

## Lecture 14: The fluctuation-dissipation theorem.

In the last lecture we derived a local version of the second law of thermodynamics:

$$\delta \frac{D_s}{Dt} = -\nabla \cdot \vec{g}_s + \sigma$$

with entropy production:

$$\sigma = \sum_{i=1}^{m_c} \vec{g}_i \cdot \vec{X}_i + \sum_{i=1}^{m_v} \vec{g}_i \cdot \vec{X}_i + \sum_{i=1}^{m_T} \vec{g}_i : \vec{X}_i$$

$\curvearrowright$ 
 $\curvearrowright$ 
 $\curvearrowright$

scalar.  
 e.g. chemical  
 reactions, bulk  
 compression

vectorial.  
 e.g. heat  
 transfer,  
 diffusion

tensorial  
 e.g. shear

Linear constitutive laws: Fluxes are linearly related to thermodynamic driving forces.

$$\text{e.g. } \vec{\Pi}_{\alpha\beta} = -\eta_s \left( \partial_\alpha v_\beta + \partial_\beta v_\alpha - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot \vec{v} \right) \text{ (isotropic system),}$$

Note that the kinetic coefficient is a scalar which reflects the underlying symmetry of the system.

Linear non-equilibrium thermodynamics will break down when gradients are large. However generally speaking relations like

$$\vec{J} \propto \nabla(\mu/T) \text{ are not correct even in the linear regime!}$$

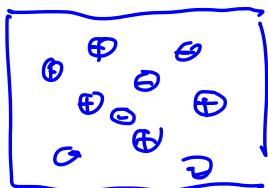
We expect that there is a time lag between setting up a gradient and the resulting flux. We expect that this time lag is on the order of  $T_{\text{relax}}$  which can typically be neglected for macroscopic properties.

How does linear non-equilibrium thermodynamics result from the microscopic degrees of freedom?

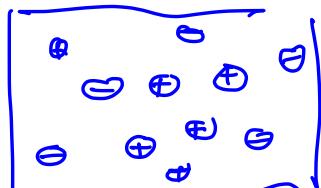
## Non-equilibrium statistical mechanics

We focus purely on systems close to equilibrium.  $\Rightarrow$  linear response theory.

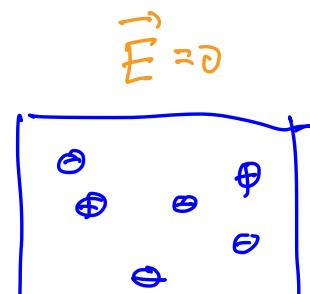
Example:  $\vec{E} = 0$



$t < t_1$

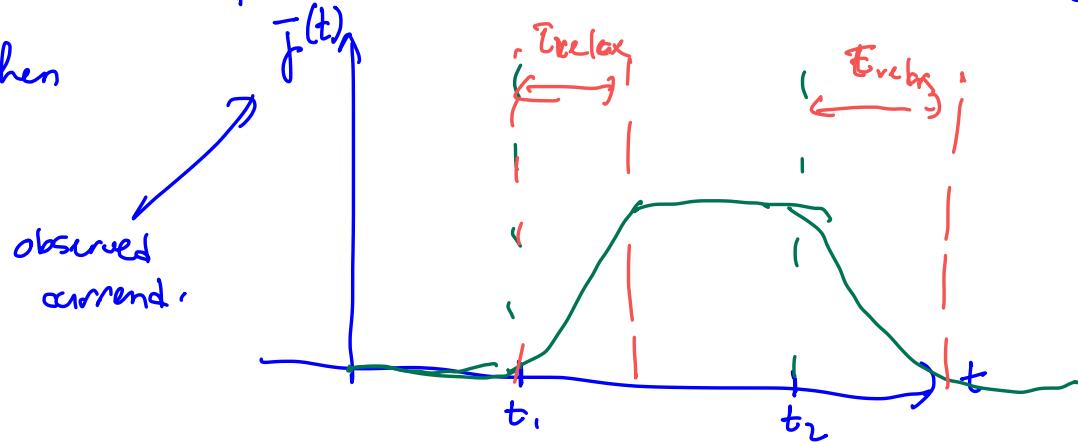


$t_1 < t < t_2$



$t > t_2$

Then



Linear regime:  $\bar{f}(t; \lambda \vec{E}) = \lambda \bar{f}(t; \vec{E})$

Here the over bar denotes a non-equilibrium ensemble average.

Consider a dynamical classical variable  $X$  (in quantum case becomes an operator).

We assume  $X$  couples to some conjugate field  $f$ .  $f = f(t)$ .

We assume

$$f(t) = \begin{cases} f & t < 0 \\ 0 & t \geq 0 \end{cases}$$

and that the field was turned on for  $t \rightarrow -\infty$

So for  $t < 0$  the system is in equilibrium with Hamiltonian

$$H_f = H_0 - f X.$$

At  $t=0$   $f$  is switched off and the system is out of equilibrium.

$$\begin{aligned} \text{We express the time evolution of } X \text{ as } X(t \geq 0) &= X(\vec{p}^N(t), \vec{r}^N(t)) \\ &= X(t; \vec{p}^N(0), \vec{r}^N(0)) \stackrel{?}{=} X(t; \vec{p}^N, \vec{r}^N) \end{aligned}$$

since  $(\vec{p}^N(t), \vec{r}^N(t))$  is known if  $(\vec{p}^N(0), \vec{r}^N(0))$  is specified via the Hamilton equations of motion. So it's sufficient to average over the initial conditions:

$$\bar{X}(t \geq 0) = \frac{1}{N!h^{3N}} \int d\vec{p}^N \int d\vec{r}^N P_f(\vec{p}^N, \vec{r}^N) X(t; \vec{p}^N, \vec{r}^N)$$

↑  
canonical probability distribution  
in the presence of  $f$ .

Thus it follows that:

$$t \geq 0: \quad \bar{X}(t) = \bar{X}(0) = \langle X \rangle_f \quad \text{and} \quad \bar{X}(t) = \langle X \rangle_0 \quad \text{for } t \rightarrow \infty$$

where  $t$  is large  
wrt  $T_{\text{relax}}$ .

### Onsager regression hypothesis

Relaxation of a system following a macroscopic perturbation must obey the same kinetic laws as the regression of spontaneous microscopic fluctuations in equilibrium.

"A system cannot distinguish between a spontaneous and an externally prepared fluctuation".

For this we need the language of time correlation functions.

Define:  $t \gg T_{\text{relax}}$   $\langle \dots \rangle \equiv \langle \dots \rangle_0$

$\delta X(t) = X(t) - \langle X \rangle$  with time evolution determined by microscopic dynamics.

Then:  $\delta X(t) = \delta X(t; \vec{p}^N, \vec{r}^N)$ .

Note that  $\langle \delta X \rangle = 0$ .

We define the correlation function:  $C(t) = \langle \delta X(0) \delta X(t) \rangle = \langle X(0) X(t) \rangle - \langle X \rangle^2$ . (auto correlation function)



We can express the autocorrelation function explicitly as

$$G(t) = \frac{1}{N!h^3N} \int d\vec{p}^N \int d\vec{r}^N P(\vec{p}^N, \vec{r}^N) \delta X(0; \vec{p}^N, \vec{r}^N) \delta X(t; \vec{p}^N, \vec{r}^N)$$

$$= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \delta X(t_0) \delta X(t_0 + t).$$

ergodicity

The autocorrelation function has several properties:

- No absolute value of time.

$$C(t) = \langle \delta X(0) \delta X(t) \rangle = \langle \delta X(t_0) \delta X(t_0 + t) \rangle$$

As a consequence of this property:

$$C(t) = \langle \delta X(-t) \delta X(0) \rangle = \langle \delta X(0) \delta X(-t) \rangle = C(-t).$$

(not necessarily valid in quantum systems!).

- For  $t$  small:  $C(0) = \langle \delta A(0) \delta A(0) \rangle = \langle (\delta A)^2 \rangle$
- For  $t$  large  $C(t) \rightarrow \langle \delta A(0) \rangle \langle \delta A(t) \rangle \quad t \rightarrow \infty$   
 $\Rightarrow C(t) \rightarrow 0 \quad (t \rightarrow \infty),$

Often autocorrelation function is of the form:

$$C(t) = C(0) e^{-|t|/\tau_{\text{relax.}}}$$

or in Fourier domain:  $\tilde{C}(\omega) = \int_{-\infty}^{+\infty} dt C(t) e^{i\omega t} = \frac{2C(0)}{1 + \omega^2 \tau^2}$

With the language of autocorrelation function we can mathematically formulate the Onsager regression hypothesis.

$$\frac{C(t)}{C(0)} = \frac{\bar{X}(t) - \langle X \rangle}{\bar{X}(0) - \langle X \rangle}$$

a type of formulation of the fluctuation-dissipation theorem.

## Proof of Onsager regression hypothesis

Suppose we have Hamiltonian:

$$H_f = H - f(t)X.$$

So for  $t \leq 0$  the Boltzmann distribution is

$$P_f = \frac{1}{Z_f} e^{-\beta H_f} ; \quad Z_f = \frac{1}{N! h^{3N}} \int d\vec{p}^N \int d\vec{r}^N e^{-\beta H_f}$$

We have that:

$$\langle X \rangle_f = \frac{1}{N! h^{3N}} \int d\vec{p}^N \int d\vec{r}^N P_f(p^N, r^N) X(p^N, r^N).$$

For  $|\beta f X| \ll 1$ :

$$e^{-\beta H_f} = e^{-\beta H_f} (1 + \beta f X + \dots)$$

$$\Rightarrow Z_f = Z (1 + \beta f \langle X \rangle + \dots) \quad \text{with } Z = Z_f \Big|_{f=0}.$$

$$\Rightarrow P_f = P (1 + \beta f X - \beta f \langle X \rangle + \dots)$$

To linear order in  $f$ , we have that  $P_f$  is still properly normalised!

$$\Rightarrow \langle X \rangle_f = \langle X \rangle + \beta f (\langle X^2 \rangle - \langle X \rangle^2) + \dots$$

$$\Rightarrow \langle X^2 \rangle - \langle X \rangle^2 = \lim_{f \rightarrow 0} \left( \frac{\partial \langle X \rangle_f}{\partial \beta f} \right).$$

$\underbrace{\text{fluctuation property}}_{\text{of unperturbed system.}}$   $\underbrace{\text{(static) response function.}}$

$\Rightarrow$  Response to an external field  $\Leftrightarrow$  equilibrium fluctuations.

Recall that for  $t > 0$

$$\bar{X}(t) = \frac{1}{N!h^N} \int d\vec{p}^N \int d\vec{r}^N P_f(\vec{p}^N, \vec{r}^N) X(t; \vec{p}^N, \vec{r}^N)$$

$$= \langle X \rangle + \beta f (\langle X(0)X(t) \rangle - \langle X \rangle^2) + \dots$$

$\therefore$  To linear order in  $f$ :  $\downarrow$  appears because averaging is over initial conditions.

$$\bar{X}(t) - \langle X \rangle = \beta f (\langle X(0)X(t) \rangle - \langle X \rangle^2) + \dots$$

$\underbrace{\quad \quad \quad}_{-C(t)}$

$$\Rightarrow C(t) = (\bar{X}(t) - \langle X \rangle) / \beta f \quad \left\{ \begin{array}{l} \bar{X}(0) = (\bar{X}(0) - \langle X \rangle) / \beta f \\ \Rightarrow \frac{C(t)}{C(0)} = \frac{\bar{X}(t) - \langle X \rangle}{\bar{X}(0) - \langle X \rangle} \end{array} \right. \quad \square$$

The fluctuation part is evident, but what does it have to do with dissipation?

### Response functions

Before we took a very specific form of  $f(t)$ . However, in linear response regime we can write

$$\bar{X}(t) = \langle X \rangle + \int_{-\infty}^{+\infty} dt' \chi(t, t') f(t') + \mathcal{O}(f^2).$$

$\chi(t, t')$  : generalized susceptibility / response function.

It quantifies how much a perturbation at time  $t'$  influences the system at a time  $t$ .

### Properties

- (i)  $\chi$  is property of the unperturbed system:  $\chi(t, t') = \chi(t - t')$
- (ii) Causality:  $\chi(t - t') = 0$  for  $t < t'$ .

What is  $\chi(t-t')$ ? Take  $f(t) = f(\beta(-t))$

Then

$$\bar{X}(t) = \langle X \rangle + \beta \int_{-\infty}^0 dt' \chi(t-t') = \langle X \rangle + \beta \int_t^{\infty} dt'' \chi(t'').$$

However, we derived before that:

$$\bar{X}(t) = \langle X \rangle + \beta f(\langle X(0)X(t) \rangle - \langle X \rangle^2)$$

$$\Rightarrow \int_t^{\infty} dt'' \chi(t'') = \beta (\langle X(0)X(t) \rangle - \langle X \rangle^2) = G(t)$$

$$\Rightarrow \chi(t) = -\beta \frac{d}{dt} G(t) \quad (t \geq 0) \quad (\text{Fluctuation-dissipation theorem}).$$

$$> 0 \quad (t < 0).$$

In the construction of our Hamiltonian, we have used that  $f$  and  $X$  are conjugate pairs.

Small perturbations then:  $\dot{f}W = -f \dot{X}$

Absorbed energy per unit time:  $P(t) = -\frac{dW}{dt} = +f(t) \frac{d\bar{X}}{dt}$ .

$$\Rightarrow P(t) = f(t) \frac{d}{dt} \left[ \langle X \rangle + \int_{-\infty}^t dt' \chi(t-t') f(t') \right]$$

since eq. average does not depend on time.  
of unperturbed system.

$$\Rightarrow -\beta f(t) \frac{d}{dt} \left[ \int_0^{\infty} dt' f(t-t') \frac{d}{dt'} G(t') \right].$$

This is a relation between power absorption (dissipation) of a system's response to an external perturbation

and the time-dependence of spontaneous fluctuations under equilibrium conditions (without perturbation).

In frequency domain:

$$P(t) = \beta \left( \frac{1}{2\pi} \right)^2 \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega' \tilde{f}(\omega) \tilde{f}(\omega') \tilde{G}(\omega') (\omega')^2 e^{-i(\omega+\omega')t} \quad \left. \right\} =$$

For monochromatic perturbation:  $f(t) = f \cos(\omega_0 t)$

$$P(t) = \beta \omega_0^2 \tilde{G}(\omega_0) f^2(t) \geq 0$$

Average over half a period:

$$\bar{P} = \omega_0 \pi^{-1} \int_0^{\pi/\omega_0} dt P(t) = \beta f^2 \omega_0^2 \tilde{G}(\omega_0) / 2.$$

Interpretation: Absorbed power as a function of  $\omega_0$  probes the frequency dependence of  $\tilde{G}(\omega_0)$ .