Lecture 13: The fluctuation-dissipation theorem.

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

$$\rho \frac{Ds}{Dt} = -\nabla \cdot \vec{J}_s + \sigma$$

with entropy production:

$$\sigma = \underbrace{\sum_{i=1}^{m_s} J_i X_i}_{\substack{\text{scalar.} \\ \text{e.g. chemical} \\ \text{reactions, bulk} \\ \text{compression}}} + \underbrace{\sum_{i=1}^{m_V} \vec{J}_i \cdot \vec{X}_i}_{\substack{\text{vectorial.} \\ \text{e.g. heat} \\ \text{transfer,} \\ \text{diffusion}}} + \underbrace{\sum_{i=1}^{m_T} \underline{\underline{J}}_i : \underline{\underline{X}}_i}_{\substack{\text{tensorial} \\ \text{e.g. shear}}}$$

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

e.g. $\Pi^{0}_{\alpha\beta} = -\eta_s \left(\partial_\alpha v_\beta + \partial_\beta v_\alpha - \frac{2}{3}\delta_{\alpha\beta} \nabla \cdot v\right)$ (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

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

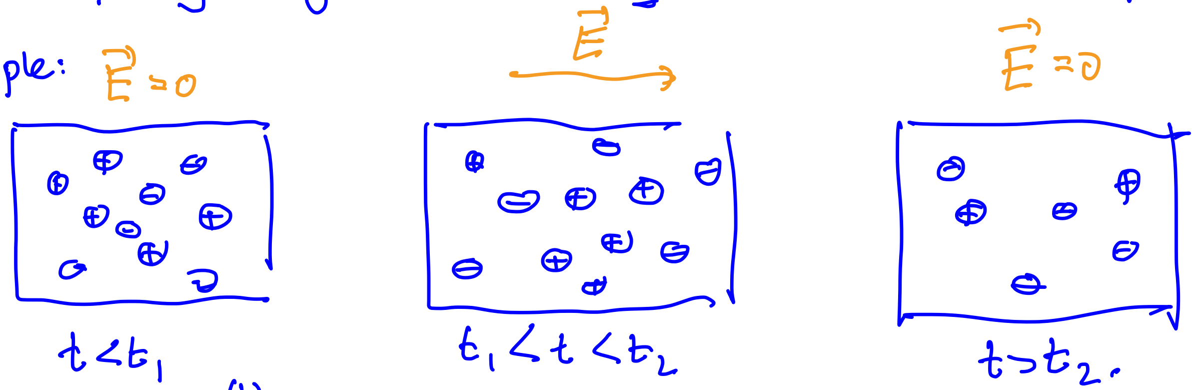
We expect that there is a time lag between setting up a gradient and the resulting flux. We expect that this time lag is on the order of T_{relax} which can typically be neglected for macroscopic properties.

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

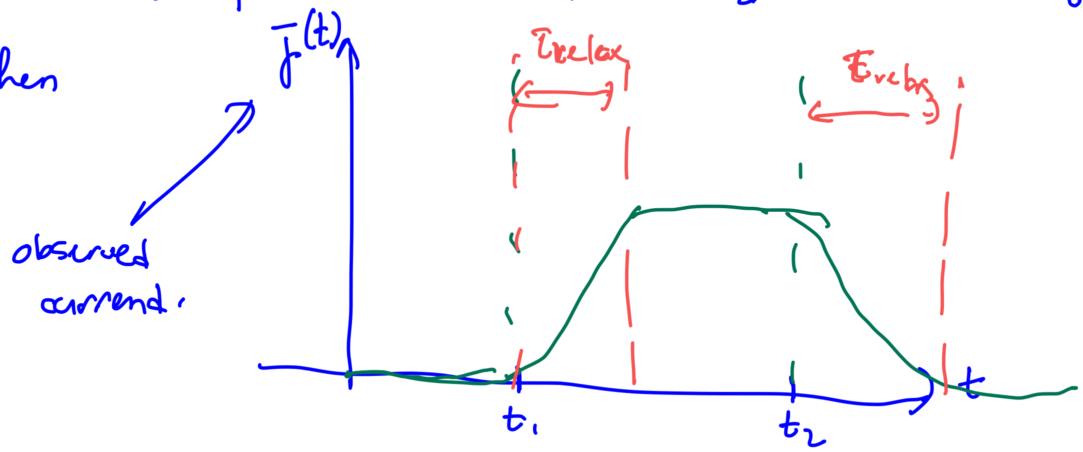
Non-equilibrium statistical mechanics

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

Example:



Then



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

Here the overbar 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 $f := f(t)$.

We assume
$$f(t) = \begin{cases} f & t < 0 \\ 0 & t > 0. \end{cases}$$
and that the field was turned on for $t \to -\infty$

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

$H_f = H_0 - fX.$

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

We express the time evolution of X as $X(t \geq 0) = X(\vec p^{\,N}(t), \vec r^{\,N}(t))$

$$= X(t;\vec p^{\,N}(0), \vec r^{\,N}(0)) \equiv X(t;\vec p^{\,N}, \vec r^{\,N})$$

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 is 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:

$t<0$: $\bar{X}(t) = \bar{X}(0) = \langle X \rangle_f$ and $\bar{X}(t) = \langle X \rangle_0$ for $t \to \infty$

where t is large wrt τ_{relax}.

Onsager regression hypothesis

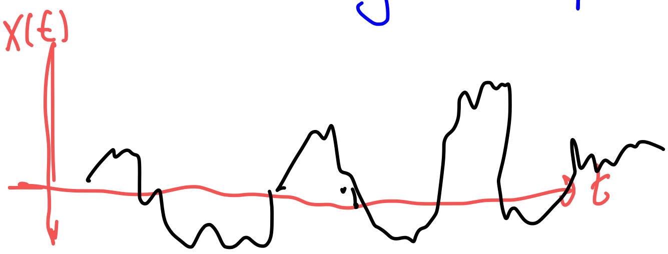
Relaxation of a system following a macroscopic perturbation must obey the same kinetic laws as the regression of spontaneous microscopic fluctuations in equilibrium.

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

$\rightsquigarrow$ For this we need the language of time correlation functions.

Define: $t \gg \tau_{relax}$ $\qquad \langle \ldots \rangle \equiv \langle \ldots \rangle_0$

$\delta X(t) = X(t) - \langle X \rangle$ 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

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

$$= \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^{\tau} dt\; \delta X(t_0)\,\delta X(t_0+t).$$

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 $C(t) \longrightarrow \langle \delta A(0)\rangle\langle \delta A(t)\rangle \quad t\to\infty$

  $$\Rightarrow\; C(t) \longrightarrow 0 \qquad (t\to\infty).$$

Often autocorrelation function is of the form:

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

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

(Lorentzian).

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

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

We have that:

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

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

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

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

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

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

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

$$\Rightarrow \underbrace{\langle X^2 \rangle - \langle X \rangle^2}_{\text{fluctuation property of unperturbed system.}} = \underbrace{\lim_{f \to 0} \left(\frac{\partial \langle X \rangle_f}{\partial \beta f} \right)}_{\text{(static) response function.}}.$$

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

Recall that for $t>0$

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

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

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

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

$$\Rightarrow C(t) = \left(\bar{X}(t) - \langle X \rangle \right) / \beta f$$
$$C(0) = \left(\bar{X}(0) - \langle X \rangle \right) / \beta f$$

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

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) χ 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 $f(t) = f\,\Theta(-t)$

Then

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

However, we derived before that:

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

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

$$\Rightarrow \quad \chi(t) = -\beta\frac{d}{dt}C(t) \quad (t\geq 0) \qquad (*)$$
$$= 0 \quad (t<0),$$

(Fluctuation-dissipation theorem).

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

Small perturbations then: $dW = -f\,d\bar{X}$

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

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

$\cancel{\langle X\rangle} = 0$ since eq. average does ~~not~~ depend on time of unperturbed system.

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

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:

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

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

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

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 ω_0 probes the frequency dependence of $\tilde{G}(\omega_0)$.