

# 15

## The Langevin and generalized Langevin equations

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### 15.1 The general model of a system plus a bath

Many problems in chemistry, biology, and physics do not involve homogeneous systems but are concerned, rather, with a specific process that occurs in some sort of medium. Most biophysical and biochemical processes occur in an aqueous environment, and one might be interested in a specific conformational change in a protein or the bond-breaking event in a hydrolysis reaction. In this case, the water solvent and other degrees of freedom not directly involved in the reaction serve as the “medium,” which is often referred to generically as a *bath*. Organic reactions occur in a variety of different solvents, including water, methanol, dimethyl sulfoxide, and carbon tetrachloride. For example, a common reaction such as a Diels-Alder reaction can occur in water or in a room-temperature ionic liquid. In surface physics, we might be interested in the addition of an adsorbate to a particular site on the surface. If a reaction coordinate (see Section 8.6) for the adsorption process can be identified, the remaining degrees of freedom, including the bulk below the surface, can be treated as the environment or bath. Many other examples fall into this general paradigm, and it is, therefore, useful to develop a framework for treating such problems.

In this chapter, we will develop an approach that allows the bath degrees of freedom to be eliminated from a problem, leaving only coordinates of interest to be treated explicitly. The resulting equation of motion in the reduced subspace, known as the *generalized Langevin equation* (1905, 1908) after the French physicist Paul Langevin (1872–1946), can only be taken as rigorous in certain idealized limits. However, as a phenomenological theory, the generalized Langevin equation is a powerful tool for understanding of a wide variety of physical processes. These include theories of chemical reaction rates (Kramers, 1940; Grote and Hynes, 1980; Pollak *et al.*, 1989; Pollak, 1990; Pollak *et al.*, 1990) and of vibrational dephasing and energy relaxation to be discussed in Section 15.4.

In order to introduce the basic paradigm of a subsystem interacting with a bath, consider a classical system with generalized coordinates  $q_1, \dots, q_{3N}$ . Suppose we are interested in a simple process that can be described by a single coordinate, which we arbitrarily take to be  $q_1$ . We will call  $q_1$  and the remaining coordinates  $q_2, \dots, q_{3N}$  the *system* and *bath* coordinates, respectively. Moreover, in order to make the notation clearer, we will rename  $q_1$  as  $q$  and the remaining bath coordinates as  $y_1, \dots, y_n$ , where  $n = 3N - 1$ . In order to avoid unnecessary complexity at this point, we will assume that

the system coordinate  $q$  is a simple coordinate, such as a distance between two atoms or a Cartesian spatial direction (in Section 15.7, we will introduce a general framework for treating the problem that allows this restriction to be lifted). The Hamiltonian for  $q$  and its conjugate momentum  $p$  in the absence of the bath can then be written simply as

$$\mathcal{H}(q, p) = \frac{p^2}{2\mu} + V(q), \quad (15.1.1)$$

where  $\mu$  is the mass associated with  $q$  and  $V(q)$  is a potential energy contribution that depends only on  $q$  and, therefore, is present even without the bath. The system is coupled to the bath via a potential  $U_{\text{bath}}(q, y_1, \dots, y_n)$  that involves both the coupling terms between the system and the bath and terms describing the interactions among the bath degrees of freedom. The total potential is

$$U(q, y_1, \dots, y_n) = V(q) + U_{\text{bath}}(q, y_1, \dots, y_n). \quad (15.1.2)$$

As an example, consider a system originally formulated in Cartesian coordinates  $\mathbf{r}_1, \dots, \mathbf{r}_N$  described by a pair potential

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \sum_{j=i+1}^N u(|\mathbf{r}_i - \mathbf{r}_j|). \quad (15.1.3)$$

Suppose the distance  $r = |\mathbf{r}_1 - \mathbf{r}_2|$  between atoms 1 and 2 is a coordinate of interest, which we take as the system coordinate. All other degrees of freedom are assigned as bath coordinates. Suppose, further, that atoms 1 and 2 have the same mass. We first transform to the center of mass and relative coordinates between atoms 1 and 2 according to

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \quad (15.1.4)$$

the inverse of which is

$$\mathbf{r}_1 = \mathbf{R} + \frac{1}{2}\mathbf{r} \quad \mathbf{r}_2 = \mathbf{R} - \frac{1}{2}\mathbf{r}. \quad (15.1.5)$$

The potential can then be expressed as

$$\begin{aligned} U(\mathbf{r}_1, \dots, \mathbf{r}_N) &= u(|\mathbf{r}_1 - \mathbf{r}_2|) + \sum_{i=3}^N [u(|\mathbf{r}_1 - \mathbf{r}_i|) + u(|\mathbf{r}_2 - \mathbf{r}_i|)] + \sum_{i=3}^N \sum_{j=i+1}^N u(|\mathbf{r}_i - \mathbf{r}_j|) \\ &= u(r) + \sum_{i=3}^N \left[ u\left(\left|\mathbf{R} + \frac{1}{2}r\mathbf{n} - \mathbf{r}_i\right|\right) + u\left(\left|\mathbf{R} - \frac{1}{2}r\mathbf{n} - \mathbf{r}_i\right|\right) \right] \\ &\quad + \sum_{i=3}^N \sum_{j=i+1}^N u(|\mathbf{r}_i - \mathbf{r}_j|), \end{aligned} \quad (15.1.6)$$

where  $\mathbf{n} = (\mathbf{r}_1 - \mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2| = \mathbf{r}/r$  is the unit vector along the relative coordinate direction. Eqn. (15.1.6) is of the same form as eqn. (15.1.2), in which the first term is

equivalent to  $V(q)$ , the term in brackets represents the interaction between the system and the bath, and the final term is a pure bath–bath interaction.

Suppose the bath potential  $U_{\text{bath}}$  can be reasonably approximated by an expansion up to second order about a minimum characterized by values  $\bar{q}, \bar{y}_1, \dots, \bar{y}_n$  of the generalized coordinates. The condition for  $U_{\text{bath}}$  to have a minimum at these values is

$$\left. \frac{\partial U_{\text{bath}}}{\partial q_\alpha} \right|_{\{q=\bar{q}, y=\bar{y}\}} = 0, \quad (15.1.7)$$

where all coordinates are set equal to their values at the minimum. Performing the expansion up to second order gives

$$\begin{aligned} U_{\text{bath}}(q, y_1, \dots, y_n) \approx & U_{\text{bath}}(\bar{q}, \bar{y}_1, \dots, \bar{y}_n) + \sum_{\alpha} \left. \frac{\partial U_{\text{bath}}}{\partial q_\alpha} \right|_{\{q=\bar{q}, y=\bar{y}\}} (q_\alpha - \bar{q}_\alpha) \\ & + \frac{1}{2} \sum_{\alpha, \beta} (q_\alpha - \bar{q}_\alpha) \left[ \left. \frac{\partial^2 U_{\text{bath}}}{\partial q_\alpha \partial q_\beta} \right|_{\{q=\bar{q}, y=\bar{y}\}} \right] (q_\beta - \bar{q}_\beta). \end{aligned} \quad (15.1.8)$$

The second term in eqn. (15.1.8) vanishes by virtue of the condition in eqn. (15.1.7). The first term is a constant that can be made to vanish by shifting the absolute zero of the potential (which is, anyway, arbitrary). Thus, the bath potential reduces, in this approximation, to

$$U_{\text{bath}}(q, y_1, \dots, y_n) = \frac{1}{2} \sum_{\alpha=1}^{n+1} \sum_{\beta=1}^{n+1} \tilde{q}_\alpha H_{\alpha\beta} \tilde{q}_\beta, \quad (15.1.9)$$

where  $H_{\alpha\beta} = \partial^2 U_{\text{bath}} / \partial q_\alpha \partial q_\beta |_{q=\bar{q}, \{y=\bar{y}\}}$  and  $\tilde{q}_\alpha = q_\alpha - \bar{q}_\alpha$  are the displacements of the generalized coordinates from their values at the minimum of the potential. Note that since we have already identified the purely  $q$ -dependent term in eqn. (15.1.6), the  $H_{11}$  arising from the expansion of the bath potential can be taken to be zero or absorbed into the  $q$ -dependent function  $V(q)$ . Since our treatment from this point on will refer to the displacement coordinates, we will drop the tildes and let  $q_\alpha$  refer to the displacement of a coordinate from its value at the minimum. Separating the particular coordinate  $q$  from the other coordinates gives a potential of the form

$$U_{\text{bath}}(q, y_1, \dots, y_n) = \sum_{\alpha} C_\alpha q y_\alpha + \frac{1}{2} \sum_{\alpha=1}^n \sum_{\beta=1}^n y_\alpha \tilde{H}_{\alpha\beta} y_\beta, \quad (15.1.10)$$

where  $C_\alpha = H_{1\alpha} = H_{\alpha 1}$  and  $\tilde{H}_{\alpha\beta}$  is the  $n \times n$  block of  $H_{\alpha\beta}$  coupling only the coordinates  $y_1, \dots, y_n$ . The potential, though quadratic, is still somewhat complicated because all of the coordinates are coupled through the matrix  $H_{\alpha\beta}$ . Thus, in order to simplify the potential, we introduce a linear transformation of the coordinates  $y_1, \dots, y_n$  to  $x_1, \dots, x_n$  via

$$y_\alpha = \sum_{\beta=1}^n R_{\alpha\beta} x_\beta, \quad (15.1.11)$$

where  $R_{\alpha\beta}$  is an orthogonal matrix that diagonalizes the symmetric matrix  $\tilde{H}_{\alpha\beta}$  via  $\tilde{H}_{\text{diag}} = R^T \tilde{H} R$ , where  $R^T$  is the transpose of  $R$  and  $\tilde{H}_{\text{diag}}$  contains the eigenvalue of  $\tilde{H}$

on its diagonal. Letting  $k_\alpha$  denote these eigenvalues and introducing the transformation into eqn. (15.1.10), we obtain

$$U_{\text{bath}}(q, x_1, \dots, x_n) = \sum_{\alpha} g_{\alpha} q x_{\alpha} + \frac{1}{2} \sum_{\alpha} k_{\alpha} x_{\alpha}^2, \quad (15.1.12)$$

where  $g_{\alpha} = \sum_{\beta} C_{\beta} R_{\beta\alpha}$ . The potential energy in eqn. (15.1.12) is known as a *harmonic bath* potential; it also contains a bilinear coupling to the coordinate  $q$ . We will henceforth refer to the coordinate  $q$  as the “system coordinate.” In order to construct the full Hamiltonian in the harmonic bath approximation, we introduce a set of momenta  $p_1, \dots, p_n$ , assumed to be conjugate to the coordinates  $x_1, \dots, x_n$ , and a set of bath masses  $m_1, \dots, m_n$ . The full Hamiltonian for the system coordinate coupled to a harmonic bath can be written as

$$\mathcal{H} = \frac{p^2}{2\mu} + V(q) + \sum_{\alpha=1}^n \left[ \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha=1}^n m_{\alpha} \omega_{\alpha}^2 x_{\alpha}^2 \right] + q \sum_{\alpha=1}^n g_{\alpha} x_{\alpha}, \quad (15.1.13)$$

where the spring constants  $k_{\alpha}$  have been replaced by the bath frequencies  $\omega_1, \dots, \omega_n$  using  $k_{\alpha} = m_{\alpha} \omega_{\alpha}^2$ . We must not forget that eqn. (15.1.13) represents a highly idealized situation in which the possible curvilinear nature of the generalized coordinates is neglected in favor of a very simple model of the bath (Deutsch and Silbey, 1971; Caldeira and Leggett, 1983).

A real bath is often characterized by a continuous distribution of frequencies  $I(\omega)$  called the *spectral density* or *density of states* (see Problem 14.9).  $I(\omega)$  is obtained by taking the Fourier transform of the velocity autocorrelation function.<sup>1</sup> The physical picture embodied in the harmonic-bath Hamiltonian is one in which a real bath is replaced by an ideal bath under the assumption that the motion of the real bath is dominated by small displacements from an equilibrium point described by discrete frequencies  $\omega_1, \dots, \omega_n$ . This replacement is tantamount to expressing  $I(\omega)$  as a sum of harmonic-oscillator spectral density functions. It is important to note that the harmonic bath does not allow for diffusion of bath particles. In general, a set of frequencies,  $\omega_1, \dots, \omega_n$ , effective masses  $m_1, \dots, m_n$ , and coupling constants to the system  $g_1, \dots, g_n$  need to be determined in order to reproduce at least some of the properties of the real bath. The extent to which this can be done, however, depends on the particular nature of the original bath. For the purposes of the subsequent discussion, we will assume that a reasonable choice can be made for these parameters and proceed to work out the classical dynamics of the harmonic-bath Hamiltonian.

## 15.2 Derivation of the generalized Langevin equation

We begin by deriving the classical equations of motion generated by eqn. (15.1.13). From Hamilton’s equations, there are

<sup>1</sup>The density of states encodes the information about the vibrational modes of the bath; however, it does not provide any information about absorption intensities.

$$\begin{aligned}
\dot{q} &= \frac{\partial H}{\partial p} = \frac{p}{\mu} \\
\dot{p} &= -\frac{\partial H}{\partial q} = -\frac{dV}{dq} - \sum_{\alpha} g_{\alpha} x_{\alpha} \\
\dot{x}_{\alpha} &= \frac{\partial H}{\partial p_{\alpha}} = \frac{p_{\alpha}}{m_{\alpha}} \\
\dot{p}_{\alpha} &= -\frac{\partial H}{\partial x_{\alpha}} = -m_{\alpha} \omega_{\alpha}^2 x_{\alpha} - g_{\alpha} q,
\end{aligned} \tag{15.2.1}$$

which can be written as the following set of coupled second-order differential equations:

$$\begin{aligned}
\mu \ddot{q} &= -\frac{dV}{dq} - \sum_{\alpha} g_{\alpha} x_{\alpha} \\
m_{\alpha} \ddot{x}_{\alpha} &= -m_{\alpha} \omega_{\alpha}^2 x_{\alpha} - g_{\alpha} q.
\end{aligned} \tag{15.2.2}$$

Eqns. (15.2.2) must be solved subject to a set of initial conditions

$$\{q(0), \dot{q}(0), x_1(0), \dots, x_n(0), \dot{x}_1(0), \dots, \dot{x}_n(0)\}$$

The second equation for the bath coordinates can be solved *in terms of the system coordinate*  $q$  by Laplace transformation, assuming that the system coordinate  $q$  acts as a kind of driving term. The Laplace transform of a function  $f(t)$ , alluded to briefly in Section 14.6, is one of several types of integral transforms defined to be

$$\tilde{f}(s) = \int_0^{\infty} dt e^{-st} f(t). \tag{15.2.3}$$

As we will now show, Laplace transforms are particularly useful for solving linear differential equations. A more detailed discussion of Laplace transforms is given in Appendix D. From eqn. (15.2.3), it can be shown straightforwardly that the Laplace transforms of  $df/dt$  and  $d^2f/dt^2$  are given, respectively, by

$$\begin{aligned}
\int_0^{\infty} dt e^{-st} \frac{df}{dt} &= s\tilde{f}(s) - f(0) \\
\int_0^{\infty} dt e^{-st} \frac{d^2f}{dt^2} &= s^2\tilde{f}(s) - f'(0) - sf(0).
\end{aligned} \tag{15.2.4}$$

Finally, the Laplace transform of a convolution of two functions  $f(t)$  and  $g(t)$  can be shown to be

$$\int_0^{\infty} dt e^{-st} \int_0^t d\tau f(\tau)g(t-\tau) = \tilde{f}(s)\tilde{g}(s). \tag{15.2.5}$$

Taking the Laplace transform of both sides of the second line in eqn. (15.2.2) yields

$$s^2 \tilde{x}_\alpha(s) - \dot{x}_\alpha(0) - s x_\alpha(0) + \omega_\alpha^2 \tilde{x}_\alpha(s) = -\frac{g_\alpha}{m_\alpha} \tilde{q}(s). \quad (15.2.6)$$

The use of the Laplace transform has the effect of turning a differential equation into an algebraic equation for  $\tilde{x}_\alpha(s)$ . Solving this equation for  $\tilde{x}_\alpha(s)$  gives

$$\tilde{x}_\alpha(s) = \frac{s}{s^2 + \omega_\alpha^2} x_\alpha(0) + \frac{\omega_\alpha^2}{s^2 + \omega_\alpha^2} \dot{x}_\alpha(0) - \frac{g_\alpha}{m_\alpha} \frac{\tilde{q}(s)}{s^2 + \omega_\alpha^2}. \quad (15.2.7)$$

We now obtain the solution to the differential equation by computing the inverse transform  $\tilde{x}_\alpha(s)$  in eqn. (15.2.7). Applying the inverse Laplace transform relations in Appendix D, recognizing that the last term in eqn. (15.2.7) is the product of two Laplace transforms, we find that the solution for  $x_\alpha(t)$  is

$$x_\alpha(t) = x_\alpha(0) \cos \omega_\alpha t + \frac{1}{\omega_\alpha} \dot{x}_\alpha(0) \sin \omega_\alpha t - \frac{g_\alpha}{m_\alpha \omega_\alpha} \int_0^t d\tau \sin \omega_\alpha(t - \tau) q(\tau). \quad (15.2.8)$$

For reasons that will be clear shortly, we integrate the convolution term by parts to express it in the form

$$\begin{aligned} \int_0^t d\tau \sin \omega_\alpha(t - \tau) q(\tau) &= \frac{1}{\omega_\alpha} [q(t) - q(0) \cos \omega_\alpha t] \\ &\quad - \frac{1}{\omega_\alpha} \int_0^t d\tau \cos \omega_\alpha(t - \tau) \dot{q}(\tau). \end{aligned} \quad (15.2.9)$$

Substituting eqn. (15.2.9) and eqn. (15.2.8) into the first line of eqn. (15.2.2) yields the equation of motion for  $q$ :

$$\begin{aligned} \mu \ddot{q} &= -\frac{dV}{dq} - \sum_\alpha g_\alpha x_\alpha(t) \\ &= -\frac{dV}{dq} - \sum_\alpha g_\alpha \left[ x_\alpha(0) \cos \omega_\alpha t + \frac{p_\alpha(0)}{m_\alpha \omega_\alpha} \sin \omega_\alpha t + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} q(0) \cos \omega_\alpha t \right] \\ &\quad - \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} \int_0^t d\tau \dot{q}(\tau) \cos \omega_\alpha(t - \tau) + \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} q(t). \end{aligned} \quad (15.2.10)$$

Eqn. (15.2.10) is in the form of an integro-differential equation for the system coordinate that depends explicitly on the bath dynamics. Although the dynamics of each bath coordinate are relatively simple, the collective effect of the bath on the system coordinate can be nontrivial, particularly if the initial conditions of the bath are randomly chosen, the distribution of frequencies is broad, and the frequencies are not all commensurate. Indeed, the bath might appear to affect the system coordinate in a seemingly random and unpredictable manner, especially if the number of bath degrees of freedom is large. This is just what we might expect for a real bath. Thus, in order to motivate this physical picture, the following quantities are introduced:

$$R(t) = - \sum_{\alpha} g_{\alpha} \left[ \left( x_{\alpha}(0) + \frac{g_{\alpha}}{m_{\alpha}\omega_{\alpha}^2} q(0) \right) \cos \omega_{\alpha} t + \frac{p_{\alpha}(0)}{m_{\alpha}\omega_{\alpha}} \sin \omega_{\alpha} t \right], \quad (15.2.11)$$

$$\zeta(t) = \sum_{\alpha} \frac{g_{\alpha}^2}{m_{\alpha}\omega_{\alpha}^2} \cos \omega_{\alpha} t, \quad (15.2.12)$$

$$W(q) = V(q) - \sum_{\alpha} \frac{g_{\alpha}^2}{m_{\alpha}\omega_{\alpha}^2} q^2. \quad (15.2.13)$$

In terms of these quantities, the equation of motion for the system coordinate reads

$$\mu \ddot{q} = - \frac{dW}{dq} - \int_0^t d\tau \dot{q}(\tau) \zeta(t - \tau) + R(t). \quad (15.2.14)$$

Eqn. (15.2.14) is known as the *generalized Langevin equation* (GLE). The quantity  $\zeta(t)$  in the GLE is called the *dynamic friction kernel*,  $R(t)$  is called the *random force*, and  $W(q)$  is identified as the potential of mean force acting on the system coordinate. Despite the simplifications of the bath inherent in eqn. (15.2.14), the GLE can yield considerable physical insight without requiring large-scale simulations. Before discussing predictions of the GLE, we will examine each of the terms in eqn. (15.2.14) and provide a physical interpretation of them.

### 15.2.1 The potential of mean force

Potentials of mean force were first discussed in Chapter 8 (see eqns. (8.6.4) and (8.6.5)). For a true harmonic bath, the potential of mean force is given by the simple expression in eqn. (15.2.13); however, as a phenomenological theory, the GLE assumes that the potential of mean force has been generated by some other means (using techniques from Chapter 8, for example the blue moon ensemble of Section 8.7 or umbrella sampling approach of Section 8.8) and attempts to model the dynamics of the system coordinate on this surface using the friction kernel and random force to represent the influence of the bath. The use of the potential of mean force in the GLE assumes a quasi-adiabatic separation between the system and bath motions. However, considering the GLE's phenomenological viewpoint, it is also possible to use the bare potential  $V(q)$  and use the GLE to model the dynamics on this surface instead. Such a model can be derived from a slightly modified version of the harmonic-bath Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2\mu} + V(q) + \sum_{\alpha=1}^n \left[ \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha=1}^n m_{\alpha}\omega_{\alpha}^2 \left( x_{\alpha} + \frac{g_{\alpha}}{m_{\alpha}\omega_{\alpha}^2} q \right)^2 \right]. \quad (15.2.15)$$

### 15.2.2 The random force

The question that immediately arises concerning the random force in eqn. (15.2.14) is why it is called “random” in the first place. After all, eqn. (15.2.11) defines a perfectly deterministic quantity. To understand why  $R(t)$  can be treated as a random process,

we note that a real bath, which contains a macroscopically large number of degrees of freedom, will affect the system in what appears to be a random manner, despite the fact that its time evolution is completely determined by the classical equations of motion. Recall, however, that the basic idea of ensemble theory is to disregard the detailed motion of every degree of freedom in a macroscopically large system and to replace this level of detail by an ensemble average. It is in this spirit that we replace the  $R(t)$ , defined microscopically in eqn. (15.2.11), with a truly random process defined by a particular time sequence of random numbers and a set of related time correlation functions satisfied by this sequence.

We first note that the time correlation functions  $\langle q(0)R(t) \rangle$  and  $\langle \dot{q}(0)R(t) \rangle$  are identically zero for all time. To see this, consider first the correlation function

$$\begin{aligned} \langle \dot{q}(0)R(t) \rangle &= \left\langle \frac{p(0)}{\mu} R(t) \right\rangle \\ &= -\frac{1}{Q} \int dp dq \exp \left\{ -\beta \left[ \frac{p^2}{2\mu} + V(q) \right] \right\} \\ &\times \int \prod_{\alpha=1}^n dx_{\alpha} dp_{\alpha} \exp \left\{ -\beta \left[ \sum_{\alpha=1}^n \left( \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha=1}^n m_{\alpha} \omega_{\alpha}^2 x_{\alpha}^2 \right) + q \sum_{\alpha=1}^n g_{\alpha} x_{\alpha} \right] \right\} \\ &\times \frac{p}{\mu} \sum_{\alpha} g_{\alpha} \left[ \left( x_{\alpha} + \frac{g_{\alpha}}{m_{\alpha} \omega_{\alpha}^2} q \right) \cos \omega_{\alpha} t + \frac{p_{\alpha}}{m_{\alpha} \omega_{\alpha}} \sin \omega_{\alpha} t \right], \end{aligned} \quad (15.2.16)$$

where the average is taken over a canonical ensemble and  $Q$  is the partition function for the harmonic-bath Hamiltonian. Since  $R(t)$  does not depend on the system momentum  $p$ , the integral over  $p$  is of the form  $\int_{-\infty}^{\infty} dp p \exp(-\beta p^2/2\mu) = 0$ , and the entire integral vanishes. It is left as an exercise to show that the correlation function  $\langle q(0)R(t) \rangle = 0$  (see Problem 15.1). The vanishing of the correlation functions  $\langle q(0)R(t) \rangle$  and  $\langle \dot{q}(0)R(t) \rangle$  is precisely what we would expect from a random bath force, and hence we require that these correlation functions vanish for any model random process. Finally, the same manipulations employed above can be used to derive autocorrelation function  $\langle R(0)R(t) \rangle$  with the result

$$\langle R(0)R(t) \rangle = \frac{1}{\beta} \sum_{\alpha} \frac{g_{\alpha}^2}{m_{\alpha} \omega_{\alpha}^2} \cos \omega_{\alpha} t = kT \zeta(t), \quad (15.2.17)$$

which shows that the random force and the dynamic friction kernel are related (see Problem 15.1). Eqn. (15.2.17) is known as the *second fluctuation dissipation theorem* (Kubo *et al.*, 1985). Once again, we require that any model random process we choose satisfy this theorem.

If the deterministic definition of  $R(t)$  in eqn. (15.2.11) is to be replaced by a model random process, how should such a process be described mathematically? There are various ways to construct random time sequences that give the correct time correlation functions, depending on the physics of the problem. For instance, the influence of a relatively high-density bath, which affects the system via only soft collisions due to



low amplitude thermal fluctuations, is different from a low-density, high-temperature bath that influences the system through mostly strong, impulsive collisions. Here, we construct a commonly used model, known as a *Gaussian random process*, for the former type of bath. Since for most potentials, the GLE must be integrated numerically, we seek a discrete description of  $R(t)$  that acts at  $M$  discrete time points  $0, \Delta t, 2\Delta t, \dots, M\Delta t$ . At the  $k$ th point of a Gaussian random process,  $R_k \equiv R(k\Delta t)$  can be expressed as the sum of a Fourier sine and cosine series

$$R_k = \sum_{j=1}^M \left[ a_j \sin\left(\frac{2\pi jk}{M}\right) + b_j \cos\left(\frac{2\pi jk}{M}\right) \right], \quad (15.2.18)$$

where the coefficients  $a_j$  and  $b_j$  are random numbers sampled from a Gaussian distribution of the form

$$P(a_1, \dots, a_M, b_1, \dots, b_M) = \prod_{k=1}^M \frac{1}{2\pi\sigma_k^2} e^{-(a_k^2 + b_k^2)/2\sigma_k^2}. \quad (15.2.19)$$

For the random force to satisfy eqn. (15.2.17) at each time point, the width,  $\sigma_k$ , of the distribution must be chosen according to

$$\sigma_k^2 = \frac{1}{\beta M} \sum_{j=0}^M \zeta(j\Delta t) \cos\left(\frac{2\pi jk}{M}\right), \quad (15.2.20)$$

which can be easily evaluated using fast Fourier transform techniques. Since the random process in eqn. (15.2.18) is periodic with period  $M$ , it clearly cannot be used for more than a single period. This means that the number of points  $M$  in the trajectory must be long enough to capture the dynamical behavior sought.

### 15.2.3 The dynamic friction kernel

The convolution integral term in eqn. (15.2.14)

$$\int_0^t d\tau \dot{q}(\tau) \zeta(t - \tau)$$

is called the *memory integral* because it depends, in principle, on the entire history of the evolution of  $q$ . Physically, this term expresses the fact that the bath requires a finite time to respond to any fluctuation in the motion of the system and that this lag affects how the bath subsequently affects the motion of the system. Thus, the force that the bath exerts on the system at any point in time depends on the prior motion of the system coordinate  $q$ . The memory of the motion of the system coordinate retained by the bath is encoded in the *memory kernel* or *dynamic friction kernel*,  $\zeta(t)$ . Note that  $\zeta(t)$  has units of mass·(time)<sup>-2</sup>. Since the dynamic friction kernel is actually an autocorrelation function of the random force, it follows that the correlation time of the random force determines the decay time of the memory kernel. The finite correlation time of the memory kernel indicates that the bath, in reality, retains memory of the

system motion for a finite time  $t_{\text{mem}}$ . One might expect, therefore, that the memory integral could be replaced, to a very good approximation, by an integral over a finite interval  $[t - t_{\text{mem}}, t]$ :

$$\int_0^t d\tau \dot{q}(\tau)\zeta(t - \tau) \approx \int_{t-t_{\text{mem}}}^t d\tau \dot{q}(\tau)\zeta(t - \tau). \quad (15.2.21)$$

Such an approximation proves very convenient in numerical simulations based on the generalized Langevin equation, as it permits the memory integral to be truncated, thereby reducing the computational overhead needed to evaluate it.

We now consider a few interesting limiting cases of the friction kernel. Suppose, for example, that the bath is able to respond infinitely quickly to the motion of the system. This would occur when the system mass,  $\mu$ , is very large compared to the bath masses,  $\mu \gg m_\alpha$ . In such a case, the bath retains essentially no memory of the system motion, and the memory kernel reduces to a simple  $\delta$ -function in time:

$$\zeta(t) = \lim_{\epsilon \rightarrow 0} \zeta_0 \delta(t - \epsilon). \quad (15.2.22)$$

The introduction of the parameter  $\epsilon$  ensures that the entire  $\delta$ -function is integrated over. Alternatively, we can recognize that for  $\epsilon = 0$ , only “half” of the  $\delta$ -function is included in the interval  $t \in [0, \infty)$ , since  $\delta(t)$  is an even function of time, and therefore, we could also define  $\zeta(t)$  as  $2\zeta_0\delta(t)$ . Substituting eqn. (15.2.22) into eqn. (15.2.14) and taking the limit gives an equation of motion for  $q$  of the form

$$\begin{aligned} \mu \ddot{q} &= -\frac{dW}{dq} - \lim_{\epsilon \rightarrow 0} \zeta_0 \int_0^t d\tau \dot{q}(\tau)\delta(t - \epsilon - \tau) + R(t) \\ &= -\frac{dW}{dq} - \lim_{\epsilon \rightarrow 0} \zeta_0 \dot{q}(t - \epsilon) + R(t) \\ &= -\frac{dW}{dq} - \zeta_0 \dot{q}(t) + R(t), \end{aligned} \quad (15.2.23)$$

where all quantities on the right are evaluated at time  $t$ . Eqn. (15.2.23) is known as the *Langevin equation* (LE), and it should be clear that the LE is ultimately a special case of the GLE. The LE describes the motion of a system in a potential  $W(q)$  subject to an ordinary dissipative friction force as well as a random force  $R(t)$ . Langevin originally employed eqn. (15.2.23) as a model for Brownian motion, where the mass disparity clearly holds (Langevin, 1908). The most common use of the LE is as a thermostating method for generating a canonical distribution (see Section 15.5). The quantity  $\zeta_0$  is known as the *static friction coefficient*, defined generally as

$$\zeta_0 = \int_0^\infty dt \zeta(t). \quad (15.2.24)$$

Note that the random force  $R(t)$  is now completely uncorrelated, as it is required to satisfy

$$\langle R(0)R(t) \rangle = 2kT\zeta_0\delta(t). \quad (15.2.25)$$

In addition, note that  $\zeta_0$  has units of mass·(time)<sup>-1</sup>.

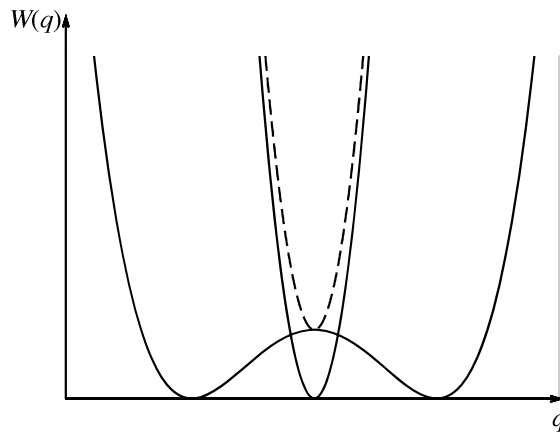
The second limiting case we will consider is a sluggish bath that responds very slowly to changes in the system coordinate. For such a bath, we can take  $\zeta(t)$  approximately constant over a long time interval, i.e.,  $\zeta(t) \approx \zeta(0) \equiv \zeta$ , for times that are short compared to the actual response time of the bath. In this case, the memory integral can be approximated as

$$\int_0^t d\tau \dot{q}(\tau)\zeta(t-\tau) \approx \zeta \int_0^t d\tau \dot{q}(\tau) = \zeta(q(t) - q(0)), \quad (15.2.26)$$

and eqn. (15.2.14) becomes

$$\mu\ddot{q} = -\frac{d}{dq} \left( W(q) + \frac{1}{2}\zeta(q - q(0))^2 \right) + R(t). \quad (15.2.27)$$

Here, the effect of friction is now manifest as an extra harmonic term in the potential



**Fig. 15.1** Example of the dynamic caging phenomenon.  $W(q)$  is taken to be the double-well potential. The potential  $\zeta(q - q_0)^2/2$  is the single-minimum solid line, and the dashed line shows the potential shifted to the top of the barrier region.

$W(q)$ , and all terms on the right are, again, evaluated at time  $t$ . This harmonic term in  $W(q)$  has the effect of trapping the system in certain regions of configuration space, an effect known as *dynamic caging*. Fig. 15.1 illustrates how the caging potential  $\zeta[q - q(0)]^2/2$  can potentially trap the particle at what would otherwise be a point of unstable equilibrium. An example of this is a dilute mixture of small, light particles in a bath of large, heavy particles. In spatial regions where heavy particle cluster forms a slowly moving spatial “cage,” the light particles can become trapped. Only rare fluctuations in the bath open up this rigid structure, allowing the light particles to escape the cage. After such an escape, however, the light particles can become trapped again in another cage newly formed elsewhere for a comparable time interval. Not unexpectedly, dynamic caging can cause a significant decrease in the rate of light-particle diffusion.