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

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

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

equilibrium correlation fctn.

i.e. fluctuations occur at near equilibrium
$\Rightarrow$ transport

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

$\rightarrow$ key steps:

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

orbit propagation:

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

Kubo formalism uses ideas of
- orbit propagator:

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

- unperturbed orbit propagator

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

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

→ example: mobility of charged Brownian particle

mobility ↔ average velocity

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

∴ 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:

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

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

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

ρ: density operator (analogous to f)

p_j: probability in j (pure)

then:

$$\boxed{\langle A\rangle} = \sum_j p_j \langle\psi_j|A|\psi_j\rangle = \sum_j p_j \, tr(|\psi_j\rangle\langle\psi_j|A)$$

$\langle A\rangle$: expectation of A

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

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

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

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

At eqbrm:

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

Dynamics:

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

Liouville operator → evolves density fctn.

$$H = H_0 + H_1$$

$$H_1 = -a(t)\, A$$

[slow fctn.] — $a(t)$

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

→ Linear Response

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

$$\updownarrow \qquad \updownarrow$$

$$H = H_0 + H_1$$

and

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

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

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

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

so

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

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

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. $\Rightarrow$ $\frac{\partial \rho}{\partial t} + \frac{i}{\hbar}[\rho, H] = 0$

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

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

parametric dep.

and since $H_1 = -a(t)\, A$

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

where,

$A_I(t'-t)$ is in interaction picture (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 ($t_0 \to -\infty$):

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

perturbed distrib.

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

$$\underbrace{\langle B(t)\rangle_a}_{\text{resp. evol'n of } B\text{, avg'd, induced by } a(t)} = tr\left[\rho(t)\, \underbrace{B}_{B \text{ is operator computing response of}}\right]$$

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

B indep. time

so

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

circular permutation (cross prod.)

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

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

eqbrm avg.

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

- can shift time arguments
- ρ_0 comm.

Finally,

response

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

susceptibility

$\tilde{\chi}$ [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 $\rightarrow$ 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:

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

→ susceptibility / response fctn ⇒ linear superposition of sinusoids at ω_{nl}

→ 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

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

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

$- A_{nq} B_{qn} e^{i\omega_{qn}t} \Big)$

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

$- x_{0n} x_{n0} e^{-i\omega_{n0}t} \Big)$

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

→ What happened to the correlation Function?

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

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

Now, $\chi_{BA} = \frac{i}{\hbar}\Theta(t)\underbrace{\langle[B(t), A]\rangle}_{\mathrm{tr}([A, \rho_0]B(t))}$

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 $-i\hbar\lambda$

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

$\Updownarrow$

Kubo canonical correlation function.

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

So

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

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)

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

$\int_0$ 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 ....