# Linear Response and Onsager Reciprocal Relations

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Based on *Kittel, Elementary statistical physics,* chapters 33-34; *Kubo,Toda and Hashitsume, Statistical Physics II*, chapter 1; and the course's notes section 7.2

## 1 Introduction

In this tutorial we shall continue to develop the theory of linear response and derive Onsager's reciprocal relations. We shall start with an overview of the fluctuations-dissipation theorem (FDT), which relates the susceptibility of a quantity to the decay of equilibrium correlations of the same quantity. Then we shall establish a relation between the response of one quantity to perturbation in a different quantity.

Both the FDT and Onsager's reciprocity relations rely on the assumption that macroscopic response and decay process occur in the same manner as the decay of equilibrium fluctuations - this assumption is called *Onsager's regression hypothesis*. It allows to study close-to-equilibrium processes using properties of equilibrium states, specifically the Boltzmann distribution (or equipartition theorem) for FDT and reversibility for Onsager's reciprocity relations.

## 2 Overview: Static and dynamic fluctuations and responses

You have already saw in class the following statements:

### 2.1 Fluctuation-response relation

Given a quantity $x$ and a conjugate field $f$, i.e. $H = H_0 - xf$, the susceptibility is

$$\chi \equiv \frac{\partial \langle x \rangle}{\partial f} = \frac{\langle x^2 \rangle - \langle x \rangle^2}{T}$$

For example, take $x$ to be the number of particles $N$ and $f$ to be the chemical potential.

## 2.2 Fluctuation-Dissipation relation in time

Given a quantity $x$ and a time dependent conjugate field $f(t)$, the susceptibility is given by

$$T\alpha\left(t,t'\right)=\frac{d}{dt'}\left\langle x(t)x(t')\right\rangle \Theta\left(t-t'\right)$$

where $\Theta\left(t-t'\right)$ is the Heaviside theta function which is 1 for $t>t'$ and 0 otherwise.

**Example**: Consider over-damped Brownian motion with harmonic potential. The Langevin equation is

$$m\ddot{x}+\lambda\dot{x}+m\omega_0^2x=f(t)+\lambda\eta(t)$$

where $f(t)$ is a driving force and $\eta(t)$ a random force with

$$\begin{aligned}\left\langle \eta(t)\right\rangle &= 0\\ \left\langle \eta(t)\eta(t')\right\rangle &= 2D\delta(t-t')\end{aligned}$$

i.e. white noise. The over-damped limit implies $\lambda$ large enough so that the inertia term can be neglected

$$\dot{x}=-\mu\left(m\omega_0^2x+f(t)\right)+\eta(t)$$

where we defined the mobility $\mu=\lambda^{-1}$. Fourier transforming

$$\begin{aligned}i\omega x(\omega) &= -\mu m\omega_0^2x(\omega)+\mu f(\omega)+\eta(\omega)\Rightarrow\\ x(\omega) &= \frac{\mu f(\omega)+\eta(\omega)}{i\omega+\mu m\omega_0^2}\end{aligned}$$

Defining the power spectrum

$$\begin{aligned}\left(z^2\right)_\omega &\equiv \left\langle\left|z\left(\omega\right)\right|^2\right\rangle=\int_{-\infty}^{\infty}\left\langle z(t)z(0)\right\rangle e^{-i\omega t}dt\\ \left\langle z(t)z(0)\right\rangle &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\left(z^2\right)_\omega e^{i\omega t}d\omega\end{aligned}$$

we get that for $f(t)=0$

$$\left(x^2\right)_\omega=\frac{\left\langle\left|\eta(\omega)\right|^2\right\rangle}{\left|i\omega+\mu m\omega_0^2\right|^2}=\frac{\left(\eta^2\right)_\omega}{\omega^2+\left(\mu m\omega_0^2\right)^2}$$

From the fact that the noise is white we get $\left(\eta^2\right)_\omega=2D$, i.e. independent of frequency (which is the reason for the name "white noise") so

$$\left(x^2\right)_\omega=\frac{2D}{\omega^2+\left(\mu m\omega_0^2\right)^2} \tag{1}$$

Inverting the Fourier transform demands some complex analysis

$$\begin{aligned}\langle x(t)x(t')\rangle &= \frac{D}{\pi}\int_{-\infty}^{\infty}\frac{e^{-i\omega t}}{\omega^2+\left(\mu m\omega_0^2\right)^2}d\omega \\ &= \frac{D}{\pi}\int_{-\infty}^{\infty}\frac{e^{-i\omega t}}{\left[\left(\omega+i\mu m\omega_0^2\right)\left(\omega-i\mu m\omega_0^2\right)\right]}d\omega\end{aligned}$$

For $t>0$ ($t<0$) we can close the contour by a large semicircle with negative (positive) imaginary part, hence

$$\langle x(t)x(t')\rangle = \frac{D}{\mu m\omega_0^2}e^{-\mu m\omega_0^2|t-t'|} \tag{2}$$

From the equipartition theorem $m\omega_0^2\left\langle x^2\right\rangle = T$ we get the Einstein relation $D=\mu T$.

On the other hand, for $f\neq 0$ we have

$$\begin{aligned}\langle x(\omega)\rangle &= \frac{\mu f(\omega)}{i\omega+\mu m\omega_0^2}\Rightarrow \\ \alpha(\omega) &= \frac{\mu}{i\omega+\mu m\omega_0^2}\Rightarrow \qquad (3)\\ \alpha(t-t') &= \mu e^{-\mu m\omega_0^2 t} \qquad (4)\end{aligned}$$

Hence we find indeed

$$\begin{aligned}\frac{d}{dt'}\langle x(t)x(t')\rangle &= \frac{\mu T}{\mu m\omega_0^2}\frac{d}{dt'}e^{-\mu m\omega_0^2|t-t'|} \\ &= \mu T e^{-\mu m\omega_0^2|t-t'|} = T\alpha(t-t')\end{aligned}$$

## 2.3 The spectral Fluctuation-Dissipation relation

Using Fourier transform in time define

$$\begin{aligned}x_\omega &= \int_{-\infty}^{\infty}x(t)e^{i\omega t}dt \\ \langle x_\omega x_{\omega'}\rangle &\equiv 2\pi\delta(\omega+\omega')\left(x^2\right)_\omega \\ \alpha_\omega &= \int_{-\infty}^{\infty}\alpha(t)e^{i\omega t}dt \\ \alpha_\omega &\equiv \alpha'+i\alpha''\end{aligned}$$

Then the FDT is formulated as

$$2T\alpha'' = \omega\left(x^2\right)_\omega$$

**Example**:

In the previous example, from (3)

$$\alpha'' = \frac{\mu\omega}{\omega^2 + \left(\mu m \omega_0^2\right)^2}$$

while from (1) we get

$$\left(x^2\right)_\omega = \frac{2\mu T}{\omega^2 + \left(\mu m \omega_0^2\right)^2} = \frac{2T}{\omega}\alpha''$$

# 3 Onsager reciprocal relations

## 3.1 General relations

When several macroscopic quantities $x_1 ... x_N$ deviate slightly from equilibrium the linear response equation is (assuming that at equilibrium $x_i = 0$)

$$\dot{x}_i = -\lambda_{ij} x_j \tag{5}$$

There is obviously also a noisy force, but for this analysis we neglect it and treat the quantities as deterministic. We wish to analyze the structure of the matrix $\lambda_{ij}$. For equilibrium fluctuations, thinking of an isolated system, we can expand the entropy in the deviations $x_i$ to find

$$\begin{aligned} S &\approx S_0 - \sum_{jk} \beta_{jk} x_j x_k \\ \beta_{jk} &= \frac{1}{2} \frac{\partial^2 S}{\partial x_j \partial x_k} \end{aligned}$$

and $\beta$ is clearly a symmetric matrix. Define the *generalized forces*

$$X_i \equiv -\frac{\partial S}{\partial x_i} = \sum_j \beta_{ij} x_j \tag{6}$$

In terms of those we can write (5) as

$$\begin{aligned} \dot{x}_i &= -\sum_j \gamma_{ij} X_j \\ \gamma &= \lambda \beta^{-1} \end{aligned}$$

Using (6) we find

$$\begin{aligned} \langle X_i x_j \rangle &= -\int d\mathbf{x} e^{S[\mathbf{x}]} \frac{\partial S}{\partial x_i} x_j \\ &= -\int d\mathbf{x} \frac{\partial}{\partial x_i} \left( e^{S[\mathbf{x}]} \right) x_j \\ &= \int d\mathbf{x} e^{S[\mathbf{x}]} \frac{\partial x_j}{\partial x_i} = \delta_{ij} \end{aligned}$$

and from this together with Eq. (6) we can deduce

$$\begin{aligned}\langle X_i X_j \rangle &= \left\langle X_i \sum_j \beta_{jk} x_k \right\rangle = \beta_{ij} \\ \langle x_i x_j \rangle &= \left\langle x_i \sum_j \left(\beta^{-1}\right)_{jk} X_k \right\rangle = \left(\beta^{-1}\right)_{ij}\end{aligned}$$

Now we invoke time reversibility (and time translation invariance), and demand that the fluctuations satisfy

$$\langle x_i(t+\tau) x_j(t) \rangle = \langle x_i(t-\tau) x_j(t) \rangle = \langle x_i(t) x_j(t+\tau) \rangle \tag{7}$$

hence

$$\begin{aligned}\frac{1}{\tau}\left(\langle x_i(t+\tau) x_j(t)\rangle - \langle x_i(t) x_j(t)\rangle\right) &= \frac{1}{\tau}\left(\langle x_i(t) x_j(t+\tau)\rangle - \langle x_i(t) x_j(t)\rangle\right) \Rightarrow \\ \langle \dot{x}_i(t) x_j(t) \rangle &= \langle x_i(t) \dot{x}_j(t) \rangle\end{aligned}$$

Finally, we assume that the thermal fluctuations follow the same decay rule (5) as perturbations caused by external forces - the *Onsager regression hypothesis.* Then we can use (7) and find

$$\begin{aligned}\langle \dot{x}_i(t) x_j(t) \rangle &= \left\langle \sum_k \gamma_{ik} X_k(t) x_j(t) \right\rangle = \gamma_{ij} \\ \langle x_i(t) \dot{x}_j(t) \rangle &= \left\langle x_i(t) \sum_k \gamma_{jk} X_k \right\rangle = \gamma_{ji}\end{aligned}$$

So the result is

$$\gamma_{ij} = \gamma_{ji} \tag{8}$$

**Remark**: The importance of the Onsager regression hypothesis is that it connects the equilibrium analysis done above to non-equilibrium phenomena such as currents. By current we mean a sustained change in a thermodynamic quantity $J_i \equiv \frac{dx_i}{dt}$ which is induced by keeping the conjugate force $X_i$ non-zero (but small). Hence Onsager reciprocal relations tell us about the relations between currents which are induced by the conjugates of other variables, such as thermoelectric effect. The next example will make this more clear.

## 3.2 Example

We will discuss now a specific example - the thermoelectric effect in which temperature gradient induces charge current and electrostatic potential difference induces heat flows. We will see how the Onsager reciprocity relations should be used, which is not so trivial in this case.

We wish to probe the connection between heat current $W$ and electric current $I$ when they are written as

$$\begin{aligned} W &= l_{11}\Delta T + l_{12}\Delta\phi \\ I &= l_{21}\Delta T + l_{22}\Delta\phi \end{aligned}$$

We will **not** find $l_{12} = l_{21}$, but instead the relation will be more subtle. Consider two connected reservoirs of heat and (charged) particles. Assume that by thermal fluctuation the first reservoir has temperature $T$ and potential $\phi = 0$ and the second temperature $T + \Delta T$ and potential $\Delta\phi$. Assume now that $dn$ electrons and energy $dU$ pass from the first reservoir to the second reservoir, and inspect how this changes the entropy. The change in entropy of the reservoirs is

$$\begin{aligned} dS_1 &= -\frac{1}{T}dU + \frac{\mu(T)}{T}dn \\ dS_2 &= \frac{1}{T+\Delta T}dU - \frac{\mu(T+\Delta T) + e\Delta\phi}{T+\Delta T}dn \\ dS &= dS_1 + dS_2 \approx \left[-\frac{\Delta T}{T^2}\right]dU + \left[-\frac{\Delta T}{e}\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) - \frac{\Delta\phi}{T}\right]edn \end{aligned}$$

Identifying $x_1 = dU$ and $x_2 = edn$ we thus find

$$\begin{aligned} X_1 &= \frac{\Delta T}{T^2} \\ X_2 &= \frac{\Delta T}{e}\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) + \frac{\Delta\phi}{T} \end{aligned}$$

Hence (now using the correspondence between fluctuations kinetic and macroscopic currents) the currents $W = \frac{dU}{dt}$ and $I = e\frac{dn}{dt}$ satisfy

$$\begin{aligned} W &= -\gamma_{11}\left[\frac{\Delta T}{T^2}\right] - \gamma_{12}\left[\frac{\Delta T}{e}\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) + \frac{\Delta\phi}{T}\right] \\ I &= -\gamma_{21}\left[\frac{\Delta T}{T^2}\right] - \gamma_{22}\left[\frac{\Delta T}{e}\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) + \frac{\Delta\phi}{T}\right] \end{aligned}$$

and Onsager reciprocal relations implies $\gamma_{12} = \gamma_{21}$.