Dynamics of Fluctuations

This section is here for your interest but is not considered examinable.

In equilibrium, the principle of **detailed balance** implies microscopic reversibility — there are no net probability currents. As a result, time evolution is symmetric: fluctuations are time-reversal invariant. Recall the dynamic correlation matrix introduced in **?@sec-correlations**

$$\langle x(\tau)y(\tau+t)\rangle = M_{xy}(t)$$

of which $M_{xx}(t)$ is the diagonal.

Therefore:

$$M_{xx}(t) = \langle x(\tau)x(\tau+t)\rangle = \langle x(\tau)x(\tau-t)\rangle = M_{xx}(-t)$$

For the cross-correlation M_{xy}, we have:

$$M_{xy}(-t) = \langle y(\tau-t)x(\tau)\rangle = \langle y(\tau)x(\tau+t)\rangle$$

(using time translation invariance of the equilibrium state). Combining this with the previous symmetry, we find:

$$M_{xy}(t) = M_{yx}(t)$$

This means the dynamic correlation matrix is symmetric in its indices — a non-trivial consequence of microscopic time-reversal symmetry.

Linear Response Theory and the Fluctuation-Dissipation Theorem

Now suppose we gently perturb the system. For example, we might apply a small thermodynamic force f_x that couples to a fluctuating variable x — like a weak magnetic field h acting on a local magnetization.

(Formally, this means adding a perturbation $-f_x x$ to the Hamiltonian.)

A typical experimental protocol applies the perturbation from $t=-\infty$ and switches it off at $t=0$. For $t>0$, the average response of another variable y is observed to decay:

$$\langle y(t)\rangle_f = R_{yx}(t)\, f_x$$

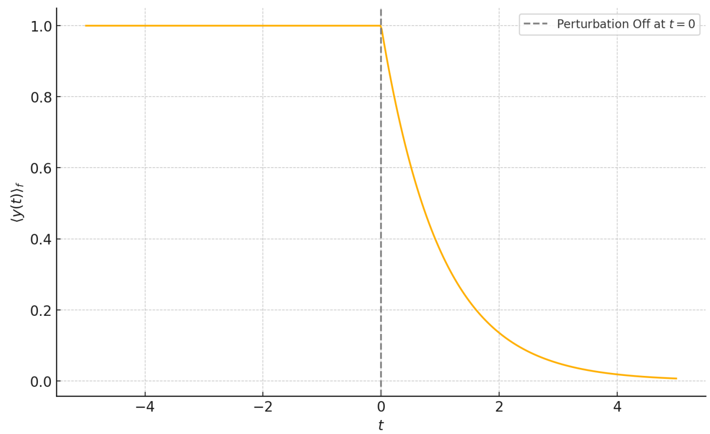


Figure 1: Effect of perturbation on a quantity which is zero in equilibrium

Here, $R_{yx}(t)$ is the **response function** describing how y responds to a small force applied to x at earlier times (for $t \geq 0$).

The key idea is this: If the perturbation is small enough, its effects are indistinguishable from those of a spontaneous fluctuation. So, the decay of the response function should mirror the decay of the correlation function of naturally occurring fluctuations.

This is the essence of the **fluctuation-dissipation theorem**:

$$k_B T \, R_{yx}(t) = M_{yx}(t)$$

This powerful result says that the system's response to a small disturbance is directly related to the correlation of fluctuations in thermal equilibrium.

The factor $k_B T$ ensures both sides of the equation have the same physical dimensions.

> *Note:* We skip the full proof, which requires formal machinery from classical mechanics (e.g., Poisson brackets) or quantum mechanics (density matrices). For more, see the final chapter of Chandler.

Onsager's Theorem

Now, recall from the previous section that the correlation matrix is symmetric:

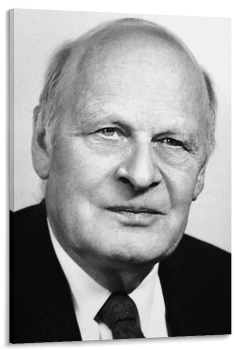
$$M_{xy}(t) = M_{yx}(t)$$

Combining this with the fluctuation-dissipation theorem gives:

$$R_{xy}(t) = R_{yx}(t)$$

This result is known as **Onsager's reciprocal relation**. It states that the response of variable x to a force acting on y is the same as the response of y to a force acting on x — provided the system is in equilibrium.

This is a deep and subtle consequence of microscopic reversibility, and Onsager's real contribution was realizing such a connection could exist. (Onsager also solved the 2D Ising model analytically and won the Nobel Prize in Chemistry in 1968.)



(a) Lars Onsager

(b) Onsager's gravestone and one-up-man-ship with colleague John Kirkwood

Figure 2: Norwegian Physicist and Nobel Laureate, Lars Onsager