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Non-markovian diffusion and Fokker–Planck equations for brownian oscillators

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A generalized diffusion equation is derived from the Mori–Kubo generalized Langevin for a brownian oscillator subject to gaussian random but in general non-markovian noise. This equation involves a time-dependent diffusion function rather than a phenomenological diffusion constant. For long times the diffusion function approaches a constant for overdamped markovian oscillators; only in the limit of extreme overdamping is the phenomenological theory recovered.

A previously derived generalized phase space Fokker–Planck equation for the brownian oscillator is shown to have incorrect short-time behaviour. The difficulty is traced to a transient systematic component of the Mori random force which is non-vanishing for classical lattices at 0 K.

Fokker–Planck and diffusion equations for the brownian oscillator are derived from a generalized Langevin representation equivalent to, but distinct from, that of Mori and Kubo. The random force in this representation lacks the systematic transient component. The Fokker–Planck and diffusion equations obtained from this alternative Langevin representation are thus correct at all times.

1. INTRODUCTION

Recently we have presented generalized Fokker–Planck equations for non-markovian free brownian particles and brownian oscillators [1]. These equations are obtained as exact transformations of the generalized Langevin equation for a brownian oscillator of mass m and frequency ω

$$\ddot{x}(t) = -\omega^2 x(t) - \int_0^t \beta(t-\tau)\mathbf{x}(\tau)\, d\tau + m^{-1}\mathbf{f}(t), \tag{1.1}$$

derived by Mori [2] and Kubo [3]. The only restrictive assumption in our derivation is that the noise term $\mathbf{f}(t)$ is gaussian random. The main result of our earlier work is the following generalized Fokker–Planck equation for the brownian oscillator phase space distribution function $P[\mathbf{x}, \mathbf{x}_0;\ \mathbf{u}, \mathbf{u}_0;\ t]$

$$\left\{\frac{\partial}{\partial t} + \mathbf{u}\cdot\frac{\partial}{\partial \mathbf{x}} - \tilde{\omega}^2(t)\mathbf{x}\cdot\frac{\partial}{\partial \mathbf{u}}\right\} P[\mathbf{x}, \mathbf{x}_0;\ \mathbf{u}, \mathbf{u}_0;\ t]$$

$$= \tilde{\beta}(t)\frac{\partial}{\partial \mathbf{u}}\cdot[\mathbf{u}P] + \frac{k_B T}{m}\tilde{\beta}(t)\frac{\partial^2 P}{\partial \mathbf{u}^2} + \frac{k_B T}{m\omega^2}[\tilde{\omega}^2(t) - \omega^2]\frac{\partial}{\partial \mathbf{u}}\cdot\frac{\partial P}{\partial \mathbf{x}}, \tag{1.2}$$

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where $\tilde{\omega}^2(t)$ and $\tilde{\beta}(t)$ are time-dependent frequency and friction functions discussed elsewhere [1] and defined here in the Appendix. Notice that equation (1.2) differs from both the phenomenological Fokker–Planck equation [4, 5] and the often derived non-markovian Fokker–Planck equations with retarded kernels [6].

This paper deals with three issues. We first develop in § 2 a generalized diffusion equation (2.10) for the brownian oscillator position distribution function from equation (1.1). [The generalized diffusion equation for a free brownian particle has been considered earlier by Dufty [7]]. The generalized diffusion equation is similar in form to the classical diffusion equation [4] but involves a time-dependent diffusion function $D(t)$ rather than a diffusion constant.

We examine in § 3 the long-time behaviour of $D(t)$. We consider $D(t)$ for three brownian oscillators; an overdamped and an underdamped markovian oscillator $[\beta(t)=2\beta\,\delta(t)]$ and a harmonically bound particle in a Debye lattice. For the latter two oscillators (both are underdamped) $D(t)$ is periodic for long times with poles and zeroes on the real time axis. Thus a diffusion equation with a constant diffusion coefficient is not approached asymptotically for these cases. For the overdamped oscillator, $D(t) \underset{t\to\infty}{\to} \tilde{D}$, a constant, asymptotically and an equation (3.14) identical in form to the phenomenological equation emerges. The effective diffusion coefficient $\tilde{D}$, equations (3.15, 3.16), differs from the Einstein result $D=k_{\mathrm{B}}T/\beta m$ except in the limit of extreme overdamping, $\omega \ll \beta$.

Our second concern here is with a flaw in equation (1.2) which was not noticed previously. We find in § 4 that equation (1.2) does not reduce properly at short times to the Liouville equation for a free harmonic oscillator. This defect arises because of an unexpected property of equation (1.1) which has apparently not been noticed previously. The Mori random force $\mathbf{f}(t)$ contains a *systematic transient* component which (*a*) shifts the frequency ω at $t=0$ to a short-time frequency ω_0 [see equation (1.3)], (*b*) causes $\mathbf{f}(t)$ to be *non-vanishing* for *classical* systems at $T=0$ K. The existence of this systematic transient term is inconsistent with our assumption that $\mathbf{f}(t)$ in equation (1.1) is gaussian random; hence the defect in equation (1.1) at short times.

Finally, in § 5, we examine the Fokker–Planck and diffusion equations derived from a generalized Langevin equation of the form [8–12]

$$\ddot{x}(t) = -\omega_0{}^2\,x(t) + \int_0^t \Theta(t-\tau)x(\tau)\,d\tau + \frac{1}{m}\,\mathbf{R}(t). \tag{1.3}$$

While equations (1.1) and (1.3) are equivalent, the individual terms in the equations differ; i.e. $\omega \neq \omega_0$, $\Theta(t-\tau)\mathbf{x}(\tau) \neq -\beta(t-\tau)\dot{\mathbf{x}}(\tau)$, and $\mathbf{R}(t) \neq \mathbf{f}(t)$. $\mathbf{R}(t)$, in particular, is rigorously gaussian for all times. Consequently the non-markovian Fokker–Planck and diffusion equations derived from equation (1.3) are valid for all times. For short times they correctly describe free harmonic motion; for long times they become identical in form to the equations derived from equation (1.1). Equation (1.3), however, has been derived only for fully harmonic systems and hence the generalized Fokker–Planck and diffusion equations derived from equation (1.3) hold only for such systems.

2. Generalized diffusion equations from the Mori–Kubo Langevin equation

We first consider the diffusion equation which is equivalent to the Mori [2]–Kubo [3] generalized Langevin equation (1.1) for the case that $\mathbf{f}(t)$ in equation

(1.1) is gaussian noise. We require as a supplement to equation (1.1) the fluctuation-dissipation result [2–3]

$$\beta(t)=\frac{\langle \mathbf{f}(t)\,.\,\mathbf{f}_0\rangle}{3k_BTm}. \tag{2.1}$$

Equation (2.1) is an expression of the detailed balance between energy loss and gain processes which enforce the decay of fluctuations from thermal equilibrium. Since the derivation of an equivalent diffusion equation from equations (2.1) and (2.2) parallels our earlier development of generalized Fokker–Planck equations [1], we will only outline the calculation here.

Solving equation (1.1) for the trajectory $\mathbf{x}(t)$ yields

$$\mathbf{x}(t)=\chi_x(t)\mathbf{x}_0+\chi_u(t)\mathbf{u}_0+m^{-1}\int_0^t \chi_u(t-\tau)\mathbf{f}(\tau)\,d\tau. \tag{2.2}$$

In equation (2.2) $\mathbf{x}_0$ and $\mathbf{u}_0$ are the initial conditions of the oscillator and $\chi_x(t)$ and $\chi_u(t)$ are brownian susceptibilities. From equation (2.2) one may verify

$$\chi_x(t)=\frac{m\omega^2}{3k_BT}\langle \mathbf{x}(t)\,.\,\mathbf{x}_0\rangle \tag{2.3}$$

and

$$\chi_u(t)=\frac{m}{3k_BT}\langle \mathbf{x}(t)\,.\,\mathbf{u}_0\rangle. \tag{2.4}$$

To obtain equation (2.3) we have used the generalized equipartition result [1]

$$\langle {x_0}^2\rangle=\frac{3k_BT}{m\omega^2}. \tag{2.5}$$

Notice that the brackets $\langle\ \rangle$ in equation (2.5) denote an average over the full oscillator plus bath canonical distribution function ; hence ω is a renormalized, rather than a primitive, oscillator frequency. We will return to this point in § 4.

Since $\mathbf{f}(t)$ is assumed Gaussian, the conditional probability distribution function for the particle position $\mathbf{x}$ given the initial conditions $\mathbf{x}_0$, $\mathbf{u}_0$ is

$$P[\mathbf{x}\,;\ \mathbf{x}_0,\mathbf{u}_0\,;\ t]=\left\{\frac{3}{2\pi A_{11}(t)}\right\}^{3/2}\exp\left\{-\frac{3}{2A_{11}(t)}[x-\chi_x(t)\mathbf{x}_0-\chi_u(t)\mathbf{u}_0]^2\right\}, \tag{2.6}$$

where [1]

$$A_{11}(t)=-\frac{3k_BT}{m}\{{\chi_u}^2(t)+\omega^{-2}({\chi_x}^2(t)-1)\}. \tag{2.7}$$

The conditional probability for $\mathbf{x}$ given an initial thermal distribution of velocities $\mathbf{u}_0$ is found by averaging equation (2.6) over the Boltzmann velocity distribution. This yields

$$P[\mathbf{x},\mathbf{x}_0\,;\ t]^-=\left\{\frac{3}{2\pi\sigma(t)}\right\}^{3/2}\exp\left\{-\frac{3}{2\sigma(t)}[\mathbf{x}-\chi_x(t)\mathbf{x}_0]^2\right\}, \tag{2.8}$$

where

$$\sigma(t)=\frac{3k_B T}{m\omega^2}[1-\chi_x^2(t)]. \tag{2.9}$$

A diffusion equation which generates $P(\mathbf{x}, \mathbf{x}_0; t)$ may be derived by the same method used elsewhere [1] to derive the generalized Fokker–Planck equations. A calculation gives

$$\frac{\partial P}{\partial t}[\mathbf{x}, \mathbf{x}_0\,;\; t]=-\frac{d\ln\chi_x(t)}{dt}\nabla\,.\,[\mathbf{x}P(\mathbf{x}, \mathbf{x}_0\,;\; t)]+D(t)\nabla^2 P(\mathbf{x}, \mathbf{x}_0\,;\; t), \tag{2.10 a}$$

where

$$D(t)=\tfrac{1}{6}\left[\dot\sigma(t)-2\sigma(t)\frac{d\ln\chi_x(t)}{dt}\right]. \tag{2.10 b}$$

Notice that equation (2.10 *a*) is identical in form to the phenomenological diffusion equation for a markovian brownian oscillator $[\beta(t)=2\beta\delta(t)]$ which is [4]

$$\frac{\partial P}{\partial t}[\mathbf{x}, \mathbf{x}_0\,;\; t]=\frac{\omega^2}{\beta}\nabla\,.\,\{\mathbf{x}P[\mathbf{x}, \mathbf{x}_0\,;\; t]\}+D\nabla^2 P[\mathbf{x}, \mathbf{x}_0\,;\; t], \tag{2.11}$$

with

$$D=\frac{k_B T}{\beta m}. \tag{2.12}$$

The coefficients in the generalized diffusion equation, however, depend on time.

3. Long-time limit of the generalized diffusion equation

We next analyse the long-time behaviour of the generalized diffusion equation (2.10 *a*). We consider three cases explicitly, a particle harmonically bound in a Debye lattice, an underdamped markovian brownian oscillator, and an overdamped markovian oscillator. For all three cases we examine the quantity [see equation (2.10)]

$$C(t)=-\frac{d\ln\chi_x(t)}{dt}. \tag{3.1}$$

This is sufficient since

$$\lim_{t\to\infty} D(t)=\frac{k_B T}{m\omega^2}C(t). \tag{3.2}$$

Equation (3.2) follows from equations (2.9) and (2.10 *b*), since $\chi_x(t)$ and $\chi_u(t)$ vanish at long times. Combining equations (2.10 *a*), (3.1), and (3.2) thus shows that for long times

$$\frac{\partial P[\mathbf{x}, \mathbf{x}_0\,;\; t]}{\partial t}=C(t)\nabla\,.\,[\mathbf{x}P[\mathbf{x}, \mathbf{x}_0\,;\; t]]+D(t)\nabla^2 P[\mathbf{x}, \mathbf{x}_0\,;\; t]. \tag{3.3}$$

Comparison of equation (3.3) with the phenomenological diffusion equation (2.12) shows that according to the phenomenological theory

$$C(t)=\beta^{-1}\omega^2. \tag{3.4}$$

We now examine $C(t)$ for the three models mentioned above.

3.1. *Debye oscillator*

For the Debye oscillator the position autocorrelation function $\chi_x(t)$ is [1]

$$\chi_x(t)=\frac{\sin \omega_0 t}{\omega_0 t}, \tag{3.5}$$

where ω_D is the Debye frequency. Thus by equation (3.1)

$$\lim_{t\to\infty} C(t)= -\omega_0 \cot \omega_0 t. \tag{3.6}$$

We see that for the Debye oscillator $C(t)$ never approaches a constant value and the phenomenological diffusion equation is not approached assymptotically. Along the real time axis $D(t)$ is periodic rather than convergent and has poles and zeroes.

3.2. *Markovian underdamped oscillator*

The asymptotic behaviour of $C(t)$ and $D(t)$ displayed by the Debye oscillator is a general feature of underdamped oscillators. As a second example we consider the markovian underdamped oscillator. For this case the generalized Langevin equation (1.2) reduces to markovian form, since $\beta(t)=2\beta\delta(t)$ and the quantity

$$\omega_1=\{\omega^2-\tfrac{1}{4}\beta^2\}^{1/2}, \tag{3.7}$$

is positive and real. The autocorrelation function $\chi_x(t)$ is [4]

$$\chi_x(t)=\exp(-\tfrac{1}{2}\beta t)\left\{\cos \omega_, t+\frac{\beta}{2\omega_1}\sin \omega_1 t\right\}, \tag{3.8}$$

and thus

$$\lim_{t\to\infty} C(t)=\left[\omega_1{}^2+\frac{\beta^2}{4\omega_1}\right]\left[\frac{\sin \omega_1 t}{\cos \omega_1 t+\dfrac{\beta}{2\omega_1}\sin \omega_1 t}\right]. \tag{3.9}$$

We see that $C(t)$ does not approach a long-time limit. Rather it again displays periodic behaviour with poles and zeroes along the real axis.

3.3. *Markovian overdamped oscillator*

For the markovian overdamped oscillator $\beta(t)=\beta\delta(t)$ and the quantity

$$\beta_1=[\tfrac{1}{4}\beta^2-\omega^2]^{1/2}, \tag{3.10}$$

is positive and real. The correlation function $\chi_x(t)$ is [4]

$$\chi_x=\exp\left(-\frac{\beta}{2}t\right)\left\{\cosh \beta_1 t+\frac{\beta}{2\beta_1}\sinh \beta_1 t\right\}, \tag{3.11}$$

and thus

$$\lim_{t\to\infty} C(t)=\frac{\beta}{2}-\beta_1. \tag{3.12}$$

Hence by equation (3.2)

$$\lim_{t\to\infty} D(t)=\frac{k_B T}{m\omega^2}\left\{\frac{\beta}{2}-\beta_1\right\}. \tag{3.13}$$

Thus for overdamped markovian oscillators the coefficients in the diffusion equation (3.3) approach constants and equation (3.3) becomes

$$\frac{\partial P[\mathbf{x}, \mathbf{x}_0\,;\ t]}{\partial t} = \frac{\omega^2}{\tilde{\beta}} \nabla \cdot \{\mathbf{x}P[\mathbf{x}, \mathbf{x}_0\,;\ t]\} + \tilde{D}\nabla^2 P[\mathbf{x}, \mathbf{x}_0\,;\ t], \tag{3.14}$$

where the effective friction coefficient $\tilde{\beta}$ is

$$\tilde{\beta} = \omega^2 \left\{\frac{\beta}{2} - \beta_1\right\}^{-1}. \tag{3.15}$$

The effective diffusion coefficient is related to $\tilde{\beta}$ by an Einstein relation ; i.e.

$$\tilde{D} = \frac{k_B T}{\tilde{\beta} m}. \tag{3.16}$$

Thus for overdamped markovian oscillators the classical equation holds. The friction coefficient appearing in the diffusion equation (3.14) is, however, a modified one, $\tilde{\beta}$. The phenomenological theory is recovered, however, in the limit of extreme overdamping $\beta \gg \omega$. Then expansion of equation (3.10) gives $\beta_1 = \beta/2 - \omega^2/\beta + \dots$ and by equation (3.15)

$$\lim_{\omega/\to\beta 0} \tilde{\beta} = \beta. \tag{3.17}$$

Combining equations (3.14) gives the classical diffusion theory of equations (2.11) and (2.12).

4. Short-time defect of the generalized Fokker–Planck equation

We now turn to the second concern of this paper, the improper short-time behaviour of the generalized Fokker–Planck equation (1.2). We will trace this improper behaviour to counter intuitive properties of the Mori random force. We will find that the Mori random force contains a systematic transient component which is non-vanishing for classical systems at 0 K. This transient component, which was implicitly neglected in our derivation of equation (1.2), shifts the apparent oscillator frequency from ω to ω_0 at short times.

The subtle behaviour of the Mori random force may be seen most easily by comparing the Langevin equations (1.1) and (1.3). This comparison is facilitated by integrating equation (1.3) by parts. This gives [10]

$$\ddot{\mathbf{x}}(t) = -\omega^2 \mathbf{x}(t) - \int_0^t \beta_R(t-\tau)\dot{\mathbf{x}}(\tau)\, d\tau + \frac{1}{m} f_R(t), \tag{4.1}$$

where [10]

$$\beta_R(t) = \frac{\langle \mathbf{R}(t) \cdot \mathbf{R}(0)\rangle}{3mk_B T}, \tag{4.2}$$

and

$$f_R(t) = \mathbf{R}(t) - m\beta_R(t)\mathbf{x}(0)\,; \tag{4.3}$$

ω is defined in equation (2.5).

Equations (4.1) and (4.2) with equation (2.5) are similar (though not identical) in structure to equations (1.1) and (2.1) with (2.5) and may be used to *illustrate* the non-intuitive properties of the Mori random force.

Let us consider a hypothetical classical system at 0 K. Naively we would identify $\mathbf{f}_R(t)$ with random heat-bath motion and thus set $\mathbf{f}_R(t)=\mathbf{0}$. This then yields for the short-time motion of $\mathbf{x}(t)$ at 0 K

$$\ddot{x}(t) = -\omega^2\mathbf{x}(t), \tag{4.4}$$

or

$$x(t) = \cos \omega t \mathbf{x}(0) + \frac{\sin \omega t}{\omega} \dot{\mathbf{x}}(0), \tag{4.5}$$

for short times.

Our identification of $\mathbf{f}_R(t)$ solely with heat-bath motion is, however, incorrect. The random force $\mathbf{R}(t)$ has only heat-bath contributions and does indeed vanish classically at $T=0$ K [10]; $\mathbf{f}_R(t)$, however, contains the additional transient term $\beta_R(t)\mathbf{x}(0)$ which is independent of heat-bath motion. When this term is properly included in equation (4.1), one finds that for classical lattices at 0 K the short-time limit of equation (4.1) is

$$\ddot{\mathbf{x}}(t) = -\omega_0^2\,\mathbf{x}(t), \tag{4.6}$$

which is expected from equation (1.3).

Thus the presence of the transient term in $\mathbf{f}_R(t)$ which is non-vanishing at $T=0$ K shifts the apparent frequency ω to a short time frequency ω_0. Identical behaviour occurs for the Mori random force $\mathbf{f}(t)$, although the analysis is more involved. The important point is that in our derivation of the generalized Fokker–Planck equation (1.2) we tacitly assumed $\mathbf{f}(t)=\mathbf{0}$ at $T=0$ K; this is implicit in our apparently innocuous assumption that $\mathbf{f}(t)$ is gaussian random. Thus the transient term was neglected and the short-time behaviour of equation (1.3) is incorrect.

This may be seen explicitly from equation (1.2) evaluated at $T=0$ K which is

$$\left\{\frac{\partial}{\partial t} + \mathbf{u}\cdot\frac{\partial}{\partial \mathbf{x}} - \bar{\omega}^2(t)\mathbf{x}\cdot\frac{\partial}{\partial \mathbf{u}}\right\} P[\mathbf{x}, \mathbf{x}_0;\ \mathbf{u}, \mathbf{u}_0;\ t]$$

$$= \bar{\beta}(t)\frac{\partial}{\partial \mathbf{u}}\cdot\{\mathbf{u}P[\mathbf{x}, \mathbf{x}_0;\ \mathbf{u}, \mathbf{u}_0;\ t]\}. \tag{4.7}$$

This equation is equivalent to the Langevin equation (1.1) with $\mathbf{f}(t)=\mathbf{0}$. This may be easily seen since equation (1.1) with $\mathbf{f}(t)=\mathbf{0}$ may be transformed to give

$$\ddot{x}(t) = -\bar{\omega}^2(t)\mathbf{x}(t) - \bar{\beta}(t)\mathbf{x}(t). \tag{4.8}$$

This transformation is carried out in the Appendix. Equations (4.7) and (4.8) are equivalent, since the first moment

$$\langle x(t)\rangle \equiv \int d\mathbf{x}\, d\mathbf{u} \mathbf{x} P[\mathbf{x}, \mathbf{x}_0;\ \mathbf{u}, \mathbf{u}_0;\ t] \tag{4.9}$$

satisfies equation (4.8) and since higher moments vanish at $T=0$ K. Notice that by equation (A 9), for short times equation (4.8) and hence (4.7) predict the incorrect equation (4.4). Thus we have shown that our earlier derivation of equation (1.2) tacitly assumes $\mathbf{f}(t)=\mathbf{0}$ at $T=0$ K and hence leads to incorrect short-time behaviour.

5. Generalized Fokker–Planck equations valid for all times

Generalized Fokker–Planck and diffusion equations valid for all times may be derived from equation (1.3). This is because the random force $\mathbf{R}(t)$ does not contain a transient systematic term and may be rigorously taken as gaussian random for all times. The derivation of the generalized Fokker–Planck and diffusion equations parallels our earlier treatment [1]; hence we will only sketch the calculation. We begin by solving equation (1.3) to give

$$\mathbf{x}(t)=\dot{\chi}(t)\mathbf{x}_0+\chi(t)\mathbf{u}_0+\frac{1}{m}\int_0^t \chi(t-\tau)\mathbf{R}(\tau)\,d\tau, \tag{5.1}$$

where the Laplace transform of $\chi(t)$, $\hat{\chi}(z)$, is given in terms of the Laplace transform of $\theta(t)$, $\hat{\theta}(z)$, by

$$\hat{\chi}(z)=[z^2+\omega^2-\hat{\Theta}(z)]^{-1}. \tag{5.2}$$

Equation (5.1) implies

$$\dot{\mathbf{x}}(t)=\ddot{\chi}(t)\mathbf{x}_0+\dot{\chi}(t)\mathbf{u}_0+\frac{1}{m}\int_0^t \dot{\chi}(t-\tau)\mathbf{R}(\tau)\,d\tau, \tag{5.3}$$

and also

$$\ddot{\mathbf{x}}(t)=\dddot{\chi}(t)\mathbf{x}_0+\ddot{\chi}(t)\mathbf{u}_0+\dot{\chi}(0)\frac{\mathbf{R}(t)}{m}+\frac{1}{m}\int_0^t \ddot{\chi}(t-\tau)\mathbf{R}(\tau)\,d\tau \tag{5.4}$$

Evaluating equations (5.1) and (5.3) at $t=0$ gives

$$\hat{\mathbf{T}}(0)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}, \tag{5.5}$$

where

$$\hat{\mathbf{T}}(t)=\begin{pmatrix}\dot{\chi}(t) & \chi(t)\\ \ddot{\chi}(t) & \dot{\chi}(t)\end{pmatrix}. \tag{5.6}$$

Evaluating equation (5.4) at $t=0$ and comparing with equation (1.3) gives

$$\dddot{\chi}(0)=-\omega_0^3. \tag{5.7}$$

From equation (5.4) and the gaussian random character of $\mathbf{R}(t)$, the probability distribution function $P[\mathbf{x}, \mathbf{x}_0;\ \mathbf{u}, \mathbf{u}_0;\ t]$ may be evaluated and the generalized Fokker–Planck equation constructed. The result is

$$\left\{\frac{\partial}{\partial t}+\mathbf{u}\cdot\frac{\partial}{\partial \mathbf{x}}-\hat{\omega}^2(t)\mathbf{x}\cdot\frac{\partial}{\partial \mathbf{u}}\right\}P[\mathbf{x}, \mathbf{x}_0;\ \mathbf{u}, \mathbf{u}_0;\ t]+\hat{\beta}(t)\frac{\partial}{\partial \mathbf{u}}\cdot[\mathbf{u}P]$$
$$+\frac{k_{\mathrm{B}}T}{m}A(t)\frac{\partial^2 P}{\partial \mathbf{u}^2}+\frac{k_{\mathrm{B}}T}{m}B(t)\frac{\partial^2 P}{\partial \mathbf{x}\,\partial \mathbf{u}}. \tag{5.8}$$

In equation (5.8)

$$\hat{\beta}(t)=-\frac{d\ \ln\det\hat{\mathbf{T}}(t)}{dt} \tag{5.9}$$

and

$$\hat{\omega}^2(t)=\frac{\ddot{\chi}^2(t)-\dot{\chi}(t)\dddot{\chi}(t)}{\det\hat{\mathbf{T}}(t)}. \tag{5.10}$$

Also

$$A(t) = \hat{\beta}(t) + \chi(t)\hat{\omega}^2(t)[1 - \omega^2\xi(t)] - \chi(t)\omega^2[\dot{\chi}(t) + \chi(t)\hat{\beta}(t)] \tag{5.11}$$

and

$$B(t) = \left\{\frac{\hat{\omega}^2(t) - \omega^2}{\omega^2} - \frac{\hat{\omega}^2(t)}{\omega^2}[1 - \xi(t)\omega^2]^2\right\} + (1 - \omega^2\, \xi(t))(\dot{\chi}(t) + \chi(t)\hat{\beta}(t)), \tag{5.12}$$

where

$$\xi(t) = \int_0^t \chi(\tau)\, d\tau. \tag{5.13}$$

Using equations (5.5)–(5.12) we find that for short times equation (5.8) reduces to

$$\left\{\frac{\partial}{\partial t} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{x}} - \omega_0{}^2\, \mathbf{x} \cdot \frac{\partial}{\partial \mathbf{u}}\right\} P[\mathbf{x}, \mathbf{x}_0\,;\ \mathbf{u}, \mathbf{u}_0\,;\ t] = 0. \tag{5.14}$$

Equation (5.14) is the Liouville equation for a *free* harmonic oscillator with the correct short-time frequency ω_0. Thus equation (5.8), unlike equation (1.2), has the proper short-time behaviour. For long times equation (5.8) simplifies to

$$\left[\frac{\partial}{\partial t} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{x}} - \hat{\omega}^2(t)\mathbf{x} \cdot \frac{\partial}{\partial \mathbf{u}}\right] P(\mathbf{x}, \mathbf{x}_0\,;\ \mathbf{u}, \mathbf{u}_0\,;\ t) = \hat{\beta}(t)\frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{u}P] + \frac{k_{\mathrm{B}}T}{m}\,\hat{\beta}(t)\,\frac{\partial^2}{\partial \mathbf{u}^2}\,P + \frac{k_{\mathrm{B}}T}{m\omega^2}\{\hat{\omega}^2(t) - \omega^2\}\frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial}{\partial \mathbf{x}}\,P. \tag{5.15}$$

Notice that equation (5.15) is identical in structure to equation (1.2), which has the correct long-time behaviour. In particular the equilibrium distribution function

$$P[\mathbf{x}, \mathbf{x}_0\,;\ \mathbf{u}, \mathbf{u}_0\,;\ t] \sim \exp\left(-\frac{1}{k_{\mathrm{B}}T}\left\{\frac{p^2}{2m} + \frac{m\omega^2\, x^2}{2}\right\}\right), \tag{5.16}$$

satisfies both equations (1.2) and (5.15); hence they both properly predict relaxation to equilibrium. We believe, in fact, that $\hat{\omega}^2(t)$, $\hat{\beta}(t)$ are identical to $\bar{\omega}^2(t)$, $\bar{\beta}(t)$ in the long-time limit and hence equations (1.2) and (5.8) are identical in the long-time limit. We have not proven this assertion, in general. We have, however, verified it for the three models discussed in § 3.

Finally, we turn to the generalized diffusion equation implicit in equation (1.3). Following our development in § 2 we find [cf. equations (2.10)]

$$\frac{\partial P[\mathbf{x}, \mathbf{x}_0\,;\ t]}{\partial t} = -\frac{d \ln \dot{\chi}(t)}{dt}\,\nabla \cdot [\mathbf{x}P(\mathbf{x}, \mathbf{x}_0\,;\ t)] + \hat{D}(t)\nabla^2\, P[\mathbf{x}, \mathbf{x}_0\,;\ t], \tag{5.17}$$

where

$$\hat{D}(t) = \tfrac{1}{6}\left[\frac{d\hat{\sigma}(t)}{dt} - 2\hat{\sigma}(t)\,\frac{d \ln \dot{\chi}(t)}{dt}\right], \tag{5.18}$$

with

$$\hat{\sigma}(t) = \frac{6k_{\mathrm{B}}T}{m}\left[1 - \frac{\omega^2}{2}\,\xi(t)\right]\xi(t). \tag{5.19}$$

For short times, both equations (2.10) and (5.17) predict $\partial P/\partial t = 0$. For long-times equation (5.17) becomes

$$\frac{\partial P[\mathbf{x}, \mathbf{x}_0 ;\ t]}{\partial t} = \hat{C}(t)\nabla \cdot [\mathbf{x}P(\mathbf{x}, \mathbf{x}_0 ;\ t)] + \hat{D}(t)\nabla^2 P[\mathbf{x}, \mathbf{x}_0 ;\ t], \tag{5.20}$$

where

$$\hat{C}(t) = -\frac{d \ln \dot{\chi}(t)}{dt}, \tag{5.21}$$

and

$$\lim_{t\to\infty} D(t) = \frac{k_B T}{m\omega^2}\hat{C}(t). \tag{5.22}$$

Notice that equations (3.1)–(3.3) are identical in structure to equations (5.20)–(5.22). The difference is that $\hat{C}(t)$ is not identical to $C(t)$. We believe that these functions become identical as $t \to \infty$. While we have not proven this assertion, it holds for the three models considered in § 3.

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Appendix

Here we derive equation (4.8) from (1.1). Notice that this amounts to transforming a non-Markovian Langevin equation (1.1) to a Markovian Langevin equation (4.8) with time-dependent coefficients. We begin with equation (2.2) with $\mathbf{f}(t) = \mathbf{0}$. This gives

$$\mathbf{x}(t) = \chi_x(t)\mathbf{x}_0 + \chi_u(t)\mathbf{u}_0. \tag{A 1}$$

Equation (A 1) implies

$$\dot{\mathbf{x}}(t) = \dot{\chi}_x(t)\mathbf{x}_0 + \dot{\chi}_u(t)\mathbf{u}_0, \tag{A 2}$$

and

$$\ddot{\mathbf{x}}(t) = \ddot{\chi}_x(t)\mathbf{x}_0 + \ddot{\chi}_u(t)\mathbf{u}_0. \tag{A 3}$$

Let us define

$$\mathbf{T}(t) = \begin{pmatrix} \chi_x(t) & \chi_u(t) \\ \dot{\chi}_x(t) & \dot{\chi}_u(t) \end{pmatrix}. \tag{A 4}$$

From equations (A 1) and (A 2) we see

$$\mathbf{T}(0) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{A 5}$$

Comparing equations (A 3) and (1.1) gives

$$\ddot{\chi}_x(0) = -\omega^2 \tag{A 6a}$$

and

$$\ddot{\chi}_u(0) = 0. \tag{A 6b}$$

Eliminating $\mathbf{x}_0$ and $\mathbf{u}_0$ from equation (A 3) using equations (A 1) and (A 2) gives equations (4.8) with

$$\tilde{\beta}(t) = -\frac{d \ln \det \mathbf{T}(t)}{dt}, \tag{A 7}$$

and

$$\tilde{\omega}^2(t) = \frac{\ddot{\chi}_u(t)\dot{\chi}_x(t) - \ddot{\chi}_x(t)\dot{\chi}_u(t)}{\det \mathbf{T}(t)}. \tag{A 8}$$

Equations (A 4) and (A 6)–(A 8) show

$$\tilde{\omega}^2(0) = \omega^2 \tag{A 9 a}$$

and

$$\tilde{\beta}(0) = 0. \tag{A 9 b}$$

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