

5 Lesson 5

5.1 Linear Response (Classical Approach)

5.1.1 The last time

We looked on the perturbed Hamiltonian

$$\mathcal{H}' = \mathcal{H} - fA, \quad (5.1)$$

and got the Onsager Fluctuation-Dissipation theorem

$$\Delta A = \beta f \langle \delta A(0) \delta A(t) \rangle_0, \quad (5.2)$$

which states that the response of the system is indistinguishable from the fluctuations in equilibrium.

5.1.2 Calculation of χ

We have also generalized the calculation to the case of $f(t)$:

$$\Delta A(t) = \int dt' \chi(t, t') f(t'). \quad (5.3)$$

In order to have causality, $\chi(t, t') = 0$ for $t' > t$.

Remark. The susceptibility χ depends on the system S only and *not* on f .

For a system S at equilibrium (stationary)

$$\chi(t, t') = \chi(t - t'), \quad (5.4)$$

therefore,

$$\chi(t, t') = \begin{cases} \chi(t - t'), & t > t' \\ 0, & t' > t \end{cases} \quad (5.5)$$

Take, for example, a step-wise f

$$f(t) = \begin{cases} f, & t > t' \\ 0, & t' > t \end{cases} \quad (5.6)$$

therefore

$$\Delta A(t) = \int_{-\infty}^0 dt' \chi(t, t') f = f \int_t^{\infty} dt' \chi(t'). \quad (5.7)$$

Hence

$$\beta \langle \delta A(0) \delta A(t) \rangle_0 = \int_t^{\infty} dt' \chi(t'), \quad (5.8)$$

and we obtain

$$\chi(t) = \begin{cases} -\beta \frac{d}{dt} \langle \delta A(0) \delta A(t) \rangle_0 & t > 0 \\ 0 & \text{otherwise} \end{cases}. \quad (5.9)$$

We could generalize this to any f .

5.1.3 Generalization

Let's generalize the Hamiltonian to any perturbation B

$$\mathcal{H}' = \mathcal{H} - fB, \quad (5.10)$$

and measure the response of A . We'd get

$$\Delta A(t) = \beta f \langle \delta B(0) \delta A(t) \rangle_0 \quad (5.11)$$

and the susceptibility depends on both A and B ,

$$\chi_{AB}(t) = \begin{cases} -\beta \frac{d}{dt} \langle \delta B(0) \delta A(t) \rangle_0 & t > 0 \\ 0 & \text{otherwise} \end{cases}. \quad (5.12)$$

5.1.4 Example: Brownian of a Particle in a Fluid

When we apply a force f_0 to the system (particle), the conjugate coordinate to the force (position x) changes, and we measure the velocity v . In this case,

$$\mathcal{H}' = \mathcal{H} - f_0 x, \quad (5.13)$$

and

$$v(t) = \int_{-\infty}^0 dt' \chi_{vx}(t-t') f(t') = f_0 \int_t^{\infty} dt' \chi_{vx}(t'). \quad (5.14)$$

Apply f_0 from $-\infty$ to 0 and $f = 0$ at $t = 0$; expect

$$v(0) = \mu f_0 \quad (5.15)$$

where μ is the mobility,

$$\mu = \frac{1}{k_B T} \int_0^{\infty} \underbrace{\langle v(t) v(0) \rangle_0}_{K_{vv}, \text{ symmetric}} dt, \quad (5.16)$$

hence

$$v(0) = f_0 \underbrace{\int_0^{\infty} dt' \chi_{vx}(t')}_{\text{out of equilibrium}} = \frac{f_0}{k_B T} \underbrace{\int_0^{\infty} \langle v(t) v(0) \rangle_0 dt}_{\text{in equilibrium}}. \quad (5.17)$$

This suggest a relation between the fluctuation out of equilibrium (linear response theory) and the correlation functions in equilibrium:

$$\boxed{\chi_{xv}(t) = \beta K_{vv}(t)}. \quad (5.18)$$

This is the Onsager relation hypothesis.

5.1.5 Proof of (5.18)

Claim.

$$\chi_{xv}(t) = -\beta \frac{d}{dt} \langle x(0) v(t) \rangle_0. \quad (5.19)$$

Proof. In the stationary case,

$$\langle x(0) v(t) \rangle_0 = \langle x(t') v(t'+t) \rangle_0. \quad (5.20)$$

Now, derive with respect to t' ,

$$0 = \frac{d}{dt'} \langle x(t') v(t'+t) \rangle_0 = \langle \dot{x}(t') v(t'+t) \rangle_0 + \langle x(t') \frac{d}{dt'} v(t'+t) \rangle_0. \quad (5.21)$$

Also,

$$\begin{aligned} \frac{d}{dt} \langle x(t') v(t'+t) \rangle_0 &= \langle x(t') \dot{v}(t'+t) \rangle_0 = -\langle \dot{x}(t') v(t'+t) \rangle_0 \\ &= -\langle v(t) v(0) \rangle_0 = -K_{vv}(t) \end{aligned} \quad (5.22)$$

hence

$$\chi_{xv}(t) = K_{vv}(t) = \frac{1}{m} e^{-t/\tau}. \quad (5.23)$$

This is the Onsager Regression Hypothesis. \square

5.2 Fluctuation-Dissipation Theorem in Fourier Space

5.2.1 Brownian Particle

Let us look on the susceptibility,

$$x(t) = \int dt' \chi(t-t') f(t'). \quad (5.24)$$

We can automatically write the the correlation function,

$$\chi_{xx}(t) = -\beta \frac{d}{dt} \langle x(t) x(0) \rangle_0 = -\beta \frac{d}{dt} K_{xx}(t). \quad (5.25)$$

Now, take a Fourier transform and get a *wrong* result

$$\tilde{\chi}_{xx}(\omega) \neq -\beta i \omega \tilde{K}_{xx}(\omega). \quad (5.26)$$

Because

$$\begin{cases} \chi_{xx}(t) & \text{is defined for } t < 0 \text{ only!} \\ K_{xx}(t) & \text{is defined for all } t. \end{cases} \quad (5.27)$$

How to solve this problem? Recall that

$$\begin{cases} \mathcal{F}[\text{real \& symmetric}] & = \text{real \& symmetric} \\ \mathcal{F}[\text{real \& odd}] & = \text{purely imaginary \& odd} \end{cases}.$$

Therefore, break $\chi_{xx}(t)$ into even and odd functions

$$\chi_{xx}(t) = \chi_e(t) + \chi_o(t) \quad (5.28)$$

and call the Fourier parts

$$\begin{cases} \tilde{\chi}_e(\omega) & = \chi'(\omega) \\ \tilde{\chi}_o(\omega) & = i\chi''(\omega) \end{cases} \quad (5.29)$$

such that

$$\chi_{xx}(\omega) = \chi'(\omega) + i\chi''(\omega). \quad (5.30)$$

Now,

$$\chi_{xx}(t) = 2\chi_o(t) = -\beta \frac{d}{dt} \langle x(t)x(0) \rangle_0 = -\beta \frac{d}{dt} K_{xx}(t) \quad (5.31)$$

hence,

$$2i\chi''(\omega) = i\beta\omega \langle x_\omega x_{-\omega} \rangle_0 \quad (5.32)$$

and, finally,

$$\boxed{\chi''(\omega) = \frac{1}{2}\omega\beta \langle |x_\omega|^2 \rangle_0.} \quad (5.33)$$

This is the FD theorem in Fourier space.

5.3 Onsager Reciprocity Relations

Assign our simple working horse, Brownian Particle, in order to make things a bit simpler. Our usual Hamiltonian,

$$\mathcal{H}' = \mathcal{H} - fx. \quad (5.34)$$

From now on f and x are not necessarily force and position, but any type of conjugated variables. We get the ‘velocity’,

$$v(t) = \dot{x}(t) = \frac{1}{k_B T} \int_0^\infty d\tau f(t-\tau) \langle \dot{x}(0) \dot{x}(\tau) \rangle_0. \quad (5.35)$$

Let’s generalize to other velocities,

$$\mathcal{H}' = \mathcal{H} - f_i x_i \quad (5.36)$$

so that

$$\dot{x}_i(t) = \beta \int_0^\infty d\tau f_j(t-\tau) \langle \dot{x}_j(0) \dot{x}_i(\tau) \rangle_0, \quad (5.37)$$

(where the order of i and j is similar to our previous discussion of A and B).

5.3.1 Principle of Dynamical Reversibility of Microscopic Processes

The macroscopic behaviour is irreversible (e. g., friction). The outlined microscopic process, however, is reversible. Any correlation can be written as

$$\langle \dot{x}_j(0) \dot{x}_i(\tau) \rangle_0 \underset{\text{reversibility}}{=} \langle \dot{x}_j(0) \dot{x}_i(-\tau) \rangle_0 \underset{\substack{\text{translation} \\ \text{in time}}}{=} \langle \dot{x}_j(\tau) \dot{x}_i(0) \rangle_0, \quad (5.38)$$

hence

$$\langle \dot{x}_j(0) \dot{x}_i(\tau) \rangle_0 = \langle \dot{x}_i(0) \dot{x}_j(\tau) \rangle_0. \quad (5.39)$$

5.3.2 Essential Ingredients of Onsager Relations

Onsager Relations. Let’s write the Onsager relations,

$$\frac{dv}{dt} = -\gamma v \implies \frac{d\dot{x}_i}{dt} = -\gamma_{ij} \dot{x}_j. \quad (5.40)$$

Remark. γ_{ij} has no reasons to be symmetric.

Define the mobility,

$$v = \dot{x} = \mu F \implies \dot{x}_i = \mu_{ij} F_j. \quad (5.41)$$

Note that for a single particle, $\gamma = \mu^{-1}$. The Onsager relations state that μ_{ij} has to be symmetric. Therefore, $\gamma_{ij} \neq \mu_{ij}^{-1}$.

Thermodynamic Equilibrium. In equilibrium we can define any transformation through the entropy:

$$\frac{1}{k_B} dS = \beta dU - \beta \sum_s f_s dx_s, \quad (5.42)$$

at equilibrium,

$$U = x_0, \quad \beta = F_0. \quad (5.43)$$

Let's set some definitions,

$$\begin{aligned} F_s &\equiv -\beta f_s \\ \Sigma &\equiv S/k_B \end{aligned} \quad (5.44)$$

such that

$$d\Sigma = \sum_s F_s dx_s \iff F_s = \frac{\partial \Sigma}{\partial x_s}. \quad (5.45)$$

At equilibrium $\Sigma = 0$ and $\bar{x}_s = 0$. Therefore, close to equilibrium,

$$\Sigma = -\frac{1}{2} S_{ij} x_i x_j \quad (5.46)$$

where S_{ij} is not necessarily symmetric, but must be *negative definite*.

Let's introduce some more terminology,

$$J_i \equiv \dot{x}_i = \frac{dx_i}{dt} \quad \text{fluxes (currents)} \quad (5.47)$$

$$F_i = \frac{\partial \Sigma}{\partial x_i} = -S_{ik} x_k \quad \text{(forces)} \quad (5.48)$$

such that

$$J_i = \mu_{ij} F_j. \quad (5.49)$$

Let's define the probability

$$P(x_0, \dots, x_n) dx_0 \dots dx_n \propto e^{\Sigma} dx_0 \dots dx_n. \quad (5.50)$$

Hence, at equilibrium,

$$\langle x_i F_j \rangle_0 = \frac{\int dx_i e^{\Sigma} \frac{\partial \Sigma}{\partial x_j} x_j}{\int dx_i e^{\Sigma}} = \delta_{ij}, \quad (5.51)$$

and we get

$$\langle x_i F_j \rangle_0 = \delta_{ij}. \quad (5.52)$$

On the other hand,

$$\langle x_i(\tau) x_j(0) \rangle = \langle x_i(-\tau) x_j(0) \rangle, \quad (5.53)$$

hence

$$\langle x_i(\tau) x_j(0) \rangle = \langle x_i(0) x_j(\tau) \rangle, \quad (5.54)$$

but

$$\frac{\langle x_i(\tau) x_j(0) \rangle - \langle x_i(0) x_j(0) \rangle}{\tau} = \frac{\langle x_i(0) x_j(\tau) \rangle - \langle x_i(0) x_j(0) \rangle}{\tau}, \quad (5.55)$$

and when $\tau \rightarrow 0$,

$$\langle \dot{x}_i(0) x_j(0) \rangle = \langle x_i(0) \dot{x}_j(0) \rangle. \quad (5.56)$$

Put in Eq. (?) and get

$$\mu_{ik} \langle F_k x_j(0) \rangle = \mu_{jk} \langle x_i(0) F_k \rangle \quad (5.57)$$

or

$$-\mu_{ik} \delta_{kj} = -\mu_{jk} \delta_{ik}, \quad (5.58)$$

and we get the Onsager relations (only at equilibrium!)

$$\mu_{ij} = \mu_{ji} \quad (5.59)$$

Remark. Outside of equilibrium μ_{ij} is not symmetric.

Generally,

$$\gamma_{ij} \mu_{jk} = S_{ik} \quad (5.60)$$

and S_{ik} is not generally symmetric.