13.11 Fluctuation and Dissipation

Let's look again at Langevin's equation (13.116) but with u as the independent variable

$$\frac{d\boldsymbol{v}(u)}{du} + \frac{\boldsymbol{v}(u)}{\tau} = \boldsymbol{a}(u). \tag{13.146}$$

If we multiply both sides by the exponential $\exp(u/\tau)$

$$\left(\frac{d\boldsymbol{v}}{du} + \frac{\boldsymbol{v}}{\tau}\right) e^{u/\tau} = \frac{d}{du}\left(\boldsymbol{v}\, e^{u/\tau}\right) = \boldsymbol{a}(u)\, e^{u/\tau} \tag{13.147}$$

and integrate from 0 to t

$$\int_0^t \frac{d}{du}\left(\boldsymbol{v}\, e^{u/\tau}\right) du = \boldsymbol{v}(t)\, e^{t/\tau} - \boldsymbol{v}(0) = \int_0^t \boldsymbol{a}(u)\, e^{u/\tau}\, du \tag{13.148}$$

then we get

$$\boldsymbol{v}(t) = e^{-t/\tau}\, \boldsymbol{v}(0) + e^{-t/\tau} \int_0^t \boldsymbol{a}(u)\, e^{u/\tau}\, du. \tag{13.149}$$

Thus the ensemble average of the square of the velocity is

$$\begin{aligned}\langle \boldsymbol{v}^2(t)\rangle = e^{-2t/\tau}\langle \boldsymbol{v}^2(0)\rangle &+ 2e^{-2t/\tau}\int_0^t \langle \boldsymbol{v}(0)\cdot \boldsymbol{a}(u)\rangle\, e^{u/\tau}\, du \\ &+ e^{-2t/\tau}\int_0^t\int_0^t \langle \boldsymbol{a}(u_1)\cdot\boldsymbol{a}(u_2)\rangle\, e^{(u_1+u_2)/\tau}\, du_1 du_2.\end{aligned} \tag{13.150}$$

The second term on the RHS is zero, so we have

$$\langle \boldsymbol{v}^2(t)\rangle = e^{-2t/\tau}\langle \boldsymbol{v}^2(0)\rangle + e^{-2t/\tau}\int_0^t\int_0^t \langle \boldsymbol{a}(u_1)\cdot\boldsymbol{a}(u_2)\rangle\, e^{(u_1+u_2)/\tau}\, du_1 du_2. \tag{13.151}$$

The ensemble average

$$C(u_1, u_2) = \langle \boldsymbol{a}(u_1)\cdot\boldsymbol{a}(u_2)\rangle \tag{13.152}$$

is an example of an **autocorrelation function**.

All autocorrelation functions have some simple properties, which are easy to prove (Pathria, 1972, p. 458):

1. If the system is independent of time, then its autocorrelation function for any given variable $\boldsymbol{A}(t)$ depends only upon the time delay s:

$$C(t, t+s) = \langle \boldsymbol{A}(t)\cdot\boldsymbol{A}(t+s)\rangle \equiv C(s). \tag{13.153}$$

2. The autocorrelation function for $s = 0$ is necessarily non-negative

$$C(t,t) = \langle \boldsymbol{A}(t)\cdot\boldsymbol{A}(t)\rangle = \langle \boldsymbol{A}(t)^2\rangle \ge 0. \tag{13.154}$$

If the system is time independent, then $C(t,t) = C(0) \geq 0$.

3. The absolute value of $C(t_1,t_2)$ is never greater than the average of $C(t_1,t_1)$ and $C(t_2,t_2)$ because

$$\langle |\boldsymbol{A}(t_1) \pm \boldsymbol{A}(t_2)|^2 \rangle = \langle \boldsymbol{A}(t_1)^2 \rangle + \langle \boldsymbol{A}(t_2)^2 \rangle \pm 2 \langle \boldsymbol{A}(t_1) \cdot \boldsymbol{A}(t_2) \rangle \geq 0 \quad (13.155)$$

which implies that

$$-C(t_1,t_2) \leq \frac{1}{2} \left(C(t_1,t_1) + C(t_2,t_2) \right) \geq C(t_1,t_2) \quad (13.156)$$

or

$$|C(t_1,t_2)| \leq \frac{1}{2} \left(C(t_1,t_1) + C(t_2,t_2) \right). \quad (13.157)$$

For a time-independent system, this inequality is $|C(s)| \leq C(0)$ for every time delay s.

4. If the variables $\boldsymbol{A}(t_1)$ and $\boldsymbol{A}(t_2)$ commute, then their autocorrelation function is symmetric

$$C(t_1,t_2) = \langle \boldsymbol{A}(t_1) \cdot \boldsymbol{A}(t_2) \rangle = \langle \boldsymbol{A}(t_2) \cdot \boldsymbol{A}(t_1) \rangle = C(t_2,t_1). \quad (13.158)$$

For a time-independent system, this symmetry is $C(s) = C(-s)$.

5. If the variable $\boldsymbol{A}(t)$ is randomly fluctuating with zero mean, then we expect both that its ensemble average vanishes

$$\langle \boldsymbol{A}(t) \rangle = \boldsymbol{0} \quad (13.159)$$

and that there is some characteristic time scale T beyond which the correlation function falls to zero:

$$\langle \boldsymbol{A}(t_1) \cdot \boldsymbol{A}(t_2) \rangle \to \langle \boldsymbol{A}(t_1) \rangle \cdot \langle \boldsymbol{A}(t_2) \rangle = 0 \quad (13.160)$$

when $|t_1 - t_2| \gg T$.

In terms of the autocorrelation function $C(u_1,u_2) = \langle \boldsymbol{a}(u_1) \cdot \boldsymbol{a}(u_2) \rangle$ of the acceleration, the variance of the velocity (13.151) is

$$\langle \boldsymbol{v}^2(t) \rangle = e^{-2t/\tau} \langle \boldsymbol{v}^2(0) \rangle + e^{-2t/\tau} \int_0^t \int_0^t C(u_1,u_2)\, e^{(u_1+u_2)/\tau}\, du_1 du_2. \quad (13.161)$$

Since $C(u_1,u_2)$ is big only for tiny values of $|u_2 - u_1|$, it makes sense to change variables to

$$s = u_2 - u_1 \quad \text{and} \quad w = \frac{1}{2}(u_1 + u_2). \quad (13.162)$$

The element of area then is by (12.6–12.14)

$$du_1 \wedge du_2 = dw \wedge ds \quad (13.163)$$