

Lecture 14: 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:

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

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

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

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

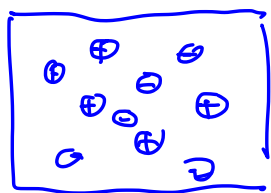
We expect that there is a time lag between setting up a gradient and the resulting flux. We expect that this time lag is on the order of τ_{relax} which can typically be neglected for macroscopic properties.

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

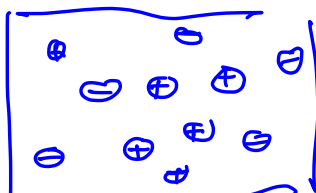
Non-equilibrium statistical mechanics

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

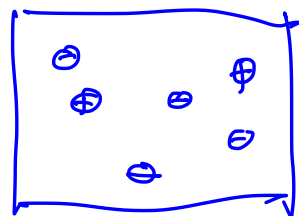
Example: $\vec{E} = 0$ \vec{E} $\vec{E} = 0$



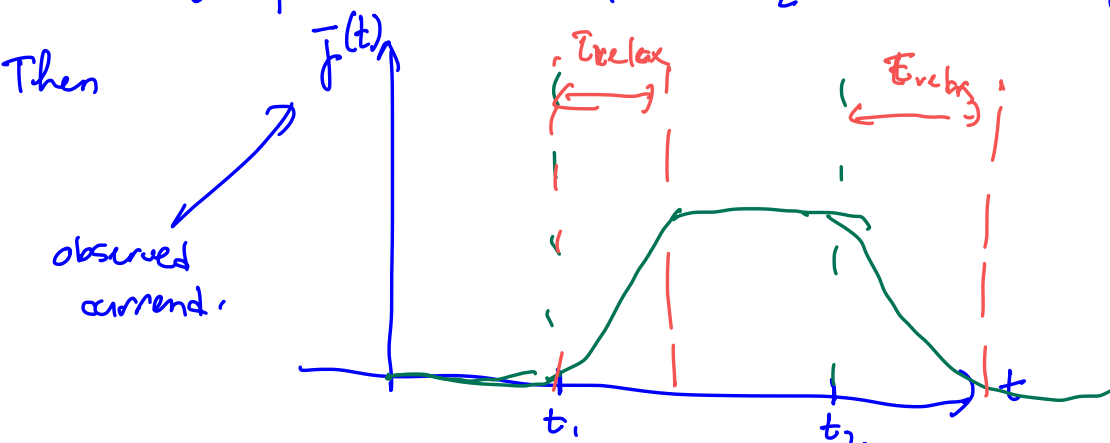
$t < t_1$



$t_1 < t < t_2$



$t > t_2$



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

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 $f \equiv f(t)$.

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

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

(3)

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:

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

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".

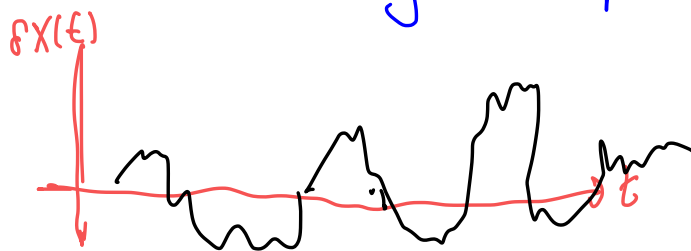
\leadsto For this we need the language of time correlation functions.

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

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

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We can express the autocorrelation function explicitly as

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

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

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.

(Lorentzian).

$$\frac{C(t)}{C(0)} = \frac{\overline{\bar{X}(t) - \langle X \rangle}}{\overline{\bar{X}(0) - \langle X \rangle}} \quad \text{a type of formulation of the fluctuation-dissipation theorem.}$$

Proof of Onsager regression hypothesis

Suppose we have Hamiltonian:

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

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

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

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

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

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

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

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

fluctuation property
of unperturbed system.

(static)
response function.

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

Recall that for $t > 0$

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

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

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

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

$$\Rightarrow C(t) = (\bar{X}(t) - \langle X \rangle) / \beta f \quad \Rightarrow \quad \frac{C(t)}{C(0)} = \frac{\bar{X}(t) - \langle X \rangle}{\bar{X}(0) - \langle X \rangle} \quad \square$$

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

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 $f(t) = f \ominus(-t)$

Then

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

However, we derived before that:

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

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

$$\Rightarrow \chi(t) = -\beta \frac{d}{dt} C(t) \quad \begin{matrix} (t \geq 0) \\ & (t < 0) \end{matrix} \quad (*) \quad (\text{Fluctuation-dissipation theorem}).$$

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

Small perturbations then: $\delta W = -f \delta X$

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

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

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

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

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).

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In frequency domain:

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

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