1.4: The Langevin Equation

Our focus in this chapter has been on the description of purely stochastic processes. However, a variety of interesting and important phenomena are subject to combinations of deterministic and stochastic processes. We concern ourselves now with a particular class of such phenomena which are described by Langevin equations. In its simplest form, a Langevin equation is an equation of motion for a system that experiences a particular type of random force. The archetypal system governed by a Langevin equation is a Brownian particle, that is, a particle undergoing Brownian motion. (For a brief description of the nature and discovery of Brownian motion, see the Appendix).

The Langevin equation for a Brownian particle in a one-dimensional fluid bath is

$$m\dot{v}(t)+\zeta v(t)=f(t) \tag{1.4.1}$$

where $v(t)=\dot{x}(t)$ is the velocity of the Brownian particle, ζ is a coefficient describing friction between the particle and the bath, m is the mass of the Brownian particle, and $f(t)$ is a random force. Though it is random, we can make a couple of useful assumptions about $f(t)$:

- The random force is equally likely to push in one direction as it is in the other, so the average over all realizations of the force is zero,

$$\langle f(t)\rangle_f=0 \tag{1.4.2}$$

- The random force exhibits no time correlation but has a characteristic strength factor g that does not change over time,

$$\langle f(t_1)\,f(t_2)\rangle_f=g\delta(t_1-t_2) \tag{1.4.3}$$

Random forces that obey these assumptions are called white noise, or more precisely, Gaussian white noise. In this case, all odd moments of f will vanish, and all even moments can be expressed in terms of two-time correlation functions: for example, the fourth moment is given by

$$\begin{aligned}\langle f(t_1)\,f(t_2)\,f(t_3)\,f(t_4)\rangle_f &= \langle f(t_1)\,f(t_2)\rangle_f\langle f(t_3)\,f(t_4)\rangle_f\\ &+\langle f(t_1)\,f(t_3)\rangle_f\langle f(t_2)\,f(t_4)\rangle_f\\ &+\langle f(t_1)\,f(t_4)\rangle_f\langle f(t_2)\,f(t_3)\rangle_f\end{aligned}$$

In general, complex systems may exhibit time-dependent strength factors $g(t)$, but we will work with the more mathematically tractable white noise assumption for the random force.

The formal solution to the Langevin equation Eq.(1.41) is

$$v(t)=v(0)e^{-\frac{\zeta}{m}t}+\frac{1}{m}\int_0^t e^{-\frac{\zeta}{m}(t-\tau)}f(\tau)d\tau \tag{1.4.4}$$

In computing the average velocity under the white noise assumption, the second term of Eq.(1.42) vanishes thanks to the condition $\langle f(t)\rangle_f=0$. So the average velocity is simply

$$\langle v(t)\rangle_f=v(0)e^{-\frac{\zeta}{m}t} \tag{1.4.5}$$

Of special interest is the velocity-velocity correlation function

$$C(t_1-t_2)=\langle v(t_1)\,v(t_2)\rangle_f \tag{1.4.6}$$

which can also be computed from Eq.(1.42). Invoking the white noise condition for $\langle f(t_1)\,f(t_2)\rangle_f$, we find that

$$\langle v(t_1)\,v(t_2)\rangle_f=\left(v(0)^2-\frac{g}{2m\zeta}\right)e^{-\frac{\zeta}{m}(t_1+t_2)}+\frac{g}{2m\zeta}e^{-\frac{\zeta}{m}(t_2-t_1)} \tag{1.4.7}$$

So far, we have only performed an average over realizations of the random force, denoted by $\langle\ldots\rangle_f$; to proceed, we may also take a thermal average $\langle\ldots\rangle_\beta$, that is, the average over realizations of different initial velocities at inverse temperature β. Equipartition tells us that $\left\langle v_0^2\right\rangle_\beta=\frac{1}{m\beta}$; if we use Eq.(1.45) to write down an expression for $\left\langle\langle v(t_1)\,v(t_2)\rangle_f\right\rangle_\beta$ and apply equipartition, we arrive at the conclusion that

$$g = \frac{2\zeta}{\beta} \tag{1.4.8}$$

which is a manifestation of the fluctuation-dissipation theorem (the fluctuations in the random force, described by g, are proportional to the dissipation of energy via friction, described by ζ).

The properties of the velocity variable v enumerated above imply that the distribution of velocities is Gaussian with exponential memory decay, like the diffusive oscillator in section 1.3, and so we can also think of this type of Brownian motion as an Ornstein-Uhlenbeck process. In particular, the probability distribution for the velocity is

$$P\left(v_0, v, t\right) = \sqrt{\frac{m\beta}{2\pi\left(1-e^{-2\gamma t}\right)}} \exp\left[-\frac{m\beta\left(v - v_0 e^{-\gamma t}\right)^2}{2\left(1-e^{-2\gamma t}\right)}\right] \tag{1.4.9}$$

We now have a thorough description of the Brownian particle's velocity, but what about the particle's diffusion? We'd like to know how far away the Brownian particle can be expected to be found from its initial position as time passes. To proceed, we calculate the mean square displacement of the particle from its initial position,

$$\begin{aligned} R^2(t) &= \left\langle (x(t) - x(0))^2 \right\rangle \\ &= \int_0^t \int_0^t \left\langle v\left(\tau_1\right) v\left(\tau_2\right) \right\rangle d\tau_2 d\tau_1 \\ &= 2\int_0^t (t-\tau) C(\tau) d\tau \end{aligned}$$

At long times, the mean square displacement behaves as

$$R^2(t) = 2t\int_0^\infty C(t) dt \tag{1.4.10}$$

This linear scaling with time is the experimentally observed behavior of Brownian particles, where the proportionality constant is called the diffusion constant D; hence, we have found an expression for the macroscopic diffusion constant D in terms of the correlation function,

$$D = \int_0^\infty C(t) dt \tag{1.4.11}$$

Eq. (1.52) is known as the Green-Kubo relation, and it implies that the mean square displacement at long times is simply

$$\lim_{t \gg 1} R^2(t) = 2Dt \tag{1.4.12}$$

This result for the mean square displacement also scales linearly with the dimensionality of the system (i.e. in three dimensions, $R^2(t) = 6Dt$).

To determine the behavior of $R^2(t)$ at short times, note that $v(t) \approx v(0)$ for short times, so that $R^2(t) = \left(\int v(t) dt\right)^2 \approx \left\langle v_0^2 \right\rangle t^2$. Therefore, the short-time limit of the mean square displacement is

$$\lim_{t \ll 1} R^2(t) = \frac{1}{m\beta} t^2 \tag{1.4.13}$$

For times in between these extremes, the formal solution to the Langevin equation for the velocity would have to be integrated. This can be done; sparing the details, the result after thermal averaging is

$$R^2(t) = \frac{2}{\beta\zeta}\left[t - \frac{1}{\gamma}\left(1 - e^{-t}\right)\right] \tag{1.4.14}$$

where $\gamma = \frac{\zeta}{m}$.

As a final note, the Langevin equation as presented in this section is often modified to describe more complex systems. The most common modifications to the Langevin equation are:

- The replacement of the friction coefficient ζ with a memory kernel $\gamma(t)$ that allows the system to have some memory of previous interactions.

- The addition of a deterministic mean force $F = -\nabla U$, which permits the system to respond to forces beyond those due to interactions with the bath.

Such modified Langevin equations, also known as Generalized Langevin equations or GLEs, will be explored in further detail in Chapter 4. The Langevin equation and its generalized counterparts provide the basis for a number of successful models of stochastic processes in chemical physics. [3]
