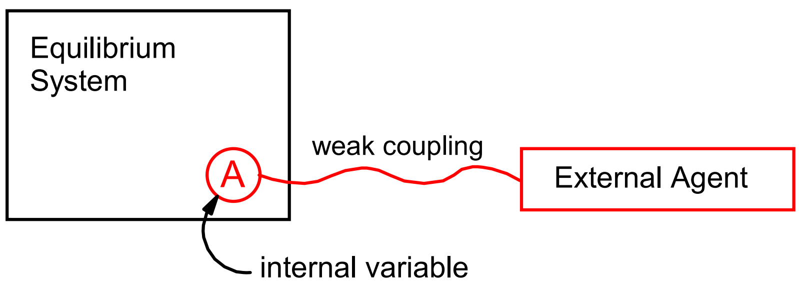
LINEAR RESPONSE THEORY

We have statistically described the time-dependent behavior of an internal variable in an equilibrium system through correlation functions, and now we would like to relate that to experimental observables. That is, how does the system respond, if you drive it from equilibrium?



> The system is moved away from equilibrium by external agent.

> The system absorbs energy from external agent.

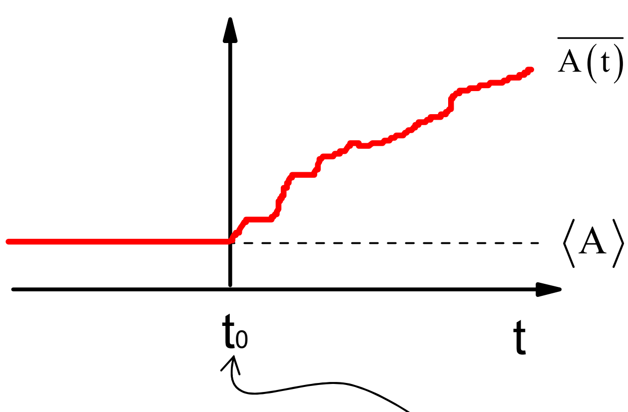
What are the time-dependent properties of the system?

$$H = H_0 - f(t)\, A$$

Internal variable

Time-dependence of external agent

Hamiltonian of equilibrium state



external force applied at t_0 moving system from $\langle A \rangle$

We average over an ensemble, **<u>each member of which is subject to same perturbation.</u>**

$\langle \ldots \rangle \equiv$ *average over equilibrium ensemble*

$\overline{\ldots} \equiv$ *average over nonequilibrium ensemble*

$\langle A \rangle \neq \overline{A(t)}$ *due to interaction*

Let's develop $\overline{A(t)}$ as an expansion in power of $f(t)$.

$$\overline{A(t)} = \left(terms\ f^{(0)}\right) + \left(terms\ f^{(1)}\right) + \ldots$$

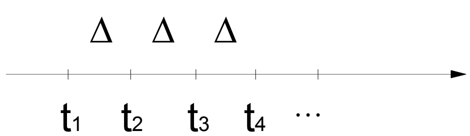
$$\overline{A(t)} = \quad \langle A \rangle \quad + \quad \int_{-\infty}^{+\infty} dt_0\ R^{(1)}(t,t_0)\ f(t_0) + \ldots$$

$R^{(1)}(t,t_0)$: Linear Response Function

The force is applied at t_0, and we observe the system at t. The linear response function is the quantity that contains the microscopic information that describes how the system responds to the applied force. We will look to find a quantum description of $R^{(1)}$.

Rationalization for an expansion of $\overline{A(t)}$ in powers of $f(t)$:

Let's break time up into infinitesimal intervals:



$$t_i = i\Delta \qquad f(t_i) = f_i$$

$$A(t_i) = A_i = A_i(\ldots, f_{i-2}, f_{i-1}, f_i)$$

Now, Taylor series expand about all $f_i = 0$

$$\overline{A(t_i)} = \underbrace{A_i(\ldots 0, 0, 0)}_{\langle A \rangle} \quad + \quad \sum_{j \le i} \left(\frac{\partial \overline{A_i}}{\partial f_j} \right)_{f_j = 0} f_j \quad + \quad \ldots$$

Value with no f applied

Sum over change due to force at all times of application

Linear term:

$$\sum_j \left(\frac{\partial \overline{A_i}}{\partial f_j} \right)_{f_j = 0} f_j \quad = \quad \sum_j j\Delta \left[\frac{1}{j\Delta} \frac{\partial A_i}{\partial f_j} \right] f_j$$

$$\lim_{\Delta \to 0} \qquad = \int_{-\infty}^{t_i} dt_j R(t_i, t_j) f(t_j)$$

Causality: The system cannot respond before the force has been applied.

$$R^{(1)}(t,t_0)=0 \quad \text{for} \quad t<t_0$$

The time-dependent change in A is

$$\delta\overline{A(t)}=\overline{A(t)}-\langle A\rangle=\int_{-\infty}^{t}dt_0\;R^{(1)}(t,t_0)\,f(t_0)$$

Stationarity: The time-dependence of the system only depends on the time interval between application of force and observation.

$$R^{(1)}(t,t_0)=R^{(1)}(t-t_0)$$

So,

$$\delta\overline{A(t)}=\int_{-\infty}^{t}dt_0\,R^{(1)}(t-t_0)f(t_0)$$

The response of the system is a convolution of the material response with the time-development of the applied force.

Usually, we define the time interval $\tau=t-t_0$

$$\delta\overline{A(t)}=\int_{0}^{\infty}d\tau\;R^{(1)}(\tau)\,f(t-\tau)$$

Impulse response. For a delta function perturbation:

$$f(t)=\lambda\delta(t-t_0)$$

$$\delta\overline{A(t)}=\lambda R^{(1)}(t-t_0)$$

Frequency-Domain Representation

$$\delta\overline{A(t)} = \int_0^{\infty} d\tau\, R^{(1)}(\tau)\, f(t-\tau)$$

Fourier Transform both sides:

$$\delta\overline{A(\omega)} \quad \int_{-\infty}^{+\infty} dt \left[\int_0^{\infty} d\tau\, R^{(1)}(\tau)\, f(t-\tau)\right] e^{i\omega t}$$

insert $\left(e^{-i\omega\tau}\, e^{+i\omega\tau}\right)$

$$\delta\overline{A(\omega)} \quad \int_{-\infty}^{+\infty} dt \int_{-\infty}^{\infty} d\tau\, e^{i\omega(t-\tau)}\, R^{(1)}(\tau)\, f(t-\tau)$$

setting $t' = t - \tau \quad dt' = dt$

$$= \underbrace{\int_{-\infty}^{+\infty} dt'\, e^{i\omega t'}\, f(t')}_{\tilde{f}(\omega)} \underbrace{\int_0^{\infty} d\tau\, R^{(1)}(\tau)\, e^{i\omega t}}_{\substack{\chi(\omega) \\ \textit{susceptibility}}}$$

Fourier-Laplace transform

F.T.

$$\delta\overline{A(\omega)} = \chi(\omega)\,\tilde{f}(\omega) \qquad \textit{spectral response}$$

A convolution of the force and response in time leads to the product of the force and response in frequency. This is a manifestation of the convolution theorem:

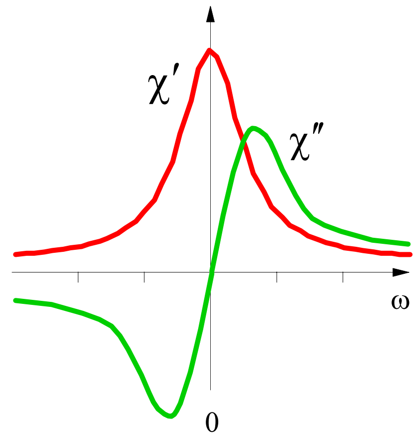
$$A(t)\otimes B(t) \equiv \int_{-\infty}^{\infty} d\tau\, A(t-\tau)\, B(\tau) = \int_{-\infty}^{\infty} d\tau\, A(\tau)\, B(t-\tau) = \mathcal{F}^{-1}\left[\tilde{A}(\omega)\,\tilde{B}(\omega)\right]$$

where $\tilde{A}(\omega) = \mathcal{F}\left[A(t)\right]$ and $\mathcal{F}[\cdots]$ is a Fourier transform.

Note that $R^{(1)}(\tau)$ is real, since the response of a system is an observable.

The susceptibility $\chi(\omega)$ is complex. We will relate $C_{AA}(\tau)$ to $R^{(1)}(\tau)$ and $\sigma_{abs}(\omega)$ to $\chi(\omega)$.

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$$



$$\chi(\omega) = \int_0^\infty d\tau\, R^{(1)}(\tau)\, e^{i\omega\tau}$$

$$= \underbrace{\int_0^\infty d\tau\, R^{(1)}(\tau)\, cos\,\omega\tau}_{\chi':\ \text{even in frequency}} + \underbrace{\int_0^\infty d\tau\, R^{(1)}(\tau)\, sin\,\omega\tau}_{\chi'':\ \text{odd in frequency}}$$

$$\chi'(\omega) = Re\left[\mathcal{F}\left(R^{(1)}(\tau)\right)\right] \qquad \chi''(\omega) = Im\left[\mathcal{F}\left(R^{(1)}(\tau)\right)\right]$$

$$\chi'(\omega) = \chi'(-\omega)$$

$$\chi''(\omega) = -\chi''(-\omega) \qquad\qquad \therefore\quad \chi(-\omega) = \chi^*(\omega)$$

Notice also

$$\chi'(\omega) = \tfrac{1}{2}\left[\chi(\omega) + \chi(-\omega)\right]$$

$$\chi''(\omega) = \tfrac{1}{2i}\left[\chi(\omega) - \chi(-\omega)\right]$$

$$\chi^*(\omega)$$

KRAMERS-KRÖNIG RELATIONS

A consequence of causality is that $\chi'(\omega)$ is not independent of $\chi''(\omega)$:

$$\chi'(\omega) = \frac{1}{\pi}\mathbb{P}\int_{-\infty}^{+\infty} \frac{\chi''(\omega')}{\omega' - \omega}\, d\omega'$$

$$\chi''(\omega) = \frac{1}{\pi}\mathbb{P}\int_{-\infty}^{+\infty} \frac{\chi'(\omega')}{\omega' - \omega}\, d\omega'$$

These are obtained from

$$\chi'(\omega) = \int_0^{\infty} R^{(1)}(t)\, cos\, \omega t\, dt$$

and

$$R^{(1)}(t) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \chi''(\omega)\, sin\, \omega t\, dt$$

Substituting:

$$\chi'(\omega) = \frac{1}{\pi}\int_0^{\infty} dt\, cos\, \omega t \int_{-\infty}^{+\infty} \chi''(\omega')\, sin\, \omega' t\, d\omega'$$

$$= \frac{1}{\pi} \lim_{R\to\infty} \int_{-\infty}^{+\infty} d\omega' \chi''(\omega') \int_0^{R} cos\, \omega t\, sin\, \omega' t\, dt$$

$$using\ \ cos\, ax\, sin\, bx = \tfrac{1}{2} sin(a+b)x + \tfrac{1}{2} sin(b-a)x$$

$$= \frac{1}{\pi} \lim_{R\to\infty} \mathbb{P}\int_{-\infty}^{+\infty} d\omega' \chi''(\omega) \tfrac{1}{2}\left[\frac{-cos(\omega'+\omega)R+1}{\omega'+\omega} - \frac{cos(\omega'-\omega)R+1}{\omega'-\omega}\right]$$

If we choose $R \to \infty$, the cosine terms vanish since they oscillate rapidly. This is equivalent to averaging over a monochromatic field. If we instead average over a single cycle: $R = 2\pi/(\omega'-\omega)$, we obtain

$$\chi'(\omega) = \frac{1}{\pi} P\int_{-\infty}^{+\infty} d\omega' \frac{\chi''(\omega')}{\omega'-\omega}$$

The other relation can be derived the same way.

Example: Classical Response

Model absorption of radiation by dipoles with a forced damped harmonic oscillator:

$$\ddot{x} + \gamma\,\dot{x} + \omega_0^2\,x = F(t)$$

For an E.M. wave: $F(t) = F_0 \cos\omega t = \dfrac{qE_0}{m}\cos\omega t$

$$x(t) = \frac{qE_0}{m}\frac{1}{\left[\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2\right]^{1/2}}\cos(\omega t + \delta)$$

$$\sin\delta = \frac{2\gamma\,\omega}{\left[\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2\right]^{1/2}}$$

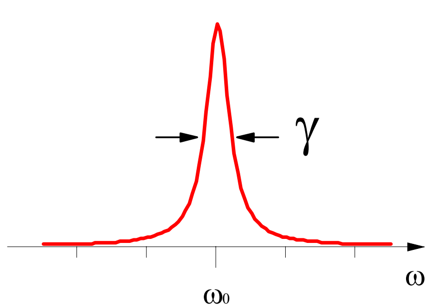
An impulsive driving force gives the response function: $x(t) = \int_0^\infty d\tau\, R^{(1)}(\tau)\, f(t-\tau)$

if $F(t) = F_0\delta(t - t_0)$, then $x(t) = F_0 R^{(1)}(t)$:

$$R^{(1)}(\tau) = \frac{1}{m\Omega}\exp\left(-\frac{\gamma}{2}\tau\right)\sin\Omega\tau \qquad \Omega = \sqrt{\omega_0^2 - \gamma^2/4}$$

$$\chi(\omega) = \frac{1}{m\left(\omega_0^2 - \omega^2 - i\gamma\omega\right)}$$

$$\chi''(\omega) = \frac{2\gamma\omega}{m\left[\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2\right]}$$



for $\gamma << \omega_0$ $\qquad \chi(\omega) \approx \dfrac{1}{2m\omega_0}\dfrac{1}{\omega - \omega_0 + i\gamma/2}$

$$\chi = \frac{1/m}{\omega_0^2 - \omega^2 + i\gamma\omega} \quad \text{for } \omega \approx \omega_0$$

$$\omega^2 - \omega_0^2 = (\omega + \omega_0)(\omega - \omega_0) \approx 2\omega_0(\omega - \omega_0) \approx 2\omega(\omega - \omega_0)$$

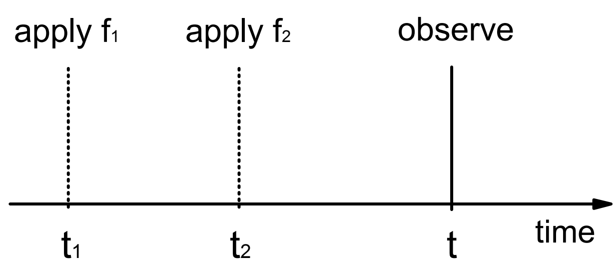
$$\chi \approx \frac{1}{2m\omega_0(\omega_0 - \omega) + i\gamma\omega} = \frac{1}{2m\omega_0}\frac{1}{(\omega_0 - \omega) + \frac{i\gamma}{2}}$$

Nonlinear Response Functions

If the system does not respond in a manner linearly proportional to the applied force, we can include nonlinear terms: the higher expansion orders in $\overline{A(t)}$. Let's look at second order:

$$\delta\overline{A(t)}^{(2)} = \int dt_1 \int dt_2 \; R^{(2)}(t;t_1,t_2)\, f_1(t_1)\, f_2(t_2)$$

Again we are integrating over the entire history of the application of two forces f_1 and f_2, including any quadratic dependence on f.



In this case, we will enforce causality through a time ordering that requires (1) that all forces must be applied before a response is observed and (2) that the application of f_2 must follow f_1:

$$t \geq t_2 \geq t_1 \qquad \text{or} \qquad R^{(2)}(t;t_1,t_2) \Rightarrow R^{(2)} \cdot \Theta(t-t_2) \cdot \Theta(t_2-t_1)$$

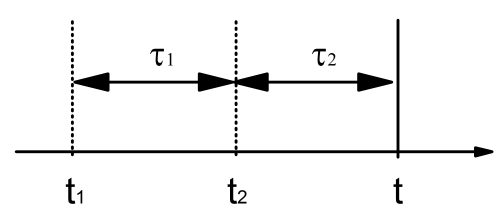
$$\delta\overline{A(t)}^{(2)} = \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 R^{(2)}(t;t_1,t_2)\, f_1(t_1)\, f_2(t_2)$$

Now we will call the system stationary so that we are only concerned with the time intervals between interactions.

$$\delta\overline{A(t)}^{(2)} = \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 \; R^{(2)}(t-t_2, t_2-t_1)\, f_1(t_1)\, f_2(t_2)$$

If we define the intervals between adjacent interactions

$$\tau_1 = t_2 - t_1 \qquad \tau_2 = t - t_2$$



$$= \int_0^{\infty} d\tau_1 \int_0^{\infty} d\tau_2 \; R^{(2)}(\tau_1,\tau_2)\, f_1(t-\tau_1-\tau_2)\, f_2(t-\tau_2)$$