Physics 210B

→ Linear Response Theory and Kubo Formalism : General Theory

(cf. Pottier, Zwanzig)

Recall:

→ seek transport coefficients →

what are they based on? what is fundamental?

- before → Boltzmann Eqn., Chapman - Enskog expansion

here

- here → linear response (Liouville Eqn.), equilibrium fluctuation correlation

$$\underline{\underline{\sigma}}(\omega) = \frac{\beta}{V}\int_0^\infty d\tau \, e^{i\omega\tau} \langle \underline{J}(\Gamma)\, \underline{J}(\Gamma(-\tau)) \rangle$$

equilibrium correlation fctn.

$$\langle \; \rangle = \int d\Gamma \, f_0$$

i.e. fluctuations occur at near equilibrium
⇒ transport

→ key steps:

from $\sum_i q_i \underline{x}_i \cdot \underline{E}$

$$\langle J(t) \rangle = \beta \int d\Gamma\, f_0\, \underline{J}(\Gamma) \int_0^{t-t_0} d\tau\, e^{-\tau \mathcal{L}_0} \left[\underline{E}(t-\tau) \cdot \underline{J}(\Gamma) \right]$$

orbit propagator:

never explicit ← $e^{-\tau \mathcal{L}_0} [\;\;] = \left[\underline{E}(\;) \cdot \underline{J}(\Gamma(\tau)) \right]$

Kubo formalism uses ideas of
- orbit propagator:

$$e^{-t\mathcal{L}} F(x, v) \to F(\underline{x}(-t), \underline{v}(-t))$$

- unperturbed orbit propagator

$\mathcal{L}_0$ → $x(-t)$, $v(-t)$ determined by H_0.

- $\mathcal{L}_1$ → propagator for perturbation $q\underline{E} \cdot \underline{x} = H_1$.

→ example: mobility of charged Brownian particle

mobility ↔ average velocity

$$\langle v \rangle_\omega = \underbrace{\mu(\omega)}_{\text{mobility}} E_\omega$$

So: mobility → velocity correlation function

$$\mu(\omega) = \int_0^\infty dt\, e^{-i\omega t} \beta q \underbrace{\langle v(0) v(t) \rangle}_{\text{velocity correlation}}$$

N.B.: $\omega \to 0$

$$\int_0^\infty dt \langle \tilde{v}(t) \tilde{v}(0) \rangle = D = \frac{\mu(0)}{\beta q} = \underbrace{\frac{\mu(0) T}{q}}_{\text{Einstein relation}}$$

but now recall showed:

$$\langle v(t) v(0) \rangle = v_{th}^2 \exp(-\underbrace{\beta}_{\text{drag.}} t/m)$$

so

$$\mu(\omega) = \int_0^\infty dt\, e^{-i\omega t}\, \cancel{\beta}\, q\, \frac{1}{m}\, e^{-\beta t/m}$$

$$= q/(i\omega m + \beta)$$

frequency dependence. (ω vs drag)

how via Chapman-Enskog?

→ Also: cumulants and diffusion (cf. next week's lectures).

Now:

→ generalize: classical and $\boxed{\text{quantum}}$ systems.

→ relate responses, susceptibilities, relaxation functions (time)

→ General Theory: (quantum FDT) etc. and structure and connections.

→ Background — Q.M. Density Operator

$$\rho = \sum_j p_j |\psi_j\rangle\langle\psi_j| \longleftrightarrow \text{analogue to } f$$

ρ: density operator; p_j: probability in j (pure) (analogous to f)

then:

$$\langle A \rangle = \sum_j p_j \langle\psi_j|A|\psi_j\rangle = \sum_j p_j \, tr\left(|\psi_j\rangle\langle\psi_j|A\right)$$

$\langle A \rangle$: expectation of A

$$= \sum_j tr\left(p_j |\psi_j\rangle\langle\psi_j|A\right)$$

$$= tr\left(\sum_j p_j |\psi_j\rangle\langle\psi_j|A\right)$$

$$\boxed{\langle A \rangle = tr(\rho A)}$$

$$\boxed{S = -tr(\rho \ln \rho)} \rightarrow \text{entropy}$$

At eqlbrm:

$$\rho_0 = \frac{1}{Z} \exp\left[-\beta H_0\right]$$

Dynamics:

$$\frac{d\rho}{dt} = -i\,\mathcal{L}\,\rho(t)$$

Liouville operator → evolves density fctn.

$$H = H_0 + H_1$$

$$-a(t)\,A$$

slow fctn.

operator ↔ canonical variables (physical quantity → i.e. V for current/resistivity)

→ Linear Response

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_1$$

$$H = H_0 + H_1$$

and

$$\rho = \rho(t) = \rho_0 + \delta\rho(t)$$

then $\frac{d\rho_0}{dt} = 0, \quad \mathcal{L}_0 \rho_0 = 0$

$$\frac{d}{dt}\delta\rho(t) = -i\mathcal{L}_1\rho_0 - i\mathcal{L}_0\,\delta\rho(t) \cancel{- i\mathcal{L}_1\,\delta\rho(t)}^{\text{h.o.}}$$

$$\delta\rho(t) = e^{-i\mathcal{L}_0 t} F(t)$$

so

$$\cancel{-i\mathcal{L}_0 e^{-i\mathcal{L}_0 t} F(t)} + e^{-i\mathcal{L}_0 t}\frac{dF}{dt} = -i\mathcal{L}_1\rho_0 \cancel{-i\mathcal{L}_0 e^{-i\mathcal{L}_0 t}F(t)}$$

$$\frac{dF(t)}{dt} = -i\,e^{i\mathcal{L}_0 t}\mathcal{L}_1\rho_0$$

so

$$F(t) = -i\int_{t_0}^{t} e^{i\mathcal{L}_0 t'}\mathcal{L}_1\rho_0\,dt'$$

and,

$$\boxed{\delta\rho(t) = -i\int_{t_0}^{t} e^{-i\mathcal{L}_0(t-t')}\mathcal{L}_1\rho_0\,dt'}$$

→ gives perturbed density (distribution fctn.)

→ simple/progress → $\mathcal{L}_0$ for evolution. Leaves ρ_0 invariant

Now, Q.M. $\Rightarrow$ $\frac{\partial \rho_0}{\partial t} + \frac{i}{\hbar}[\rho_0, H] = 0$

$$i\mathcal{L}_1 \rho_0 = \frac{i}{\hbar}[H_1, \rho_0]$$

$\Leftrightarrow$ $\mathcal{L}_1$ advances $\left\{\begin{array}{l}\text{orbits} \\ \text{particles}\end{array}\right.$ / ρ_0 according to H_1

and since $H_1 = -\underset{\substack{\uparrow \\ \text{parametric dep.}}}{a(t)}\, A$

$$\boxed{\begin{aligned} \delta\rho(t) &= \frac{i}{\hbar}\int_{t_0}^{t} a(t')\, e^{-i\mathcal{L}_0(t-t')}\left[A, \rho_0\right] \\ &= \frac{i}{\hbar}\int_{t_0}^{t} a(t')\left[A_I(t'-t), \underset{\substack{\uparrow \\ \text{inv}}}{\rho_0}\right] dt' \end{aligned}}$$

where,

$A_I(t'-t)$ is in <u>interaction picture</u> (Heisenberg)

i.e.

$$\boxed{A_I(t)} = e^{i\mathcal{L}_0 t} A = \boxed{e^{iH_0 t/\hbar} A e^{-iH_0 t/\hbar}}$$

Finally, $(t_0 \to -\infty)$:

$$\boxed{\delta\rho(t) = \frac{i}{\hbar}\int_{-\infty}^{t} a(t')\,[A_I(t'-t), \rho_0]\,dt'}$$

perturbed distrib.

Now to compute linear response of operator B (represents any canonical variable)

$$\langle B(t)\rangle_a = tr[\rho(t)\, B]$$

evol'n resp. B, avg'd, induced by $a(t)$

B is operator computing response of

$$= \underbrace{\langle B\rangle}_{\cancelto{0}{tr(\rho_0 B)}} + tr[\delta\rho(t)\, B]$$

B indep time

so

$$\langle B(t)\rangle_a = \frac{i}{\hbar}\int_{-\infty}^{t} a(t')\, tr\left([A_I(t'-t), \rho_0]\, B\right) dt'$$

circular permutation (cross prod.)

$$= \frac{i}{\hbar}\int_{-\infty}^{t} a(t')\, tr\left([B, A_I(t'-t)]\, \rho_0\right)$$

$$\langle B(t)\rangle_a = \frac{i}{\hbar}\int_{-\infty}^{t} a(t')\, tr\big([B, A_I(t'-t)]\underbrace{\rho_0}_{\text{eqbm avg.}}\big)$$

$$\boxed{\langle B(t)\rangle_a = \frac{i}{\hbar}\int_{-\infty}^{t} a(t')\,\underbrace{\langle[B^I(t-t'), A]\rangle}\, dt'}$$

- can shift time arguments
- ρ_0 cnv.

Finally,

response

$$\boxed{\langle B(t)\rangle_a = \int_{-\infty}^{+\infty} \underbrace{\tilde{\chi}_{BA}(t-t')}_{\text{susceptibility}}\, a(t')\, dt'}$$

$$\boxed{\tilde{\chi}_{\text{[redacted]}\,B,A} = \frac{i}{\hbar}\,\Theta(t)\,\langle[B(t), A]\rangle}$$

General

** Kubo Formula **

- if $H_1 = -a(t)A$, then $\tilde{\chi}_{BA}$ is susceptibility of B, [redacted] computed with $\delta\rho = \delta\rho(A)$ i.e. from: $tr(B\,\delta\rho)$

- if $[H, A] = [H, B] = 0 \rightarrow [A, B] = 0$ and $\tilde{\chi}_{BA} \rightarrow 0$
- avg is over ρ_0
- classical counterpart:

$$\frac{i}{\hbar}[B(t), A] \longrightarrow \{B, A\}, \quad \text{avg over } \rho_0$$

- general.
- for several perturbations → add. (linear response).

Expressing as sum over eigenstates: $\Pi_n = \langle \phi_n | \rho_0 | \phi_n \rangle$

$$\tilde{\chi}_{BA}(t) = \frac{i}{\hbar}\Theta(t)\sum_n \langle \phi_n | [B(t), A] \rho_0 | \phi_n \rangle$$

$$= \frac{i}{\hbar}\Theta(t)\sum_n \langle \phi_n | (B(t)A - AB)\rho_0 | \phi_n \rangle$$

$$= \frac{i}{\hbar}\Theta(t)\sum_{n,l} \Pi_n \left(B_{nl} A_{ln} e^{i\omega_{nl}t} - A_{nl} B_{ln} e^{i\omega_{ln}t} \right)$$

$$\omega_{nl} = (\epsilon_n - \epsilon_l)/\hbar$$

and symmetrizing second term:

$$\boxed{\tilde{\chi}_{BA}(t) = \frac{i}{\hbar}\Theta(t)\sum_{n,\ell}(\Pi_n - \Pi_\ell)\, B_{n\ell} A_{\ell n}\, e^{i\omega_{n\ell}t}}$$

→ susceptibility / response fctn → linear superposition of sinusoids at $\omega_{n\ell}$

→ finite d-o-f ⇒ H_0 spectrum discrete

$\tilde{\chi}_{B,A}$ ⟺ sum of sinusoids

⇒ $\boxed{\text{undamped!}}$

system has infinite memory!

Atom perturbed by electric field.

Eg. What is response function of an atom (atomic system) perturbed (polarized) by electric field. Unperturbed is in $|\phi_0\rangle$.

⇝ $\underline{H}_1 = -\underline{E}(t)\cdot q\,\underline{X}$

Recall: $\chi_{BA}(t) = \frac{i}{\hbar}\Theta(t)\langle[B(t), A]\rangle$

here: $\underline{A} = \underline{x}$ (via $\underline{H}_1$)

$\underline{B} = \underline{x}(t)$ i.e. polarization is $\underline{x}(t)$ trajectory

so

$$\text{Resp Fctn} = \chi_{x,x} = \frac{i}{\hbar}\Theta(t)\langle\phi_0|[x(t), x]|\phi_0\rangle$$

Now,
$$\chi_{BA} = \frac{i}{\hbar}\Theta(t)\sum_{n,q}\Pi_n\left(B_{nq}A_{qn}e^{i\omega_{nq}t} - A_{nq}B_{qn}e^{i\omega_{qn}t}\right)$$

$$= \frac{i}{\hbar}\Theta(t)\sum_n\left(x_{0n}x_{n0}e^{i\omega_{0n}t} - x_{0n}x_{n0}e^{-i\omega_{n0}t}\right)$$

$$= \Theta(t)\frac{2}{\hbar}\sum_n|\langle\phi_0|x|\phi_n\rangle|^2\sin\omega_{n0}t$$

→ What happened to the correlation Function?

⇒ Relation to Canonical Correlation Function [redacted] ⟺ Rewrite commutator in simpler way!

⇝ T, $\rho_0 \equiv \sum_n \underbrace{p_n}_{\frac{1}{Z} e^{-\beta E_n}} |\phi_n\rangle\langle\phi_n|$

Now, $\chi_{BA} = \frac{i}{\hbar}\theta(t)\langle\underbrace{[B(t), A]}_{}\rangle$

$\sim \mathrm{tr}\left([A, \rho_0]\, B(t)\right)$

to compute use identity:

$$[A, e^{-\beta H_0}] = e^{-\beta H_0}\int_0^{\beta} e^{\lambda H_0}[H_0, A]\, e^{-\lambda H_0}\, d\lambda$$

– show via matrix elements ⟺ tedious

– leads to "Kubo Transform"

but : $[H_0, A] = i\hbar \dot{A}$

so identity $\Rightarrow$

$$[A, \rho_0] = -i\hbar \rho_0 \int_0^\beta e^{\lambda H_0} \dot{A} e^{-\lambda H_0} d\lambda$$

so, for response:

$$\chi_{BA}(t) = \Theta(t) \int_0^\beta \langle e^{\lambda H_0} \dot{A} e^{-\lambda H_0} B(t) \rangle d\lambda$$

and if define:

$$A(i\hbar\lambda) \equiv e^{\lambda H_0} A e^{-\lambda H_0}$$

i.e. operator at imaginary time $-i\hbar\lambda$

$$\boxed{K_{BA}(t) = \frac{1}{\beta} \int_0^\beta \langle A(-i\hbar\lambda) B(t) \rangle d\lambda}$$

$\Downarrow$

Kubo canonical correlation function.

$A(-i\hbar\lambda) \equiv$ operator at imag. time.

so

$$\boxed{\underbrace{\chi_{BA}(t)}_{\text{resp. function}} = \beta\,\Theta(t)\,\underbrace{K_{BA}(t)}_{\text{canonical correlator}}}$$

General, QM counterpart of:

$$\underline{\underline{\sigma}}(\omega) = \int_0^\infty e^{i\omega\tau} \langle \underline{J}(0)\,\underline{J}(-\tau)\rangle \frac{\beta}{V}$$

→ Generalized Susceptibility

i.e. have: correlation ↔ response fctn.

response ↔ susceptibility
(F.T.)

So → general form susceptibility ?

have $a(t)$ applied

$$\langle B(\omega)\rangle_a = \chi_{BA}(\omega)\, a(\omega)$$

so, define generalized susceptibility as: (FT)

$$\chi_{BA}(\omega+i\epsilon) = \int_0^\infty \chi_{BA}(t)\, e^{i\omega t}\, e^{-\epsilon t}\, dt \qquad \epsilon > 0$$

conv.

so

$$\chi_{BA}(\omega) = \lim_{\epsilon\to 0} \chi_{BA}(\omega+i\epsilon)$$

so if

$$\chi_{BA}(t) = \frac{i}{\hbar}\,\Theta(t) \sum_{n\ell} (\Pi_n - \Pi_\ell)\, B_{n\ell} A_{\ell n}\, e^{i\omega_{n\ell} t}$$

$\Rightarrow$

$$\boxed{\chi_{BA}(\omega) = \frac{1}{\hbar} \sum_{n,\ell} (\Pi_n - \Pi_\ell)\, B_{n\ell} A_{\ell n} \lim_{\epsilon\to 0} \frac{1}{\omega_{\ell n} - \omega - i\epsilon}}$$

susceptibility.

- poles - resonances $\omega_{\ell,n}$

- general QM. derivation

Lots more ....