Linear response theory

We had already seen that response of an equilibrium system to external force can be obtained from equilibrium correlation functions

Will formalise this idea more

Consider system described by $\hat{H}$ in equilibrium at $t=-\infty$ and then perturbed by a time dependent perturbation described by operator $\hat{A}$

$$\hat{H}(t) = \hat{H} - \lambda(t)\hat{A}$$

Initial state at $t=-\infty$

$$\hat{\rho}(t=-\infty) = \hat{\rho}_{eq} = e^{-\beta \hat{H}}$$

Evolution of the system described by Liouville equation

$$i\hbar \frac{\partial}{\partial t}\hat{\rho}(t) = \left[\hat{H}, \hat{\rho}(t)\right]$$

Since $\hat{H}$ in $\rho_{eq} = e^{-\beta \hat{H}}$ and $\hat{H}$ governing the evolution of unperturbed system are identical, equilibrium state is time translation invariant.

Now for general perturbation it is hard to ... of perturbation will drive system out of equilibrium, and then also evolution under $\hat{H}$ will be non-trivial.

However if we consider small perturbations, can expand

$$\rho(t) = \hat{\rho}_{eq} + \lambda \hat{\rho}_{neq}(t)$$

$$O(\lambda) \quad i\hbar \frac{\partial}{\partial t} \hat{\rho}_{neq}(t) = [\hat{H}, \hat{\rho}_{neq}(t)] - f(t) [\hat{A}, \hat{\rho}_{eq}]$$

So we find ...

$$i\hbar \frac{\partial}{\partial t} e^{\frac{i}{\hbar}\hat{H}t} \hat{\rho}_{neq}(t) e^{-\frac{i}{\hbar}\hat{H}t} = -f(t) e^{+\frac{i}{\hbar}\hat{H}t} [\hat{A}, \hat{\rho}_{eq}] e^{-\frac{i}{\hbar}\hat{H}t}$$

which using $\hat{\rho}_{neq}(t=-\infty) = 0$

$$\hat{\rho}_{neq}(t) = \frac{i}{\hbar} e^{-\frac{i}{\hbar}\hat{H}t} \int_{-\infty}^{t} dt' f(t') e^{+\frac{i}{\hbar}\hat{H}t'} [\hat{A}, \hat{\rho}_{eq}] e^{-\frac{i}{\hbar}\hat{H}t'} e^{+\frac{i}{\hbar}\hat{H}t}$$

In particular if we now measure an observable $\hat{B}$

$$\langle\hat{B}\rangle = \mathrm{tr}\left[\hat{B}\hat{\rho}\right]$$

$$= \langle\hat{B}\rangle_{eq} + \frac{i}{\hbar}\,\mathrm{tr}\Big[\, e^{\frac{i}{\hbar}\hat{H}t}\,\hat{B}\,e^{-\frac{i}{\hbar}\hat{H}t}\int_{-\infty}^{t} dt'\, f(t')\; e^{\frac{i}{\hbar}\hat{H}t'}\left[\hat{A},\hat{\rho}_{eq}\right]e^{-\frac{i}{\hbar}\hat{H}t'}\Big]$$

or equivalently in interaction picture

$$\hat{A}_I(t) = e^{\frac{i}{\hbar}\hat{H}t}\,\hat{A}_S\,e^{-\frac{i}{\hbar}\hat{H}t} \quad \text{and} \quad \hat{\rho}^{eq}_I = e^{\frac{i}{\hbar}\hat{H}t}\,\hat{\rho}_{eq}\,e^{-\frac{i}{\hbar}\hat{H}t} = \hat{\rho}^{S}_{eq}$$

$$\langle\hat{B}\rangle = \langle\hat{B}\rangle_{eq} + \frac{i}{\hbar}\int_{-\infty}^{t} dt'\,\mathrm{tr}\left[\hat{B}_I(t)\left[\hat{A}_I(t'),\hat{\rho}_{eq}\right]\right] f(t')$$

using $\mathrm{tr}\left[A[B,C]\right] = \mathrm{tr}\left[ABC - ACB\right]$

$$= \mathrm{tr}\left[ABC - BAC\right] = \mathrm{tr}\left[[A,B]C\right]$$

$$\langle\hat{B}\rangle = \langle\hat{B}\rangle_{eq} + \frac{i}{\hbar}\int_{-\infty}^{t} dt'\, f(t')\;\mathrm{tr}\left[\hat{\rho}_{eq}\left[\hat{B}_I(t),\hat{A}_I(t')\right]\right]$$

or

$$\langle\hat{B}\rangle = \langle\hat{B}\rangle_{eq} + \frac{i}{\hbar}\int_{-\infty}^{t} dt'\, f(t')\;\left\langle\left[\hat{B}_I(t),\hat{A}_I(t')\right]\right\rangle_{eq}$$

We again see that response to perturbation is determined by equilibrium correlation functions

Now if we can prove this result ground
fun of linear response to [illegible] (Kubo formula)

$$\langle B \rangle_{neq} - \langle B \rangle_{eq} = \int_{-\infty}^{+\infty} \chi_{BA}(t-t')\, f(t')\, dt'$$

we refer the complex susceptibility / admittance (response function)

$$\chi_{BA}(t) = \frac{i}{\hbar} \left\langle \left[B_I(t), A_I(0) \right] \right\rangle_{eq} \Theta(t)$$

where we used time translation invariance
of equilibrium average

Now often we want to know response in Fourier space, we should consider Fourier ponderation

However we need to respect $f(t) \to 0$ for $t \to -\infty$ so that system is in equilibrium initially

Can be achieved as usual with the $i\varepsilon$ prescription

$$\tilde{\chi}_{BA}(\omega) = \lim_{\varepsilon \to 0^+} \int_{-\infty}^{+\infty} dt \, \chi_{BA}(t) \, e^{i\omega t} e^{-\varepsilon t}$$

So

$$\tilde{\chi}_{BA}(\omega) = \lim_{\varepsilon \to 0} \frac{i}{\hbar} \int_{-\infty}^{+\infty} dt \, \theta(t) \left\langle \left[B_I(t), A_I(0) \right] \right\rangle_{eq} e^{i\omega t} e^{-\varepsilon t}$$

Now lets evaluate this in eigenbasis of Hamiltonian

$$\left\langle \left[B_I(t), A_I(0) \right] \right\rangle_{eq} = \mathrm{tr} \left[\rho_{eq} \left[B_I(t), A_I(0) \right] \right]$$

$$= \sum_n \langle n | \rho_{eq} \left[B_I(t), A_I(0) \right] | n \rangle$$

$$= \sum_n \frac{e^{-\beta E_n}}{Z(\beta)} \langle n | \left[B_I(t), A_I(0) \right] | n \rangle$$

$$= \sum_{nn'} \frac{e^{-\beta E_n}}{Z(\beta)} \Big[\langle n | B_I(t) | n' \rangle \langle n' | A_I(0) | n \rangle - n \leftrightarrow n' \Big]$$

$$= \sum_{nn'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{Z(\beta)} \underbrace{\langle n | B_I(0) | n' \rangle}_{B_{nn'}} \underbrace{\langle n' | A_I(0) | n \rangle}_{A_{n'n}}$$

$$e^{\frac{i(E_n - E_{n'})t}{\hbar}}$$

Define $\omega_{nn'} = \frac{E_n - E_{n'}}{\hbar} = -\omega_{n'n}$

$$\langle [B_I(t), A_I(0)] \rangle_{eq} = \sum_{nn'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{Z(\beta)} B_{nn'} A_{n'n} e^{i\omega_{nn'}t}$$

So performing the integral

$$\int_{-\infty}^{+\infty} dt\, \Theta(t)\, e^{i(\omega - \omega_{n'n} + i\varepsilon)t}$$

$$\overset{\varepsilon \to 0}{=} \frac{+i}{(\omega - \omega_{n'n} + i\varepsilon)}$$ lower bound only

we then get

$$\tilde{\chi}_{BA}(\omega) = \frac{1}{\hbar} \sum_{nn'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{Z(\beta)} B_{nn'} A_{n'n} \lim_{\varepsilon \to 0^+} \frac{1}{\omega_{n'n} - \omega - i\varepsilon}$$

which is called spectral representation / Lehmann representation

Similarly if we don't care about the response (which involves causal $\Theta(t)$ function) can directly look at spectral function

$$\rho_{BA}(t) = \frac{1}{\hbar} \left\langle \left[B_I(t), A(0) \right] \right\rangle_{eq}$$

Now integrating over t to go to frequency space, gives δ-fctn

$$\tilde{\rho}_{BA}(\omega) = \frac{2\pi}{\hbar} \sum_{nn'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{Z(\beta)} B_{nn'} A_{n'n} \, \delta(\omega - \omega_{n'n})$$

We can use this kind of analysis to establish all kinds of relations between correlation functions, e.g.

$$\frac{1}{2\pi} \lim_{\epsilon \to 0} \int d\omega' \frac{\tilde{\rho}_{BA}(\omega')}{\omega' - \omega - i\epsilon} = \tilde{\chi}_{BA}(\omega)$$

Now while the spectral function microscopically characterizes the structure of possible excitations of the system, there is a further relation to actual fluctuations of an equilibrium system.

Namely if instead of commutator we consider the symmetrized two-point function

$$\tilde{F}_{BA}(t) = \frac{1}{2} \Big\langle \underbrace{\{ B_H(t), A(0) \}_+}_{\text{anti-commutator}} \Big\rangle_{eq}$$

then

$$\tilde{F}_{BA}(\omega) = \frac{2\pi}{\hbar} \sum_{nn'} \frac{e^{-\beta E_n} + e^{-\beta E_{n'}}}{2 Z(\beta)} B_{nn'} A_{n'n} \cdot \delta(\omega - \omega_{n'n})$$

Now using $\dfrac{e^{-a} + e^{-b}}{e^{-a} - e^{-b}} = \dfrac{1 + e^{a-b}}{1 - e^{a-b}}$

we find $a - b = \beta(E_n - E_{n'}) = -\beta \hbar \omega_{n'n}$

$$\tilde{F}_{BA}(\omega) = \frac{\hbar}{2} \frac{1 + e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \tilde{\rho}_{BA}(\omega)$$

$$= \frac{\hbar}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right) \tilde{\rho}_{BA}(\omega)$$

So in particular for $\beta\hbar\omega \ll 1$ $\coth(x) \sim \frac{1}{x}$

$$\tilde{F}_{BA}(\omega) = \frac{k_B T}{\omega} \tilde{\rho}_{BA}(\omega)$$

which is classical KMS relation