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Nonlinear Generalized Langevin Equations

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Exact generalized Langevin equations are derived for arbitrarily nonlinear systems interacting with specially chosen heat baths. An example is displayed in which the Langevin equation is nonlinear but approximately Markovian.

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The purpose of this paper is the derivation of a class of generalized Langevin equations describing the motion of a system interacting with a heat bath. No restriction is placed on the properties of the system: in particular, its equations of motion may be arbitrarily nonlinear. The heat bath is a collection of harmonic oscillators, and the interaction has a special form.

The possibility of a derivation of this sort was suggested by work of Ford *et al.*[1] on the statistical mechanical theory of Brownian motion. Mori[2] has shown how to derive linearized generalized Langevin equations for arbitrary systems close to thermal equilibrium. Little is known, however, about Brownian motion in nonlinear systems, so that explicit examples of the type treated here may be useful as illustrations of what may be expected.

Although our derivation can be carried out within the framework of conventional Hamiltonian dynamics, we use instead a form of "generalized

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dynamics" which does not explicitly distinguish between canonical coordinates and momenta. This new form has the advantage of compactness of notation and greater generality than Hamiltonian dynamics. It was used, e.g., by Kerner[3] in his development of the statistical mechanics of interacting biological species.

At the end of the paper we give a specific example of our general results in the conventional Hamiltonian form.

The state of the system is determined by a set of system variables, denoted collectively by the vector X. Similarly, the state of the bath is determined by the vector Y. At time t these vectors become X_t and Y_t.

We want to find an equation of motion for the system vector X_t when the initial bath vector Y_0 has a certain statistical distribution.

The equations of motion of X_t and Y_t are specified as follows. We introduce a function $H(X, Y)$ which is analogous to the Hamiltonian function. This is separated into a system part $H_s(X)$ which depends only on the state of the system, and a bath part $H_b(X, Y)$ which depends on the state of both system and bath:

$$H(X, Y) = H_s(X) + H_b(X, Y) \tag{1}$$

Next we introduce two *antisymmetric* matrices A (in the system space) and B (in the bath space). Then the equations of motion are given by

$$dX/dt = A \cdot \nabla_x(H_s + H_b) \tag{2}$$

$$dY/dt = B \cdot \nabla_y H_b \tag{3}$$

It is easy to verify that $H(X, Y)$ is a constant of motion; this is a consequence of the antisymmetry of A and B.

The matrix A may be an arbitrary function of X, but B is a constant matrix.

We note that Hamilton's equation may be written in this form. Suppose, e.g., that the system variables are $X = (Q, P)$, where Q and P are a coordinate and its conjugate momentum. Then if H is a Hamiltonian function, A is the matrix

$$A = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{4}$$

When there are many pairs of coordinates and momenta, then A can be represented as the direct product of such matrices.

The system function H_s is an arbitrary function of X. For the bath function H_b we take a quadratic form. Let K be a symmetric nonsingular matrix in the bath space. Let $a(X)$ be an arbitrary vector function of X in the bath space. Then we define the bath function as

$$H_b(X, Y) = \tfrac{1}{2}[Y - a(X)]^T \cdot K \cdot [Y - a(X)] \tag{5}$$

The transpose of a vector or matrix is denoted by the superscript T.

The equation of motion of the bath variables is now

$$dY/dt = B \cdot K \cdot [Y - a(X)] \tag{6}$$

Suppose that we know the time dependence of X_t. Then this may be solved as a linear inhomogeneous differential equation:

$$Y_t = \exp(tB \cdot K) \cdot Y_0 - \int_0^t dt' \exp(t'B \cdot K) \cdot B \cdot K \cdot a(X_{t-t'}) \tag{7}$$

An integration by parts leads to another form,

$$\begin{aligned} Y_t - a(X_t) &= \exp(tB \cdot K) \cdot [Y_0 - a(X_0)] \\ &\quad + \int_0^t dt' \exp(t'B \cdot K) \cdot (d/dt')\, a(X_{t-t'}) \end{aligned} \tag{8}$$

Now we turn to the equation of motion of the system. For convenience of notation we define

$$V(X) = A \cdot \nabla_x H_s(X) \tag{9}$$

and we introduce the matrix $W(X)$, defined by

$$W(X) = \nabla_x a^T(X) \tag{10}$$

The equation of motion of X becomes

$$dX/dt = V(X) - A \cdot W(X) \cdot K \cdot [Y - a(X)] \tag{11}$$

By using the matrix W, we may also write

$$(d/dt')a(X_{t-t'}) = -W^T(X_{t-t'}) \cdot \dot{X}_{t-t'} \tag{12}$$

To proceed, we recognize that X is a function of t. In the right-hand side of Eq. (11) we substitute Eq. (8). This leads to

$$\begin{aligned} dX_t/dt = V(X_t) &+ \int_0^t dt'\, A \cdot W(X_t) \cdot K \cdot \exp(t'B \cdot K) \cdot W^T(X_{t-t'}) \cdot \dot{X}_{t-t'} \\ &- A \cdot W(X_t) \cdot K \cdot \exp(tB \cdot K) \cdot [Y_0 - a(X_0)] \end{aligned} \tag{13}$$

This is essentially our final result. The motion of X_t is expressed in terms of its own history from zero to t, and the bath variables enter only through their initial values.

However, a further change in notation will put our result into a more transparent form. We define a "noise" source by

$$F(t) = -K \cdot \exp(tB \cdot K) \cdot [Y_0 - a(X_0)] \tag{14}$$

The statistical properties of the noise are determined as follows. We consider an ensemble of initial states, in which X_0 is held fixed but the initial bath variables Y_0 are drawn at random from a canonical distribution characterized by a temperature T:

$$\mathrm{Prob}(Y_0/\mathrm{given}X_0) \sim \exp(-H_b/kT) \tag{15}$$

In this ensemble the mean and dispersion of Y_0 are

$$\begin{aligned} \langle Y_0 \rangle &= a(X_0) \\ \langle [Y_0 - a(X_0)][Y_0 - a(X_0)]^T \rangle &= kTK^{-1} \end{aligned} \tag{16}$$

Note that $F(t)$ is a linear combination of variables that have a Gaussian distribution, so that $F(t)$ has itself a Gaussian distribution. The mean and dispersion of the noise are

$$\begin{aligned} \langle F(t) \rangle &= 0 \\ \langle F(t)F^T(t') \rangle &= kTL(t - t') \\ L(t) &= K \cdot \exp(tB \cdot K) \end{aligned} \tag{17}$$

This defines the "friction coefficient" $L(t)$.
In deriving this expression for $L(t)$, we used the identity

$$K^{-1} \cdot [\exp(tB \cdot K)]^T = \exp(-tB \cdot K) \cdot K^{-1} \tag{18}$$

which can be verified, e.g., by series expansion of both sides.

The resulting generalized Langevin equation is

$$\begin{aligned} dX_t/dt = V(X_t) &+ \int_0^t dt' \, A \cdot W(X_t) \cdot L(t') \cdot W^T(X_{t-t'}) \cdot \dot{X}_{t-t'} \\ &+ A \cdot W(X_t) \cdot F(t) \end{aligned} \tag{19}$$

Equation (17) is the fluctuation-dissipation theorem relating the noise intensity to the transport coefficient.

The preceding derivation has led to the desired result, but it is somewhat formal and abstract. As an illustration of the structure of the generalized Langevin equation, we consider next a special case.

The system is a particle in a potential. The coordinate and conjugate momentum are Q and P, the mass is M, and the potential is $U(Q)$. The system function—or Hamiltonian—is

$$H_s = (P^2/2M) + U(Q) \tag{20}$$

The bath oscillators have coordinates and momenta q_j and p_j, where $j = 1, 2, \ldots, N$. The oscillators have unit mass, and the jth oscillator has a frequency ω_j. Then the bath function—or Hamiltonian—is

$$H_b = \sum \tfrac{1}{2} p_j^2 + \sum \tfrac{1}{2}\omega_j^2 (q_j - \gamma_j Q/\omega_j^2)^2 \tag{21}$$

With some effort, this Hamiltonian system can be rewritten in the generalized dynamics notation used in the preceding derivation. In particular, the vector $a(X)$, which describes the coupling of system to bath, is linear in the system coordinate. Because of the simplicity of the example, however, it is probably easier to repeat the entire derivation explicitly in Hamiltonian form.

Either way, one obtains the generalized Langevin equation

$$\begin{aligned} M\, dQ_t/dt &= P_t \\ dP_t/dt &= -\, U'(Q_t) - \int_0^t dt'\, \zeta(t') P_{t-t'}/M + \mathscr{F}(t) \end{aligned} \tag{22}$$

As before, the noise $\mathscr{F}(t)$ is a linear combination of all oscillator coordinates and momenta. The friction coefficient $\zeta(t)$ is

$$\zeta(t) = \sum (\gamma_j/\omega_j)^2 \cos \omega_j t \tag{23}$$

The fluctuation-dissipation theorem takes the form

$$\langle \mathscr{F}(t) \rangle = 0, \qquad \langle \mathscr{F}(t)\mathscr{F}(t') \rangle = kT\zeta(t - t') \tag{24}$$

The friction is linear in the system momentum, and the friction coefficient is a simple function of the frequencies ω_j and the coupling constants γ_j.

This generalized Langevin equation is exact. It differs from the type obtained by Mori's scheme[2] in the presence of an arbitrary nonlinear force $-U'(Q)$. Further, its validity is not restricted to small departures from thermal equilibrium.

Our Langevin equation is non-Markovian; the frictional term contains a memory function $\zeta(t)$. As noticed by Ford *et al.*[1] in a similar connection, a special choice of frequencies and coupling constants can lead to an equation that is approximately Markovian. (In distinction to their work, we do not restrict ourselves to a model of the lattice dynamics type.)

First, we suppose that there are very many oscillators in the heat bath, with a distribution of frequencies. Then, we treat the frequency distribution as continuous. (The only serious effect here is the elimination of Poincaré recurrences at very long times.) We use a frequency distribution of the Debye type,

$$g(\omega) = \begin{cases} 3\omega^2/\omega_d^2, & \omega < \omega_d \\ 0, & \omega > \omega_d \end{cases} \tag{25}$$

where ω_d is a cutoff frequency. Sums over oscillator frequencies are replaced by integrals according to

$$\sum \rightarrow N \int d\omega \; g(\omega) \tag{26}$$

Further, we suppose that all coupling constants are equal,

$$\gamma_j = \gamma / N^{1/2} \tag{27}$$

In this approximation the friction coefficient becomes

$$\zeta(t) = (3\gamma^2/\omega_d^2)(\sin \omega_d t)/t \tag{28}$$

If the system momentum varies sufficiently slowly over times of the order of $1/\omega_d$, then a delta-function approximation may be used for $\zeta(t)$,

$$\zeta(t) \simeq 2\zeta_0 \, \delta(t); \qquad \zeta_0 = 3\pi\gamma^2/2\omega_d^2 \tag{29}$$

This leads to the Markovian approximation

$$dP_t/dt = -U'(Q_t) - \zeta_0 P_t/M + \mathscr{F}(t) \tag{30}$$

The preceding example shows that it is possible to obtain an approximately Markovian, but nonlinear, Langevin equation from a Hamiltonian model.

The further special case where $U = \frac{1}{2}Q^2 + \frac{1}{4}\beta Q^4$ was studied recently by Bixon and Zwanzig[4] as an example of fluctuation-renormalization of a transport equation.

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