1 General Development of the Langevin Equation

1.1 The Reservoir

Systems that undergo Brownian motion turn out to be part of a general problem in physics, namely, a “small” system with few degrees of freedom coupled to a “large” thermal (or heat) bath which describes the environment the system is immersed in. This heat bath is called a “reservoir”. A thermodynamic reservoir is a system with an extremely large number (ideally infinte) degrees of freedom. It is not useful to attempt a detailed mathematical description of the dynamics of the reservoir. By partitioning and the use of coarse-grained variables the effects of the reservoir on the small system can be modeled using statistical methods.

The Langevin equation has been used as a phenomenological equation of motion to describe a system of dynamical variables interacting with a surrounding heat bath. A complete description of the environmental variables is far to complex. Besides, the system evolution is our interest not that of the heat bath, but the role of the environment-system interaction is important. A simple illustration of this idea is contained in Fig. 1. In general a total coupled

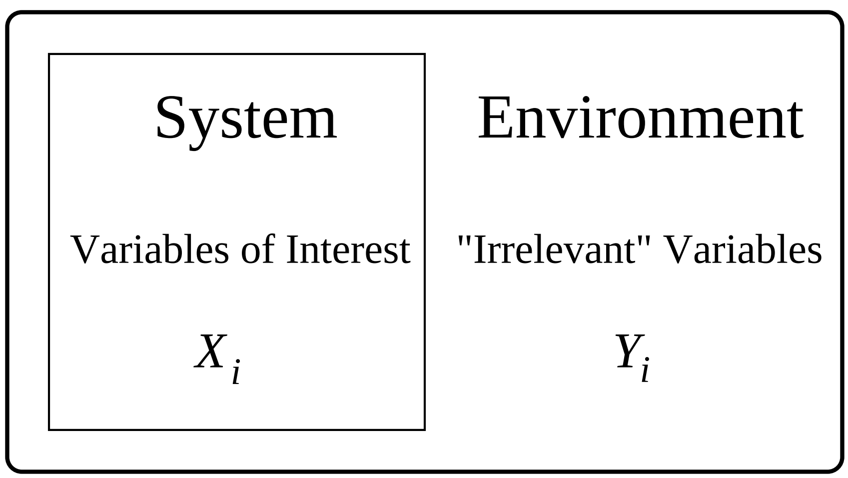

Figure 1: Picture illustrating the partitioning of the system variables to be studied from the variables describing the environment which will not be directly taken into account.

system Hamiltonian can be written down with the form, $H(X,Y) = H(X)+H(Y)+V(X,Y)$. The objective is to eliminate the environment variables, $\{Y_i\}$, to produce an equation of motion for the system variables, $\{X_i\}$, with damping. The damping or “dissipation” will be modeled through the potential energy $V(X,Y)$. Therefore it is important to understand the thermodynamics of the environment (i.e. heat bath) interacting with the system.

2 Developing the Equation of Motion

There have been many researchers who have described Brownian motion of a particle immersed in a heat bath using methods from statistical mechanics. The Langevin equation is one method used to study a dynamical particle under going Brownian motion. The following is a development of the Langevin equation of motion in one dimension.

Consider a particle of mass m with a center-of-mass coordinate as a function of time $x(t)$. The corresponding velocity of the particle is $\mathsf{v} \equiv dx/dt$. This particle is embedded in an environment which is at absolute temperature T. It would be impractical to describe in detail the interaction of all the degrees of freedom of the environment with the center-of-mass coordinate x. However these other degrees of freedom can be modeled as a heat reservoir at some temperature T. The interactions between x and the reservoir can be combined into a net force $\mathbf{F}(t)$ which can be used in finding the time dependence of x. The particle velocity v usually will be different from its mean value in equilibrium. The starting point is Newton's second law of motion;

$$m\frac{d\mathsf{v}}{dt} = \mathbf{F}_e(t) + \mathbf{F}(t) \; , \qquad (1)$$

where $\mathbf{F}_e(t)$ denotes the sum of all externally applied conservative forces. To continue, a method to describe $\mathbf{F}(t)$ is needed.

$\mathbf{F}(t)$ depends on the positions and motions of all the atoms in the medium surrounding the particle. This means that $\mathbf{F}$ is a rapidly varying function of time with the fluctuations being very irregular. Thus a precise functional dependence of $\mathbf{F}$ on t is impossible. The only way to move forward is to formulate the problem in statistical terms. Consider an ensemble of many similarly prepared systems each consisting of a particle and heat bath. For each case $\mathbf{F}(t)$ is a random function of time. Now a key point must be made about the time scales involved in the problem. The fluctuations in $\mathbf{F}(t)$ can be characterized by a "correlation time" τ_c which is approximately the mean time between two successive extrema of $\mathbf{F}$. The time τ_c is quite small on a macroscopic scale (i.e. about the mean time between collisions, ~ 100 fs). The variations in $\mathbf{F}$ will be as likely positive as negative such that the ensemble average $\bar{\mathbf{F}}(t)$ vanishes. However at any point in time $\bar{\mathbf{F}}$ will be slowly varying in a way as to restore the particle to equilibrium. This means that the total force can be divided into two pieces because of the time scales of their variations.

$$\mathbf{F} = \bar{\mathbf{F}} + \mathbf{F}' \; , \qquad (2)$$

where $\mathbf{F}'$ denotes the rapidly fluctuating part and whose average value is zero. From equation (1) it can be seen that since $\mathbf{F}(t)$ is a rapidly varying function of time, then the velocity must also vary with time. It is assumed that the velocity v has a rapidly fluctuating component superimposed onto a slowly varying motion. Therefore the velocity can be decomposed like the force into two pieces;

$$\mathsf{v} = \bar{\mathsf{v}} + \mathsf{v}' \ , \tag{3}$$

where v' is the part that rapidly fluctuates and whose mean value vanishes. The slow varying part $\bar{\mathsf{v}}$ is important because it is what determines the behavior of the particle over long time periods.

The slow varying part of the total force $\bar{\mathbf{F}}$ must be a function of $\bar{\mathsf{v}}$ such that $\bar{\mathbf{F}}(\bar{\mathsf{v}}) = 0$ in equilibrium when $\bar{\mathsf{v}}$ goes to zero. It will be assumed that $\bar{\mathsf{v}}$ is small enough, so that after expanding $\bar{\mathbf{F}}(\bar{\mathsf{v}})$ in a power series in $\bar{\mathsf{v}}$ only the linear term is needed. Therefore $\bar{\mathbf{F}}$ will have the general form;

$$\bar{\mathbf{F}} = -\alpha\bar{\mathsf{v}} \ , \tag{4}$$

where α is a positive constant (called the friction coefficient) and the minus sign means that the force $\bar{\mathbf{F}}$ acts to reduce $\bar{\mathsf{v}}$ to zero as time increases. Substituting the slow part of (2) and its definition (4) into Newton's equation of motion (1) yields,

$$m\frac{d\bar{\mathsf{v}}}{dt} = \mathbf{F}_e + \bar{\mathbf{F}} = \mathbf{F}_e - \alpha\bar{\mathsf{v}} \ . \tag{5}$$

This result can be modified by adding the rapidly varying parts of v' and $\mathbf{F}'$ into (5) and noting that $\alpha\bar{\mathsf{v}} \approx \alpha\mathsf{v}$, because the rapidly varying part of the friction force $-\alpha\mathsf{v}'$ is negligible compared to $\mathbf{F}'(t)$ fluctuations. Making this substitution gives,

$$m\frac{d\mathsf{v}}{dt} = \mathbf{F}_e(t) - \alpha\mathsf{v} + \mathbf{F}'(t) \ . \tag{6}$$

Equation (6) is a stochastic differential equation called the "Langevin equation." In the Langevin equation the force $\mathbf{F}(t)$ is explicitly decomposed into a slowly varying part $-\alpha\mathsf{v}$ and a fluctuating part $\mathbf{F}'(t)$. $\mathbf{F}'(t)$ is purely random with a mean value $\langle\mathbf{F}'(t)\rangle = 0$ irrespective of the position or velocity of the particle. Also, the Langevin force is stationary, Ergodic, Gaussian and Markovian. Given the initial conditions, the Langevin equation describes the time evolution of the particle. The presents of the frictional force $-\alpha\mathsf{v}$ implies the existence of physical processes that allow the dissipation of energy associated with the center-of-mass coordinate x to the other degrees of freedom of the environment. In order to understand the frictional force better, a relationship between dissipation and the fluctuating force must be found.

3 The Fluctuation-Dissipation Theorem

Einstein's theoretical work on Brownian motion brought together quantities which seemed unrelated at the time, that is friction and temperature. In 19$^{\text{th}}$ century theoretical physics, these were uncorrelated concepts. It turns out that the physics contained in the Einstein relation is extremely general and applies to many physical systems. We call this bit of physics the *Fluctuation-Dissipation theorem.* Now we will give a derivation that follows Reif.

Consider a time interval τ which is small compared to the period of the applied forces $\mathbf{F}_e(t)$, but is large compared to the collision or correlation time, $\tau \gg \tau_c$. Rewriting (1) in its integral form with a difference form for the differential $d\mathsf{v}$,

$$m\big[\mathsf{v}(t+\tau) - \mathsf{v}(t)\big] = \int_t^{t+\tau} \big[\mathbf{F}_e(t') + \mathbf{F}(t')\big]\,dt' \approx \mathbf{F}_e(t)\,\tau + \int_t^{t+\tau} \mathbf{F}(t')\,dt' \ . \tag{7}$$

Now averaging over the heat bath variables yields,

$$m\big[\,\langle \mathsf{v}(t+\tau)\rangle - \langle \mathsf{v}(t)\rangle\,\big] = \mathbf{F}_e(t)\,\tau + \int_t^{t+\tau} \langle \mathbf{F}(t')\rangle \ dt' \ . \tag{8}$$

Now the problem is to find an expression for $\langle \mathbf{F}(t')\rangle$. If the motion of the particle with its effect on the environment is not considered, then the mean of the force is merely the static equilibrium value $\langle \mathbf{F}\rangle_0 = 0$. This approximation is too simplistic, since it would not yield a slowly varying velocity that tended to restore the particle to thermal equilibrium. An estimate of how the changes in the velocity of the particle affect $\langle \mathbf{F}\rangle$ is required.

The following argument is paraphrased from Reif. To proceed, a method is needed for the system described by x to interact with the environment through the force $\mathbf{F}$. Consider that at some time t the system is in equilibrium with $\langle \mathbf{F}\rangle = 0$ and the particle has a velocity $\mathsf{v}(t)$ which is associated with state i having a probability denoted by W_i^0. At a small delta time $t' = t + \tau'$ later the particle has a velocity $\mathsf{v}(t+\tau')$ and this change in the particle's velocity disturbs the internal equilibrium of the environment. For a sufficiently small τ', the mean force $\langle \mathbf{F}(t')\rangle$ is dependent on the state at time t, however after a time τ_c the environment (heat reservoir) has reestablished equilibrium conditions consistent with the state of the particle having velocity $\mathsf{v}(t+\tau')$. At this point the reservoir is equally likely to be in any one of its Ω accessible states. Suppose after a time interval $\tau > \tau_c$ the particle velocity changes by $\Delta\mathsf{v}(\tau')$ and the heat reservoir's energy correspondingly changes from E' to $E' + \Delta E'(\tau')$. Then the number of accessible states that the heat reservoir could possibly assume changes from $\Omega(E')$ to $\Omega(E' + \Delta E')$. In equilibrium the probability of the system occupying state i is proportional to the corresponding number of accessible states for the reservoir. The probability of the same configuration i occurring at the times t and $t+\tau'$ is;

$$\frac{W_i(t+\tau')}{W_i^0} = \frac{\Omega(E'+\Delta E')}{\Omega(E')} = \boldsymbol{e}^{\beta\,\Delta E'} \;, \tag{9}$$

where $\beta \equiv (\partial \ln \Omega / \partial E') = (k_B T)^{-1}$ is the temperature parameter of the heat reservoir. The physical interpretation of (9) is that the probability of the system being found in a given state in the future is increased if more energy becomes available to the reservoir. Rearranging (9) assuming that $\Delta E'$ is small over times on the order of τ' and little energy is transferred per collision gives,

$$W_i(t') = W_i^0 \boldsymbol{e}^{\beta\,\Delta E'} \approx W_i^0(1+\beta\,\Delta E') \;. \tag{10}$$

Now taking the mean of $\mathbf{F}$ at $t' = t+\tau'$ yields,

$$\langle \mathbf{F}(t') \rangle = \sum_i W_i(t')\mathbf{F}_i = \sum_i W_i^0(1+\beta\,\Delta E')\mathbf{F}_i = \langle \mathbf{F} \rangle_0 + \langle \beta\,\Delta E'\,\mathbf{F} \rangle_0 \;. \tag{11}$$

Remembering that $\langle \mathbf{F} \rangle_0 = 0$ leaves,

$$\langle \mathbf{F}(t') \rangle = \beta\,\langle \mathbf{F}\Delta E' \rangle_0 \;. \tag{12}$$

The average of (12) is not in general zero. To use this result in (8), the integration time τ must be sufficiently long such that $\tau \geqq \tau' = t'-t \gg \tau_c$ making the approximation (12) good when used in the integrand of (8).

The energy increase $\Delta E'$ in the reservoir during the time $\tau' = t'-t$ is the negative of the work done by the force $\mathbf{F}$ on the particle. Therefore;

$$\Delta E' = -\int_t^{t'} \mathsf{v}(t'')\mathbf{F}(t'')\,dt'' \approx -\mathsf{v}(t)\int_t^{t'} \mathbf{F}(t'')\,dt'' \;, \tag{13}$$

where the approximation that $\mathsf{v}(t)$ is essentially constant over the time interval τ. Substituting (13) into (12) yields,

$$\langle \mathbf{F}(t') \rangle = -\beta\Big\langle \mathbf{F}(t')\,\mathsf{v}(t')\int_t^{t'} \mathbf{F}(t'')\,dt'' \Big\rangle_0 = -\beta\,\bar{\mathsf{v}}(t)\int_t^{t'} \big\langle \mathbf{F}(t')\mathbf{F}(t'')\big\rangle_0 dt'' \;. \tag{14}$$

First $\mathsf{v}(t)$ was averaged over separately from $\mathbf{F}$ since it varies much more slowly than $\mathbf{F}(t)$. Now substitute (14) into (8) after defining the time difference $\mathsf{s} = t''-t'$. Thus,

$$m\big[\,\langle \mathsf{v}(t+\tau)\rangle - \langle \mathsf{v}(t)\rangle\,\big] = \mathbf{F}_e(t)\,\tau - \beta\,\bar{\mathsf{v}}(t)\int_t^{t+\tau} dt' \int_{t-t'}^{0} \langle \mathbf{F}(t')\mathbf{F}(t'+\mathsf{s})\rangle_0\,d\mathsf{s} \;. \tag{15}$$

The last term on the right of equation (15) is slowly varying and leads to “dissipation” (also called “damping”). If the external force is zero, then the dissipation will drive the mean velocity $\bar{\mathsf{v}}$ to zero as time increases.

The ensemble average in the integrand of (15),

$$K(s) \equiv \langle \mathbf{F}(t')\mathbf{F}(t'')\rangle_0 = \langle \mathbf{F}(t')\mathbf{F}(t'+s)\rangle_0 \ , \tag{16}$$

is called the autocorrelation function of $\mathbf{F}(t)$. It is sometimes called a "dissipative memory kernel". The autocorrelation function is defined by the time difference s, and therefore independent of the time t', which describes a stationary process. $K(s)$ is nonzero for s when functions $\mathbf{F}(t')$ and $\mathbf{F}(t'+s)$ overlap. Therefore $K(s)$ is a highly peaked, symmetric function. Also $K(s) \approx 0$ if $s > \tau_c \ll \tau$.

The assumption made at the beginning was that $\bar{v}$ does not vary much on time scales the order of τ. Then the left side of (15) is relatively small, hence a "coarse-grained" time derivative can be defined and applied to equation (15);

$$\begin{aligned} \frac{d\bar{v}}{dt} &\equiv \frac{\langle v(t+\tau)\rangle - \langle v(t)\rangle}{\tau} \ , \\ &= \frac{1}{m}\left\{ \mathbf{F}_e(t) - \frac{\beta\,\bar{v}(t)}{\tau}\int_t^{t+\tau} dt' \int_{t-t'}^{0} K(s)\,ds \right\} \ . \end{aligned} \tag{17}$$

Next change the limits on the integrals in (17) by determining the domain of integration.

$$\int_t^{t+\tau} dt' \int_{t-t'}^{0} K(s)\,d(s) = \int_{-\tau}^{0} ds \int_{t-s}^{t+\tau} K(s)\,dt' = (\tau + s)\int_{-\tau}^{0} K(s)\,ds \ . \tag{18}$$

Since s can be neglected compared to τ, and the lower limit of the last integral can be replaced by $-\infty$ with negligible error, thus (18) becomes,

$$\approx \tau \int_{-\infty}^{0} K(s)\,ds = \frac{\tau}{2}\int_{-\infty}^{\infty} K(s)\,ds \ . \tag{19}$$

The right integral limits in (19) is due to the symmetry property of the autocorrelation function $K(s)$. As defined in (16), the equilibrium ensemble $K(s)$ is independent of the time t'. Proof of the symmetry property follows;

$$\begin{aligned} K(s) = \langle \mathbf{F}(t)\mathbf{F}(t+s)\rangle = \langle \mathbf{F}(t'-s)\mathbf{F}(t')\rangle = \langle \mathbf{F}(t')\mathbf{F}(t'-s)\rangle = \langle \mathbf{F}(t)\mathbf{F}(t-s)\rangle \ , \\ K(s) = K(-s) \ . \end{aligned} \tag{20}$$

The second equality is arrived at by substituting $t + s = t'$. The next step is an interchange of terms. The final step involves replacing t' by t. All steps are allowed because the averages are independent of t' or t.

Now (17) can be written in the form;

$$m\frac{d\bar{v}}{dt} = \mathbf{F}_e(t) + \alpha\,\bar{v}(t) \ , \tag{21}$$

where the friction constant is explicitly given by,

$$\alpha \equiv \frac{1}{2k_B T} \int_{-\infty}^{\infty} \langle \mathbf{F}(0)\mathbf{F}(s) \rangle_0 \, ds \; . \tag{22}$$

The relation (22) defining α is known as the "fluctuation-dissipation theorem". This is an explicit expression for the friction constant in terms of the autocorrelation function of the fluctuating force $\mathbf{F}(t)$ in thermal equilibrium. It can be seen that (21) is the same as (5) and the present analysis provides greater insight into how the frictional force arises from the fluctuating force.