Lecture 14: The fluctuation-dissipation theorem II.

Systems close to equilibrium $\Leftrightarrow$ linear response regime.

For a dynamical variable $X(t) = X(t; \underbrace{\vec{p}^N, \vec{r}^N}_{\text{initial conditions}})$ that linearly couples to an external force $f(t)$ in the Hamiltonian, i.e. $H' = H - fX$, we found that

$$\frac{C(t)}{C(0)} = \frac{\bar{X}(t) - \langle X\rangle}{\bar{X}(0) - \langle X\rangle} \Leftrightarrow \chi(t) = \begin{cases} -\beta \frac{d}{dt} C(t) & t \geq 0 \\ 0 & t < 0 \end{cases}$$

Onsager regression hypothesis — Fluctuation-dissipation theorem.

The fluctuation-dissipation theorem is often formulated in frequency space.

Spectral analysis of fluctuations

Recall that we defined the autocorrelation function as

$$C(t) = \langle \delta X(0) \delta X(t)\rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T d\tau\, \delta X(\tau)\, \delta X(\tau + t)$$

We introduce a quantity called the spectral density defined as

$$S(\omega) = \lim_{T\to\infty} \left\langle \frac{1}{T} \left|\delta \tilde{X}_T(\omega)\right|^2 \right\rangle \quad (*)$$

Here the windowed Fourier transform is given by:

$$\delta \tilde{X}_T(\omega) = \int_{-T/2}^{T/2} dt\, e^{i\omega t}\, \delta X(t).$$

Here we take $\delta X(t) \in \mathbb{R} \Leftrightarrow \widetilde{\delta X}_T^*(\omega) = \delta \tilde{X}_T(-\omega)$.

We ask ourselves two questions: (i) Does the limit $(*)$ exist?

(ii) How does $S(\omega)$ relate to $C(t)$?

Let us evaluate:

$$\langle |\widetilde{\delta X_T(\omega)}|^2 \rangle = \int_{-T/2}^{T/2} dt'' \int_{-T/2}^{T/2} dt' \, \langle \delta X(t'') \delta X(t') \rangle e^{i\omega(t''-t')}$$

$$= \int_{-T/2}^{T/2} dt' \int_{-T/2}^{T/2} dt'' \, G(t''-t') e^{i\omega \underbrace{(t''-t')}_{=:t}} = \int_{-T/2}^{T/2} dt' \int_{-T/2+t'}^{T/2-t'} dt \, G(t) e^{i\omega t}$$

$$= \int_{-T}^{T} dt \int_{-T/2+|t|/2}^{T/2-|t|/2} dt' \, G(t) e^{i\omega t} = \int_{-T}^{+T} dt \, (T-|t|) G(t) e^{i\omega t}.$$

Therefore, $S(\omega) = \lim_{T\to\infty} \int_{-T}^{T} dt \, e^{i\omega t} G(t) \left(1 - \frac{|t|}{T}\right)$

$$= \lim_{T\to\infty} \int_{-\infty}^{+\infty} dt \, e^{i\omega t} G(t) \left(1-\frac{|t|}{T}\right) \Theta(T-|t|)$$

$$\xrightarrow{\text{Lebesgue dominated convergence theorem}} \; = \int_{-\infty}^{+\infty} dt \, e^{i\omega t} G(t).$$

Therefore, the limit exists and it turns out that $S(\omega)$ is the Fourier transform of $G(t)$. This is called the Wiener-Khinchin theorem.

This is all we have to say about the fluctuation part of the fluctuation dissipation theorem.

What about the dissipative part in Fourier space?

Properties of response function $\chi(t)$

We restrict our attention to cases where $f(t)$ and $X(t)$ are real.

By the definition

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

$\chi(t,t') = \chi(t-t')$ is real as well). What does this mean for the Fourier transform?

We have $\tilde{\chi}(\omega) = \int_{-\infty}^{+\infty} dt\, \chi(t)\, e^{i\omega t}$ and we write: $\tilde{\chi}(\omega) = \tilde{\chi}'(\omega) + i\tilde{\chi}''(\omega)$

where $\tilde{\chi}'(\omega) = \mathrm{Re}[\tilde{\chi}(\omega)]$ and $\tilde{\chi}''(\omega) = \mathrm{Im}[\tilde{\chi}(\omega)]$.

- Imaginary part can be written as

$$\tilde{\chi}''(\omega) = -\frac{i}{2}\left[\tilde{\chi}(\omega) - \tilde{\chi}^*(\omega)\right] \underset{\chi(t) = \chi^*(t)}{=} -\frac{i}{2}\int_{-\infty}^{\infty} dt\, \chi(t)\left[e^{i\omega t} - e^{-i\omega t}\right]$$

$$= -\frac{i}{2}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\underbrace{\left[\chi(t) - \chi(-t)\right]}_{\text{not invariant under } t \to -t}.$$

$\Rightarrow$ $\chi''(\omega)$ arises from dissipative processes.

Furthermore, we observe that $\chi''(-\omega) = -\chi''(\omega)$. since

- Real part can be written as

$$\tilde{\chi}'(\omega) = \frac{1}{2}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\underbrace{\left[\chi(t) + \chi(-t)\right]}_{\text{"mechanical"}}$$

Furthermore, $\tilde{\chi}'(-\omega) = \tilde{\chi}'(\omega)$.

For this reason $\tilde{\chi}'(\omega)$ is called the reactive part of the response function

$\tilde{\chi}''(\omega)$ is called the dissipative part of the response function.

This becomes especially clear in the context of the fluctuation-dissipation theorem.

$$\chi(t) = \begin{cases} -\beta \frac{d}{dt} C(t) & t > 0 \\ 0 & t < 0 \end{cases} \qquad \chi(-t) = \begin{cases} 0 & t > 0 \\ \beta \frac{d}{dt} C(t) & t < 0. \end{cases}$$

$$\chi(t) - \chi(-t) = -\beta \frac{d}{dt} C(t) \quad \forall t$$

The Fourier transform of $\chi(t) - \chi(-t)$ is $2i\tilde{\chi}''(\omega)$.

and of $\frac{d}{dt} G(t)$ is $-i\omega S(\omega)$.

$$\Rightarrow \boxed{\tilde{\chi}''(\omega) = +\frac{\omega\beta}{2} S(\omega)}$$

Fluctuation-dissipation theorem in frequency space.

In last lecture we considered the absorbed power and have shown that LHS relates to dissipation!

In the quantum-mechanical derivation is a bit more technical (commutators, imaginary-time formalism) and we find

$$S(\omega) = +2\hbar\,[n_B(\omega) + 1]\,\tilde{\chi}''(\omega)$$

$n_B(\omega)$ is the Bose-Einstein distribution.

Remark: Sometimes you see in the literature the FD theorem with an opposite sign as the above. This stems from a different definition of the Fourier transform.

Causality and the Kramers-Kronig relations

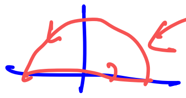
Recall that we impose the causality condition $\chi(t) = 0$ for $t < 0$

We can compute $\chi(t)$ from its Fourier transform:

$$\chi(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}\,\tilde{\chi}(\omega) \quad (*)$$

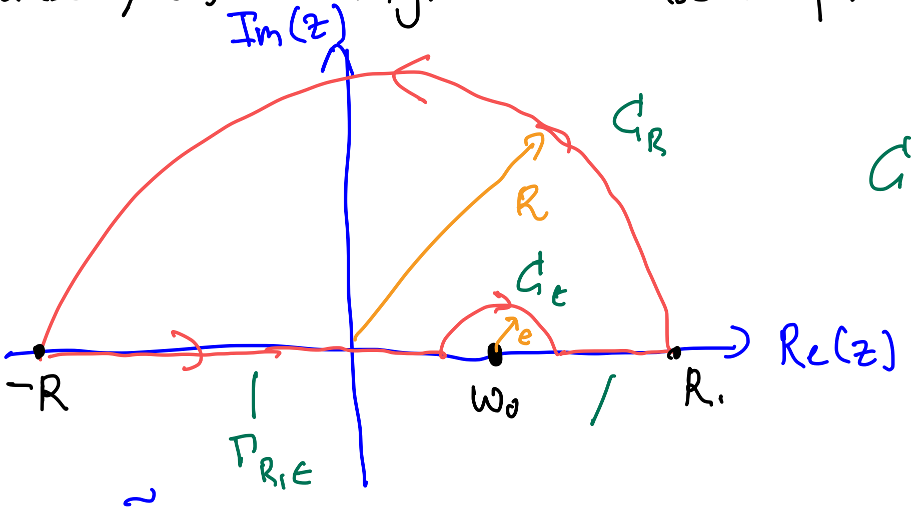
Furthermore, we take $\int_0^{\infty} dt\, \chi(t) < \infty$

(Finite force must give a finite response)



We can compute the integral (*) by closing the contour in the upper half complex plane. Since $\chi(t)=0$ for $t<0$ we conclude that for the analytic continuation $\tilde{\chi}(z)$; $z=\omega+i\eta$, there are no poles for $\eta>0$. In other words $\tilde{\chi}(\omega+i\eta)$ is analytic for $\eta>0$.

Because $\tilde{\chi}(z)$ is analytic we can use the following trick:



$G = G_R \cup \Gamma_{R,\epsilon} \cup G_\epsilon$

Because $\tilde{\chi}(z)$ is analytic in the upper half plane and the contour G does not enclose any poles, we find:

$$0 = \oint_G \frac{\tilde{\chi}(z)}{z-\omega_0} = \lim_{R\to\infty}\Big(\underbrace{\int_{G_R}}_{=0 \text{ e.g. Jordan's lemma}} + \int_{\Gamma_{R,\epsilon}} + \int_{G_\epsilon}\Big)\frac{\tilde{\chi}(z)}{z-\omega_0}\,dz,$$

$$=\left(\int_{-\infty}^{\omega_0-\epsilon} + \int_{\omega_0+\epsilon}^{\infty}\right)\frac{\tilde{\chi}(\omega)}{\omega-\omega_0}\,d\omega + \int_{G_\epsilon} dz\,\frac{\tilde{\chi}(z)}{z-\omega_0}$$

Now take $\epsilon\downarrow 0$, then

$$0 = \mathcal{P}\int_{-\infty}^{\infty} d\omega\,\frac{\tilde{\chi}(\omega)}{\omega-\omega_0} + \underbrace{\lim_{\epsilon\downarrow 0}\int_{G_\epsilon} dz\,\frac{\tilde{\chi}(z)}{z-\omega_0}}_{\text{we parametrize using } z=\omega_0+\epsilon e^{i\theta}} \qquad (**)$$

$$\int_{C_\epsilon} \frac{\tilde{\chi}(z)}{z-\omega_0}\,dz = \int_{\pi}^{0} d\theta \, \frac{\tilde{\chi}(\omega_0+\epsilon e^{i\theta})}{\epsilon e^{i\theta}}\, i\epsilon e^{i\theta}$$

Taylor

$$= -i\int_{0}^{\pi} d\theta \left[\tilde{\chi}(\omega_0) + \mathcal{O}(\epsilon)\right] \rightarrow -i\pi\,\tilde{\chi}(\omega_0) \text{ for } \epsilon \downarrow 0$$

$$\Rightarrow \quad \tilde{\chi}(\omega_0) = \frac{1}{i\pi}\, \mathcal{P}\int_{-\infty}^{+\infty} \frac{\tilde{\chi}(\omega)}{\omega-\omega_0}\, d\omega.$$

We conclude that:

$$\boxed{\begin{aligned} \tilde{\chi}'(\omega_0) &= \frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} d\omega\, \frac{\tilde{\chi}''(\omega)}{\omega-\omega_0} \\ \tilde{\chi}''(\omega_0) &= -\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} d\omega\, \frac{\tilde{\chi}'(\omega)}{\omega-\omega_0} \end{aligned}}$$

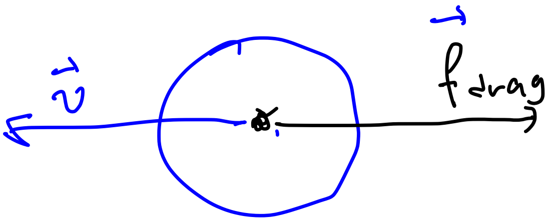
Kramers-Kronig relations

$\tilde{\chi}'(\omega)$ and $\tilde{\chi}''(\omega)$ are not independent !

The generalized Langevin equation

One of the most familiar non-equilibrium phenemenon is that of friction.

Consider a particle moving in a fluid:

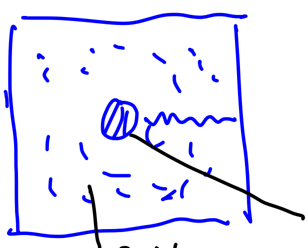


The fluid exerts a drag force $\vec{f}_{drag} = -\gamma v$ on the particle.

γ : friction constant.

Here, we want to provide a simple model for the friction constant γ.

We consider a "tagged" particle coupled to a bath



We consider the following Hamiltonian:

$$H = H_0(x) - xf + H_b(y_1, \dots, y_N).$$

oscillator Hamiltonian of tagged particle

bath Hamiltonian.

We assume a linear coupling between bath and particle:

$$f = \sum_i c_i y_i \qquad c_i \in \mathbb{R} \qquad i = 1, \dots, N.$$

x: primary degree of freedom

$\{y_i\}$: secondary degrees of freedom.

$$H_0 = \frac{1}{2} m \dot{x}^2 + V(x).$$

H_b: collection of harmonic oscillators.

Let us denote $f_b(t)$ as the force provided by a pure bath.
The presence of the tagged particle changes this behaviour within linear response theory as:

$$f(t) = f_b(t) + \int_{-\infty}^{+\infty} dt \, \chi_b(t-t') \, x(t')$$

and we know from the fluctuation-dissipation theorem that:

$$\chi_b(t-t') = \begin{cases} -\beta \dfrac{d}{d(t-t')} C_b(t-t') & t > t' \\ 0 & t < t'. \end{cases}$$

where $C_b(t) = \langle \delta f(0) \delta f(t) \rangle_b = \sum_{i,j} c_i c_j \langle \delta y_i(0) \delta y_j(t) \rangle_b$

Now we find the following equation of motion for the primary variable:

$$m\ddot{x}(t) = -\frac{dV}{dx} + f_b(t) + \int_{-\infty}^{+\infty} dt'\, \chi_b(t-t')\, x(t').$$

random or fluctuating force from bath.

nonlocal term because tagged particle influences bath degrees of freedom.

$$\overset{\text{causality}}{=} -\frac{dV}{dx} + f_b(t) + \int_{-\infty}^{t} dt'\, \chi_b(t-t')\, x(t')$$

$$\overset{\text{FDT}}{=} -\frac{dV}{dx} + f_b(t) \pm \beta \int_{-\infty}^{t} dt' \frac{d}{dt'} C_b(t-t')\, x(t')$$

$$\underset{\text{P.I.}}{=} -\frac{d\tilde{V}}{dx} + \delta f(t) - \beta \int_{0}^{t} dt'\, C_b(t-t')\, \dot{x}(t').$$

Generalized Langevin equation.

where $\tilde{V}(x) = V(x) - \beta C_b(0) x^2/2$

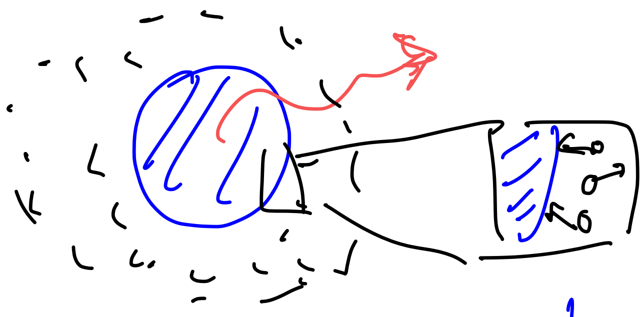
$\delta f(t) = f_b(t) - \beta C_b(t) x(0).$

Potential of mean force (bath-averaged potential on primary coordinate)

Friction is a result of fluctuating forces!

"Second fluctuation-dissipation theorem"

The model describes (1D) Brownian motion.



Suppose we approximate $\int_{0}^{t} dt'\, C_b(t')\, \dot{x}(t-t') \approx \dot{x}(t) \int_{0}^{\infty} dt'\, C_b(t')$ and $\tilde{V} = 0$

(Markovian approximation)

neglecting memory.

In the Markovian approximation:

$$m\dot{v}(t) \simeq f_b(t) - \gamma v(t)$$ Langevin equation.

with $v(t) = \dot{x}(t)$.

It turns out that: $$\gamma = \beta \int_0^\infty dt \, \langle \delta f(t) \delta f(0) \rangle .$$ (More details on tutorials).

Tagged particle experience random forces that buffet the particle about. Particle gains kinetic energy that is removed by frictional dissipation.

Within Langevin equation, we find $\langle v(0) v(t) \rangle = \langle v^2 \rangle e^{-(\gamma/m)t}$.

However if we include the effects of memory, we find

$\langle v(0) v(t) \rangle \sim t^{-3/2}$ Long-time tails.

Measured in experiment!

$$\langle \Delta x^2(t) \rangle = \underbrace{2D}_{\text{Diffusion coefficient}} t - \frac{4D\Delta}{\sqrt{\pi}} t^{1/2} + \dots$$