \nabla_R \omega)\, dX \tag{2.22}$$

and thus

$$\nabla_R \omega = \int \tilde{\rho}_e \nabla_R \Phi\, dX$$

The term $QLy(t)$ in Eq. (2.20b) becomes

$$\begin{aligned} QLy(t) &= W(t)\, QL\tilde{\rho}_e + Q\tilde{\rho}_e LW(t) \\ &= W(t)\, L\tilde{\rho}_e + \lambda\tilde{\rho}_e \nabla_R(\Phi - \omega)\cdot\nabla_P W(t) \\ &= \lambda\tilde{\rho}_e \nabla_R(\Phi - \omega)\cdot(\nabla_P + \beta\mathbf{P}/M)\, W(t) \end{aligned} \tag{2.23}$$

Thus, Eqs. (2.20) become

$$\dot{W}(t) = \tilde{L}_s W(t) + \lambda\nabla_P \cdot \int \nabla_R \Phi z(t)\, dX \tag{2.24a}$$

$$\dot{z}(t) = QLQz(t) + \lambda\tilde{\rho}_e \nabla_R(\Phi - \omega)\cdot(\nabla_P + \beta\mathbf{P}/M)\, W(t) \tag{2.24b}$$

where

$$\tilde{L}_s \equiv L_s + \lambda\nabla_R\omega\cdot\nabla_P = -\mathbf{P}/M\cdot\nabla_R + \nabla_R(V + \lambda\omega)\cdot\nabla_P \tag{2.25}$$

is an effective Liouvillian corresponding to the Hamiltonian

$$\tilde{H}_s = P^2/2M + V(\mathbf{R}) + \lambda\omega(\mathbf{R}, \lambda) \tag{2.26}$$

Equations (2.24) are exact. Note that $\omega(\mathbf{R}, \lambda)$ can be expanded as a power series in λ starting with a λ^0 term. Since $\mathsf{P}\rho_e = \rho_e$, $z_e = 0$, and since $\tilde{L}_s W_e = (\nabla_P + \beta\mathbf{P}/M)\, W_e = 0$, the terms in Eqs. (2.24) involving W and z are separately equal to zero at equilibrium.

Substitution of the formal solution to Eq. (2.24b) into (2.24a) yields

$$\begin{aligned} \dot{W}(\mathbf{R}, \mathbf{P}, t) &= \tilde{L}_s W(t) + \lambda\nabla_P\cdot\int \nabla_R\Phi\, e^{QLQt} z(0)\, dX \\ &\quad + \lambda^2\nabla_P\cdot\int_0^t d\tau \int dX \nabla_R\Phi\, e^{QLQ\tau}\, \tilde{\rho}_e \nabla_R(\Phi - \omega)\cdot(\nabla_P + \beta\mathbf{P}/M)\, W(t - \tau) \end{aligned} \tag{2.27}$$

The first term on the rhs of Eq. (2.27) is a streaming or Euler term; the second term is an initial value term; and the third term involves a time-dependent correlation function. Again, Eq. (2.27) is an exact equation and each term on the rhs is zero at equilibrium.

Since Eq. (2.27) is exact, it is equivalent to Newton's laws for the overall system. It is in a suggestive form for reduction to a generalized Fokker–Planck equation when λ is small. This reduction is facilitated by the special properties of the projection operator, Eq. (2.17). These special properties are:

1. Since $\mathsf{P}\rho_e = \rho_e$, $z(t) \to 0$ as $t \to \infty$.
2. The streaming and dissipative terms in Eq. (2.27) are separately equal to zero in equilibrium.
3. The initial value term in Eq. (2.27) becomes negligible for $t > \tau_b$ because of the properties of the propagator $e^{QLQt}Q$ for essentially all initial conditions.
4. The last term on the rhs can be significantly simplified because of the properties of this propagator.

Other choices of projection operators have been previously used, but they have limited applicability since they do not have properties 1 and 2 and thus cannot be used for systematic expansions of Eqs. (2.24) or (2.27) in powers of λ.

3. A GENERALIZED FOKKER–PLANCK EQUATION

In this section, we obtain a generalized Fokker–Planck Equation from Eq. (2.27) which is valid in the weak coupling limit in which λ is small, t large, and $\lambda^2 t$ of arbitrary size. In carrying out this procedure, we must be careful not to neglect any terms which contribute to the $\lambda^2 t$ dependence of W. Extensions to higher orders in λ are straightforward even though they are complicated algebraically.

We first turn our attention to the initial value term in Eq. (2.27). The propagator $e^{QLQt}Q$ can be written

$$e^{QLQt}Q = \left[e^{L_0 t} + \lambda \int_0^t e^{L_0(t-\tau)} QL_I Q e^{L_0 \tau} \, d\tau + O(\lambda^2) \right] Q \tag{3.1}$$

where we have used the fact that $QL_0 Q = L_0 Q$. The propagator $e^{L_b t}$ has the property

$$\int dX \, Ce^{L_b t} QBz(0) = 0 \tag{3.2}$$

for $t > \tau_b$, where C and B are dynamical variables involving bath coordinates and/or momenta. This property follows from the assumption that the isolated bath relaxes to equilibrium on the time scale τ_b. Therefore, the initial value term in Eq. (2.17) is of order λ for $t < \tau_b$, λ^2 for $2\tau_b > t > \tau_b$, λ^3 for $3\tau_b > t > 2\tau_b$, etc. For a similar argument, see Mazur and Oppenheim.[21] For $\lambda \ll 1$, $\lambda\tau_b$ is negligible and the initial value term in Eq. (2.27) can be neglected.

The λ dependence of the last term on the rhs of Eq. (2.27) arises from the explicit factor of λ^2, the propagator $e^{QLQ\tau}$, the distribution function $\tilde{\rho}_e$, the potential of mean foce ω, and the distribution function $W(t-\tau)$. The λ-dependent terms in $\tilde{\rho}_e$ and $\nabla_R \omega$ will contribute to $O(\lambda^3 t)$ and thus we can substitute

$$\tilde{\rho}_e \nabla_R(\Phi - \omega) \simeq \rho_b^{(0)} \widehat{\nabla_R \Phi} \tag{3.3}$$

where

$$\widehat{\nabla_R \Phi} \equiv \nabla_R \Phi - \int \rho_b^{(0)} \nabla_R \Phi \, dX \tag{3.4}$$

The λ-dependent terms arising from an expansion of the propagator $e^{QLQ\tau}$ similar to Eq. (3.1) must be treated as perturbations if an appropriate transport equation is to be obtained (see, e.g., van Kampen and Oppenheim[2]). Since τ_s and τ_b may be comparable, we cannot neglect the time displacement of $W(t-\tau)$ in this term. Because of the properties of the propagator $e^{L_b \tau} Q$, the correlation function in this term is zero for times greater than τ_b and $W(t-\tau)$ can be written

$$W(t-\tau) \simeq [\exp(-\tilde{L}_s \tau)] \, W(t) \tag{3.5}$$

up to $O(\lambda^2)$, which follows from Eq. (2.27).

Finally, we can now approximate Eq. (2.27) by

$$\begin{aligned} \dot{W}(t) = \tilde{L}_s W(t) + \lambda^2 \nabla_P \cdot \int_0^\infty d\tau \int dX \, \nabla_R \Phi \\ \times \{\exp[(\tilde{L}_s + L_b)\tau]\} \, \rho_b^{(0)} \widehat{\nabla_R \Phi} \cdot (\nabla_P + \beta \mathbf{P}/M)[\exp(-\tilde{L}_s \tau)] \, W(t) \end{aligned} \tag{3.6}$$

for $t > \tau_b$. Equation (3.6) is correct through $O(\lambda^2 t)$. Indeed, it contains some parts of higher order terms due to the presence of the $\tilde{L}_s$ Liouvillians which, in principle, contain terms to all orders in λ. We have used the propagators $\exp(\tilde{L}_s \tau)$ in Eq. (3.6) in order to ensure that W_e is an exact solution to Eq. (3.6) to all orders in λ.

Again, the streaming and dissipative parts of Eq. (3.6) are separately equal to zero when $W(t) = W_e$. Because of the dissipative nature of the second term on the rhs of Eq. (3.6), $W(t) \to W_e$ as $t \to \infty$. The relaxation of $W(t)$ to W_e described by Eq. (3.6) is correct to order $\lambda^2 t$, but there are higher order terms $(\lambda^3 t)$ in the time dependence which have been omitted. These properties of Eq. (3.6) are due to the choice of the projection operator in Eq. (2.17).

Equation (3.6) can be written

$$\dot{W}(t) = \tilde{L}_s W(t) + \lambda^2 \nabla_P \cdot \int_0^\infty d\tau \, \langle \nabla_R \Phi \widehat{\nabla_R \Phi(-\tau)} \rangle_0 \times [e^{\tilde{L}_s \tau} \nabla_P e^{-\tilde{L}_s \tau} + \beta \mathbf{P}(-\tau)/M] \, W(t) \tag{3.7}$$

where the notation $\langle \cdot \rangle_0$ implies an average over $\rho_b^{(0)}$, $\nabla_R \Phi(-\tau) \equiv [\nabla_R \Phi(\mathbf{r}, \mathbf{R})](-\tau)$, and

$$\mathbf{r}(-\tau) = e^{+L_b \tau} \mathbf{r}, \qquad \mathbf{R}(-\tau) = e^{+\tilde{L}_s \tau} \mathbf{R}$$

Before applying Eq. (3.7) to a particular situation, we must retain $\tilde{L}_s$ to an appropriate order in λ.

The operator acting on $W(t)$ in Eq. (3.7) can be approximated in the following way:

$$\begin{aligned} e^{-\tilde{L}_s \tau} W(\mathbf{R}, \mathbf{P}, t) &= W(\mathbf{R}(\tau), \mathbf{P}(\tau), t) + O(\lambda^2) \\ \nabla_P e^{-\tilde{L}_s \tau} W(\mathbf{R}, \mathbf{P}, t) &= \nabla_P \mathbf{P}(\tau) \cdot \nabla_{\mathbf{P}(\tau)} W + \nabla_P \mathbf{R}(\tau) \cdot \nabla_{\mathbf{R}(\tau)} W + O(\lambda^2) \\ e^{+\tilde{L}_s \tau} \nabla_P e^{-\tilde{L}_s \tau} W(\mathbf{R}, \mathbf{P}, t) &= [e^{\tilde{L}_s \tau} \nabla_\mathbf{P} P(\tau)] \cdot \nabla_P W(\mathbf{R}, \mathbf{P}, t) \\ &\quad + [e^{\tilde{L}_s \tau} \nabla_P \mathbf{R}(\tau)] \cdot \nabla_R W(\mathbf{R}, \mathbf{P}, t) + O(\lambda^2) \end{aligned} \tag{3.8}$$

The error introduced into Eq. (3.7) by this approximation is of order λ^4.

If the characteristic time of the system τ_s is much longer than τ_b, Eq. (3.7) can be approximated by

$$\dot{W}(t) = \tilde{L}_s W(t) + \lambda^2 \int_0^\infty d\tau \, \langle \nabla_R \Phi e^{L_b \tau} \widehat{\nabla_R \Phi} \rangle_0 \colon \nabla_P (\nabla_P + \beta \mathbf{P}/M) \, W(t) \tag{3.9}$$

which is the usual Fokker–Planck equation.

In the next section, we solve Eq. (3.7) for a simple example which clarifies important aspects of the time dependences inherent in this equation.

4. HARMONIC OSCILLATOR WITH LINEAR COUPLING

In this section we analyze Eq. (3.7), through second order in λ, for the simple case of a one-dimensional overall system in which the system is a harmonic oscillator linearly coupled to the bath. Here,

$$H_s = P^2/2M + \tfrac{1}{2} M \Omega^2 R^2 \tag{4.1}$$

and

$$\Phi(R, r) = R \phi(r) \tag{4.2}$$

Without loss of generality, we assume that

$$\langle \phi \rangle_0 = 0 \tag{4.3}$$

To second order in λ, Eq. (3.7) becomes

$$\begin{aligned} W(t) &= \left(-P \frac{\partial}{\partial R} + M\Omega_1^2 R \frac{\partial}{\partial P} \right) W(t) \\ &\quad + \lambda^2 \frac{\partial}{\partial P} \int_0^\infty d\tau \, \langle \phi(\tau)\phi \rangle_0 \left[e^{+\tilde{L}_s \tau} \left(\frac{\beta P}{M} + \frac{\partial}{\partial P} \right) e^{-\tilde{L}_s \tau} W(t) \right] \end{aligned} \tag{4.4}$$

where

$$\tilde{L}_s = -P/M \, \partial/\partial R + M\Omega_1^2 R \, \partial/\partial P \tag{4.5}$$

and

$$\Omega_1^2 = \Omega^2 - \beta\lambda^2/M \langle \phi^2 \rangle_0 \tag{4.6}$$

Substitution of the results

$$\begin{aligned} R(\tau) &\equiv e^{-\tilde{L}_s \tau} R = R \cos \Omega_1 \tau + P/M\Omega_1 \sin \Omega_1 \tau \\ P(\tau) &\equiv e^{-\tilde{L}_s \tau} P = P \cos \Omega_1 \tau - M\Omega_1 R \sin \Omega_1 \tau \end{aligned} \tag{4.7}$$

into Eq. (3.8) and then into Eq. (3.7) yields

$$\begin{aligned} \dot{W}(t) &= -\frac{P}{M} \frac{\partial W(t)}{\partial R} + M\Omega_1^2 R \frac{\partial W(t)}{\partial P} \\ &\quad + \lambda^2 \Gamma_1 \frac{\partial}{\partial P} \left(\frac{\beta P}{M} + \frac{\partial}{\partial P} \right) W(t) \\ &\quad + \lambda^2 \Gamma_2 \frac{\partial}{\partial P} \left(\beta M \Omega_1^2 R + \frac{\partial}{\partial R} \right) W(t) \end{aligned} \tag{4.8}$$

where

$$\Gamma_1 = \int_0^\infty d\tau \, \langle \phi(\tau)\phi \rangle_0 \cos \Omega_1 \tau \tag{4.9}$$

$$\Gamma_2 = \int_0^\infty d\tau \, \frac{\langle \phi(\tau)\phi \rangle_0}{M\Omega_1} \sin \Omega_1 \tau \tag{4.10}$$

As was mentioned in Section 3, if $\Omega_1^{-1} \gg \tau_b$, $\Gamma_2 \to 0$, and we recover the standard Fokker–Planck equation.

Notice that for this particular example, the last term of Eq. (4.8) involves a correction to the frequency in addition to the shift coming from the Euler term. This correction is of a dynamic nature; namely, the equilibrium distribution function will be independent of it. This point will be clarified later once the exact solution of Eq. (4.8) is obtained.

In order to solve Eq. (4.8), we will follow very closely the method outlined by Chandrasekhar.[22] For convenience, we set $M=1$ in the following.

We first write down the associated subsidiary system of Eq. (4.8) (i.e., the equations for the first moments of the distribution):

$$\dot{P}=\tilde{\Omega}^2 R-\lambda^2\beta\Gamma_1 P \tag{4.11}$$

$$\dot{R}=P \tag{4.12}$$

where

$$\tilde{\Omega}^2=\Omega_1^2(1+\lambda^2\beta\Gamma_2) \tag{4.13}$$

Now, we introduce as variables two first integrals of Eqs. (4.11) and (4.12), that is,

$$\xi=(R\mu_1-P)e^{-\mu_2 t} \tag{4.14a}$$

$$\eta=(R\mu_2-P)e^{-\mu_1 t} \tag{4.14b}$$

where

$$\mu_1=-\frac{\lambda^2\Gamma_1\beta}{2}+i\left[\tilde{\Omega}^2-\left(\frac{\lambda^2\Gamma_1\beta}{2}\right)^2\right]^{1/2} \tag{4.15a}$$

$$\mu_2=-\frac{\lambda^2\Gamma_1\beta}{2}-i\left[\tilde{\Omega}^2-\left(\frac{\lambda^2\Gamma_1\beta}{2}\right)^2\right]^{1/2} \tag{4.15b}$$

are the roots of the secular equation of the system (4.11) and (4.12),

$$\mu^2+\lambda^2\beta\Gamma_1\mu+\tilde{\Omega}^2=0 \tag{4.16}$$

where we have assumed that Ω is $O(1)$, giving rise to complex roots.

In these variables, and by making the further transformation

$$W(\xi,\eta;t)=e^{\lambda^2\Gamma_1\beta t}\chi(\xi,\eta;t) \tag{4.17}$$

Eq. (4.8) becomes

$$\begin{aligned}\frac{\partial\chi(t)}{\partial t}&=\lambda^2(\Gamma_1-\Gamma_2\mu_1)e^{-2\mu_2 t}\frac{\partial^2}{\partial\xi^2}\chi(t)\\&+\lambda^2(\Gamma_1-\Gamma_2\mu_2)e^{-2\mu_1 t}\frac{\partial^2}{\partial\eta^2}\chi(t)\\&+\lambda^2[2\Gamma_1-\Gamma_2(\mu_1+\mu_2)]e^{-(\mu_1+\mu_2)t}\frac{\partial^2}{\partial\eta\,\partial\xi}\chi(t)\end{aligned} \tag{4.18}$$

The solution of Eq. (4.18) for the initial condition

$$\chi(t=0)=\delta(\xi-\xi_0)\,\delta(\eta-\eta_0) \tag{4.19}$$

that is, corresponding to $W(P, R;\ t=0)=\delta(P-P_0)\,\delta(R-R_0)$, where $\xi_0=R_0\mu_1-P_0$ and $\eta_0=R_0\mu_2-P_0$, is

$$\chi(\xi, \eta, t, \xi_0, \eta_0)=\frac{1}{2\Pi\Delta^{1/2}}\exp\left\{-\frac{1}{\Delta}\left[v(t)(\xi-\xi_0)^2+u(t)(\eta-\eta_0)^2 - w(t)(\xi-\xi_0)(\eta-\eta_0)\right]\right\} \tag{4.20}$$

where

$$v(t)=\lambda^2(\Gamma_1-\Gamma_2\mu_2)\frac{1-e^{-2\mu_1 t}}{2\mu_1} \tag{4.21a}$$

$$u(t)=\lambda^2(\Gamma_1-\Gamma_2\mu_1)\frac{1-e^{-2\mu_2 t}}{2\mu_2} \tag{4.21b}$$

$$w(t)=\lambda^2[2\Gamma_1-\Gamma_2(\mu_1+\mu_2)]\,\frac{1-e^{-(\mu_1+\mu_2)t}}{\mu_1+\mu_2} \tag{4.21c}$$

$$\Delta=4u(t)\,v(t)-w^2(t) \tag{4.21d}$$

Hence, the normalized solution $W(t)$ in the variables P and R, whose initial condition is $W(0)=\delta(P-P_0)\,\delta(R-R_0)$, is

$$W(P, R, t; P_0, R_0) = \frac{\mu_1+\mu_2}{2\Pi\Delta^{1/2}}\,e^{\lambda^2\beta\Gamma_1 t} \times \chi((R\mu_1-P)e^{-\mu_2 t}, (R\mu_2-P)e^{-\mu_1 t}, t; (R_0\mu_1-P_0), (R_0\mu_2-P_0)) \tag{4.22}$$

Although it is evident that $W(t)$ is a Gaussian function in P and R, its time dependence is somewhat complicated and not very illuminating. Nevertheless, we can look at the time evolution of its moments and at some limiting cases.

First of all we note that when $t\to\infty$, we obtain the equilibrium distribution function W_e, valid up to second order in λ,

$$W_e(P, R)=\frac{\exp[-\beta(P^2/2+\frac{1}{2}\Omega_1^2R^2)}{\int dP\,dR\exp[-\beta(P^2/2+\frac{1}{2}\Omega_1^2R^2)]} \tag{4.23}$$

that is, $\tilde{L}_s W_e=0$.

Note that at equilibrium the frequency of the oscillator is given by Ω_1 only [see Eq. (4.6)]; that is, only the streaming shift contributes, as predicted.

In order to analyze the time dependence, we calculate two of the second moments of the distribution, $\overline{P^2(t)}$ and $\overline{R^2(t)}$:

$$\overline{P^2(t)} = \int dP\, dR\, P^2 W(P, R, t) \tag{4.24a}$$

$$\overline{R^2(t)} = \int dP\, dP\, dR\, R^2 W(P, R, t) \tag{4.24b}$$

which give

$$\begin{aligned}\overline{P^2(t)} = e^{-\lambda^2\beta\Gamma_1 t}&\left[-\frac{\tilde{\Omega}^2}{\omega} R_0 \sin \omega t + P_0\left(\cos \omega t - \frac{\lambda^2\beta\Gamma_1}{2\omega}\sin \omega t\right)\right]^2 \\ &+\frac{1}{\beta}\left(1 + e^{-\lambda^2\beta\Gamma_1 t}\left\{-1 + \frac{\lambda^2\beta\Gamma_1}{2\omega}\sin 2\omega t\right.\right. \\ &\left.\left.+\frac{1}{\omega^2}\left[\omega^2 - \left(\frac{\lambda^2\beta\Gamma_1}{2}\right)^2 - \frac{\tilde{\Omega}^4}{\Omega_1^2}\right]\sin^2 \omega t\right\}\right)\end{aligned} \tag{4.25a}$$

$$\begin{aligned}\overline{R^2(t)} = e^{-\lambda^2\beta\Gamma_1 t}&\left[R_0\left(\cos \omega t + \frac{\lambda^2\beta\Gamma_1}{2\omega}\sin 2\omega t\right) + \frac{1}{\omega} P_0 \sin \omega t\right]^2 \\ &+\frac{1}{\beta\Omega_1^2}\left(1 + e^{-\lambda^2\beta\Gamma_1 t}\left\{-1 + \frac{\lambda^2\beta\Gamma_1}{2\omega}\sin 2\omega t\right.\right. \\ &\left.\left.+\frac{1}{\omega^2}\left[\tilde{\Omega}^2 - \Omega_1^2 + \left(\frac{\lambda^2\beta\Gamma_1}{2}\right)^2\right]\sin^2 \omega t\right\}\right)\end{aligned} \tag{4.25b}$$

where

$$\omega = [\tilde{\Omega}^2 - (\lambda^2\beta\Gamma_1/2)^2]^{1/2} \tag{4.26}$$

From Eqs. (4.25) and (4.26) we find that the time evolution is given by the expected exponential relaxation, times an oscillatory term. The frequency of such oscillations, apart from the standard shift of the friction coefficient, is given by $\tilde{\Omega}$, that is, the frequency that involves both the streaming and the "dissipative" term; see Eq. (4.13). This is the dynamical shift to the frequency to which we referred earlier. It is a dynamical effect since its presence can only be detected while the system is relaxing toward equilibrium and does not affect the stationary state. We emphasize once more that this effect is due to the fact that the natural time scale of the system is comparable with the relaxation time of the bath.

In the weak coupling limit, Eqs. (4.25) become

$$\overline{P^2(t)} \simeq e^{-\lambda^2\beta\Gamma_1 t}(P_0 \cos \omega t - R_0/\Omega \sin \omega t)^2 + 1/\beta(1 - e^{-\lambda^2\beta\Gamma_1 t}) \tag{4.27a}$$

$$\overline{R^2(t)} \simeq e^{-\lambda^2\beta\Gamma_1 t}(R_0 \cos \omega t + P_0/\Omega \sin \omega t)^2 + 1/\beta\Omega^2(1 - e^{-\lambda^2\beta\Gamma_1 t}) \tag{4.27b}$$

with

$$\omega \simeq \Omega + \lambda^2/2(\beta\Omega\Gamma_2 - \beta\langle\phi^2\rangle_0/\Omega) \tag{4.28}$$

The frequency ω contains a dynamic shift $\sim \lambda^2\beta\Omega\Gamma_2/2$ and a statistical shift $\sim -\lambda^2\beta\langle\phi^2\rangle_0/2\Omega$, neither of which can be neglected on the $\lambda^2 t$ time scale.

5. SUMMARY AND CONCLUSIONS

The main aim of this paper has been to derive the relaxation properties of a small system weakly coupled to a heat bath in a systematic fashion using classical mechanics. This is accomplished by introducing the projection operator P [Eq. (2.17)], where

$$\mathsf{P}B = \tilde{\rho}_e \int B \, dX \tag{5.1}$$

where $\tilde{\rho}_e$ is the equilibrium conditional distribution function for the bath in the presence of fixed system coordinates and momenta. The introduction of an effective system Hamiltonian [Eq. (2.26)] and its Liouvillian [Eq. (2.15)] including the potential of mean force facilitates the derivation. An exact equation for the time dependence of the reduced distribution function of the system is obtained [Eq. (2.27)]. This equation can be approximated to any order in λ, the strength of the system–bath interaction. To order λ^2, a generalized Fokker–Planck equation is obtained.

The general results are applied to the specific problem in which the system is a harmonic oscillator linearly coupled to a bath. It is demonstrated that the system relaxes to equilibrium in an oscillating fashion with a frequency that is shifted from the frequency of the isolated oscillator by dynamic as well as statistical shifts. The dynamic shifts do not appear in the equilibrium distribution function, whereas the statistical shifts do.

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