6 Equilibrium dynamics

Fluctuation–dissipation theorem. The evolution of the system state associated with Langevin dynamics can be mapped onto the evolution of the probability distribution of the system state in the form of the Fokker–Planck equation

$$\frac{\partial}{\partial t}p(\mathbf{s},t) = \frac{\partial}{\partial \mathbf{s}} \cdot \left[p(\mathbf{s},t)\frac{\partial H(\mathbf{s})}{\partial \mathbf{s}} + T\frac{\partial p(\mathbf{s},t)}{\partial \mathbf{s}} \right] = \hat{\mathcal{H}}p(\mathbf{s},t) \tag{1}$$

where we have defined the linear operator

$$\hat{\mathcal{H}} = \frac{\partial}{\partial \mathbf{s}} \cdot \left[\frac{\partial H(\mathbf{s})}{\partial \mathbf{s}} + T\frac{\partial}{\partial \mathbf{s}} \right] = -\boldsymbol{\nabla} \cdot \hat{\mathbf{J}} \tag{2}$$

1. Argue that the total probability $\int d\mathbf{s}\, p(\mathbf{s},t)$ is conserved in time.

2. Argue that a formal solution to evolving the probability distribution from a time 0 to a time t is given by

$$p(\mathbf{s},t) = e^{\hat{\mathcal{H}}t}p(\mathbf{s},0) \tag{3}$$

3. The Green function $G_{\mathbf{s}_0}(\mathbf{s},t)$ is the solution to the Fokker–Planck equation for an initial condition $\delta(\mathbf{s}-\mathbf{s}_0)$. Show that

$$p(\mathbf{s},t) = \int d\mathbf{s}_0\, p(\mathbf{s}_0,0)G_{\mathbf{s}_0}(\mathbf{s},t) \tag{4}$$

4. Show that $p_{st}(\mathbf{s}) = \frac{1}{Z}e^{-\beta H(\mathbf{s})}$ is a stationary solution to the Fokker–Planck equation.

5. Assuming $t' \leqslant t$, show that

$$C(t,t') = \frac{\langle \mathbf{s}(t)\cdot\mathbf{s}(t')\rangle}{N} = \int d\mathbf{s}'\, p(\mathbf{s}',t') \int d\mathbf{s}\, G_{\mathbf{s}'}(\mathbf{s},t-t')\frac{\mathbf{s}\cdot\mathbf{s}'}{N} \tag{5}$$

   If t' is large enough that $p(\mathbf{s},t')$ has reached a stationary distribution, argue that $C(t,t') = C(t-t')$ is a function only of the difference in times.

   Hint: one state is sampled from the distribution of configurations that have evolved from time 0 to time t', while the other is sampled from the distribution of configurations that have evolved from *the particular state* at time t' to time t.

6. Assuming $t \geqslant t'$ and that t' is large enough that $p(\mathbf{s},t')$ is stationary, show that

$$\frac{\partial}{\partial t}C(t-t') = -\int d\mathbf{s}'\, p_{st}(\mathbf{s}') \int d\mathbf{s}\, G_{\mathbf{s}'}(\mathbf{s},t-t')\frac{\partial H(\mathbf{s})}{\partial \mathbf{s}} \cdot \mathbf{s}' \tag{6}$$

   Hint: Looking at Fokker–Plank, what is $\frac{\partial}{\partial t}G_{\mathbf{s}_0}(\mathbf{s},t)$? Look for opportunities for integration by parts.

7. To study the response function, consider adding an external field to the Hamiltonian, with $H_{\mathbf{h}}(\mathbf{s}) = H(\mathbf{s}) - \mathbf{h} \cdot \mathbf{s}$. Argue that the field-dependent Fokker–Planck operator is

$$\hat{\mathcal{H}}_{\mathbf{h}} = \hat{\mathcal{H}} - \mathbf{h} \cdot \frac{\partial}{\partial \mathbf{s}} \tag{7}$$

8. If the external field depends on time, argue that formal solutions to the Fokker–Planck equation are now

$$p(\mathbf{s}, t) = e^{\int_0^t dt' \hat{\mathcal{H}}_{\mathbf{h}(t')}} p(\mathbf{s}, 0) \tag{8}$$

9. Assuming $t \geqslant t'$, show that

$$\begin{aligned} R(t, t') &= \frac{1}{N} \sum_{i=1}^{N} \left. \frac{\delta \langle s_i(t) \rangle}{\delta h_i(t')} \right|_{\mathbf{h}=0} \\ &= -\frac{1}{N} \sum_{i=1}^{N} \int d\mathbf{s}' \, \frac{\partial}{\partial s_i'} p(\mathbf{s}', t') \int d\mathbf{s} \, G_{\mathbf{s}'}(\mathbf{s}, t - t') s_i \end{aligned} \tag{9}$$

If t' is large enough that $p(\mathbf{s}, t')$ is stationary, argue that $R(t, t') = R(t-t')$ is a function of the time difference only, and that

$$R(t - t') = \beta \int d\mathbf{s}' \, p_{st}(\mathbf{s}') \int d\mathbf{s} \, G_{\mathbf{s}'}(\mathbf{s}, t - t') \mathbf{s} \cdot \frac{\partial H(\mathbf{s}')}{\partial \mathbf{s}'} \tag{10}$$

Hint: Evolve $\mathbf{s}(t)$ from time 0 in two chunks: one until t', and one from t' to t. Where does the variation with respect to $\mathbf{h}$ act?

10. The Onsager reciprocal relation tells us that in equilibrium, $\langle A(t)B(t') \rangle = \langle A(t')B(t) \rangle$ for any operators A and B. Use this to argue that in equilibrium $R(\tau) = -TC'(\tau)$.