2.1: Response, Relaxation, and Correlation

At the beginning of the 21st century, the thermodynamics of systems far from equilibrium remains poorly understood. However, it turns out that many nonequilibrium phenomena can be described rather well in terms of equilibrium fluctuations; this is especially true of systems near equilibrium $[1, 2]$.

By designating a system as "near equilibrium", we mean that the system is perturbed from its equilibrium state by some time-dependent external force $f(t)$. The external force is deterministic, not random; typical examples include mechanical forces and forces due to an applied electric or magnetic field. This force drives the expectation values of some of the system's observables away from their equilibrium values. For example, a typical observable A affected by the external force might be the system's velocity or its magnetic moment. If the response of the observable A to the external force $f(t)$ satisfies the linearity property

$$\delta A(\lambda f(t), t) = \lambda \delta A(f(t), t) \tag{2.1.1}$$

where $\delta A = A - \langle A \rangle_{eq}$ and λ describes the strength of the force, then we call the time-dependent behavior of A the linear response of A to the external force $f(t)$. The linearity property Eq.(2.1) implies that the shape of the response curve A vs. t is independent of the value of λ in the case of linear response.

After achieving a short-lived nonequilibrium steady state (between t_2 and t_3 in Figure 2.1), the system is allowed to relax back to equilibrium. This process is also known as regression. Linear response and regression of a system driven from equilibrium are both described in terms of the **time correlation function** of the observable A, and so we turn first to the definition and properties of the time correlation function $[3, 4]$.

The time correlation function $C_{AA}(t, t')$ of the observable A is defined by

$$C_{AA}(t, t') = \langle A(t) A(t') \rangle = \frac{\mathrm{Tr}[A(t) A(t') \rho_{eq}]}{\mathrm{Tr}[\rho_{eq}]} \tag{2.1.2}$$

Here, ρ_{eq} denotes the equilibrium density matrix of the system; hence the average denoted by $\langle\rangle$ is the ensemble average. This function describes how the value of A at time t is correlated to its

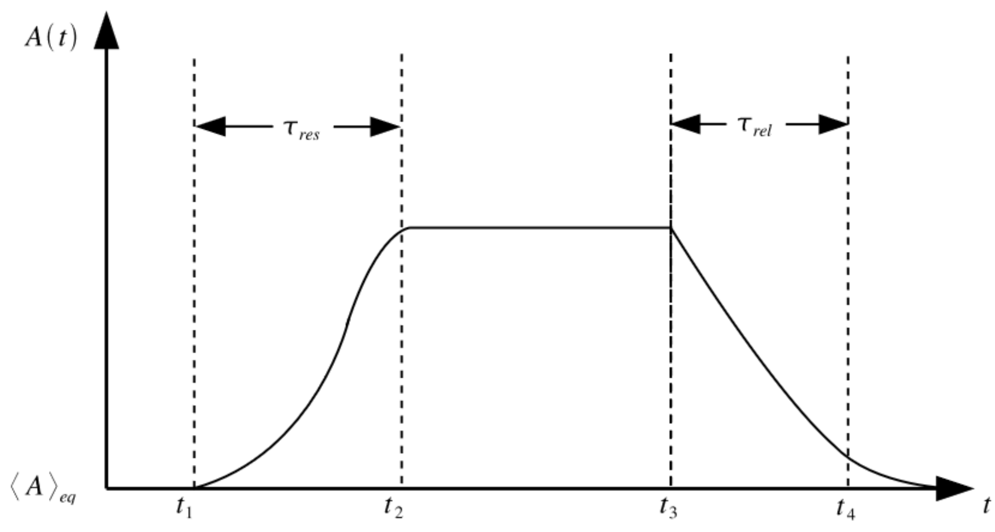

Figure 2.1: Response, nonequilibrium steady state, and relaxation

value at time t'; it is sometimes referred to as the autocorrelation function of A to distinguish it from correlation functions between A and other observables.

For a system which is time-translational invariant, we often choose for convenience to set $t' = 0$ and to drop the subscript on C_{AA}, so that the time correlation function becomes simply

$$C(t) = \langle A(t) A(0) \rangle \tag{2.1.3}$$

The correlation function may in general take on complex values. This result is in keeping with our phenomenological understanding of quantum mechanics in the following way. In order to measure the correlation function of an observable A, the quantity A must be measured twice (first at time zero, then again at time t). However, the first measurement at $t=0$ collapses the system wavepacket, and the state that would have been exhibited by the unperturbed system at time t becomes irrecoverable.

We now identify some important features and properties of correlation functions.

1. All inner products $\langle X \mid Y\rangle$ satisfy the Schwarz inequality

$$|\langle X \mid Y\rangle|^2 \leq \left\langle X^2\right\rangle\left\langle Y^2\right\rangle \tag{2.1.4}$$

Thus the correlation function for any relaxation process has the property

$$C^2(t)=|\langle A(t) \mid A(0)\rangle|^2 \leq \left\langle A^2(t) A^2(0)\right\rangle \leq \left\langle A^2(0)\right\rangle^2=C^2(0) \tag{2.1.5}$$

The second inequality above arises from the fact that $A^2(t)<A^2(0)$ for relaxation processes when $t>0$. More concisely, the Schwarz inequality implies that

$$|C(t)| \leq C(0) \tag{2.1.6}$$

3. Correlation functions are time-invariant, that is, their value depends only on the time interval between the two measurements of the observable:

$$\langle A(t) A(0)\rangle=\left\langle A\left(t-t_0\right) A\left(t_0\right)\right\rangle=\langle A(0) A(-t)\rangle \tag{2.1.7}$$

4. Time-invariance imparts the following identities on the time derivative of a time correlation function:

$$\dot{C}(t)=\langle\dot{A}(t) A(0)\rangle=-\langle A(0) \dot{A}(-t)\rangle=-\langle A(t) \dot{A}(0)\rangle \tag{2.1.8}$$

5. If the equilibrium value of A is $\langle A\rangle_{eq}=0$, then the long-time limit of the correlation function is zero,

$$\lim_{t \rightarrow \infty}\langle A(t) A(0)\rangle=\langle A\rangle_{eq}\langle A(0)\rangle=0 \tag{2.1.9}$$

6. For quantum systems, the time-invariance properties imply that $C(-t)=C^*(t)$. In the classical limit, the correlation function is always real-valued, so this relation becomes $C(-t)=C(t)$ and $C(t)$ is thus even. The fact that classical correlation functions are real-valued should seem sensible because we can (and do) measure correlation functions every day for classical systems, for example, when we try to steady a cord dangling from the ceiling. In this case, we determine the appropriate time and place to apply an external steadying force by looking for time correlations between the various motions the cord undergoes. Note that $C(t)$ is odd with $C(0)=0$ for classical time correlation functions.
7. For ergodic systems, the time correlation function can be calculated as a time average instead of an ensemble average:

$$\langle A(t) A(0)\rangle=\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau A\left(t+\tau^{\prime}\right) A\left(\tau^{\prime}\right) d \tau^{\prime} \tag{2.1.10}$$

Since most systems amenable to analysis by the methods of statistical mechanics are inherently ergodic, we are generally free to choose whichever formulation is easier to work with. The time average is often easier to implement experimentally because it only requires integration along a trajectory rather than a simultaneous sampling of every state accessible to the system.

Example: The classical linear harmonic oscillator with mass m and frequency ω obeys the equation of motion

$$\ddot{x}+\omega^2 x=0 \tag{2.1.11}$$

If we provide initial conditions $x(0)$ and $\dot{x}(0)=v(0)$, then this equation of motion has the closed-form solution

$$x(t)=x(0) \cos \omega t+\frac{v(0)}{\omega} \sin \omega t \tag{2.1.12}$$

Taking the inner product of $x(t)$ with the initial value $x(0)$, we find

$$\langle x(t) x(0)\rangle=\left\langle x^2(0)\right\rangle \cos \omega t+\frac{\langle v(0) x(0)\rangle}{\omega} \sin \omega t \tag{2.1.13}$$

The second term is zero because $\langle x(0)\rangle=0$, so the time correlation function is just

$$C(t)=\left\langle x^2(0)\right\rangle \cos \omega t \tag{2.1.14}$$

Finally, invoking the equipartition result $\left\langle x^{2}(0)\right\rangle=\frac{kT}{m\omega^{2}}$, where k is the Boltzmann constant, the correlation function for the classical linear harmonic oscillator is

$$C(t)=\frac{kT}{m\omega^{2}}\cos\omega t \tag{2.1.15}$$