Physics 210 B

Goal of large part of course: Transport Coefficients.

III.) Linear Response Theory / Kubo Formalism; Quasilinear Theory

i.) Linear Response and Kubo Formalism — OV

(Follows: Dorfman, Kubo, Zwanzig)

"Look at him – a grown man, and he's still doing linear theory!?"

— overheard at a conference..

⇒ What is linear response theory about?

- seek transport coefficients (induced by / for) response to weak perturbation. (How weak is 'weak'?).

- Upshot: Kubo Formula (generalizes previous)

For current, and conductivity:

$$\underset{\substack{\uparrow\\ \text{conductivity}\\ \text{(tensor)}}}{\underline{\underline{\sigma}}(\omega)} = \frac{\beta}{V}\int d\tau\, e^{-i\omega\tau} \underset{\substack{\uparrow\\ \text{equilibrium fluctuation}\\ \text{correlation function!}}}{\langle \underline{\tilde{J}}(0)\underline{\tilde{J}}(\tau)\rangle}$$

(brackets ...)

i.e. generic result: F-T. of equilibrium
correlation function yields
transport coefficient — here $\underline{\underline{\sigma}}(\omega)$
(note frequency dependence!)

why care?:

- systematic, fundamental (Liouville Thm.)

- relates (weakly) non-equilibrium response to equilibrium fluctuation correlation function.

- frequently easy to measure equilibrium fluctuation spectra
correlations

F.T. of spectra $\Leftrightarrow$ correlation function $\Rightarrow$ transport coefficient

- useful for calculating / relating:

{ response
correlation
susceptibility
transport

- What's New? Chapman-Enskog, etc. are all fundamentally linear response theories!!

Yes, but:

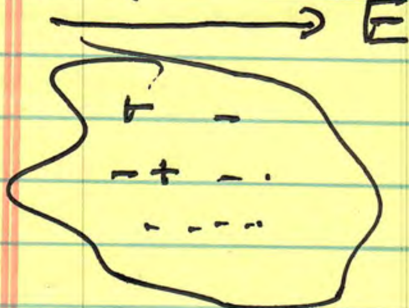
→ rooted in <u>fundamental</u>, <u>exact</u> equation → Liouville (but calculate)

→ reveals fundamentals of response, transport, etc. Eg.: Onsager Symmetry (proof via Linear Response Theory).

→ relates non-equilibrium response to equilibrium fluctuation correlation.

→ Response and Kubo Formula →
Case Study of Conductivity

Consider:



- system of charged, neutral particles (Atoms)

- E(t) applied

N.B. How compute conductivity, a/a Chapman-Enskog?

System described by:

$$\partial_t f + \{f, H\} = 0$$

Liouville Eqn (most basic)

$f = f_{eq} + \delta f$, $\{A, B\} = \sum_i \left[\frac{\partial A}{\partial \underline{x}_i} \cdot \frac{\partial B}{\partial \underline{p}_i} - \frac{\partial A}{\partial \underline{p}_i} \cdot \frac{\partial B}{\partial \underline{x}_i} \right]$

$\delta f \sim E$

Poisson Bracket

For Hamiltonian:

base state

$$\begin{cases} H = H_0 + H_1 \\ H_0 = \sum_i \frac{p_i^2}{2m} + \underbrace{\sum_{\substack{i,j \\ i \neq j}} \phi_{ij}}_{\text{Coulomb}} \end{cases}$$

perturbation

$$H_1 = \sum_i -Z_i \left(\underbrace{\underline{r}}_{\text{phase space variable}} \cdot \underline{E}(t) \right)$$

ext. parameter

energy due external field

N.B.: $\underline{E}(t) \rightarrow$ smooth, slow.
(space)

$$f = f_0 + \delta f \quad , \quad f_0 = \underbrace{\frac{1}{Z}}_{\text{norm.}} e^{-\beta H_0}$$

$$\beta \equiv 1/T$$

then,

$$\partial_t (f_0 + \delta f) + \left\{ f_0 + \delta f, \; H_0 + H_1 \right\} = 0$$

l.o.

$$\partial_t f_0 + \left\{ f_0, H_0 \right\} = 0$$

i.e. Base state is Hamiltonian $\rightarrow$ Liouville Theorem

Ψ.

$O(1)$:

$$\partial_t \delta f + \{f_1, H_0\} = -\{f_0, H_1\}$$

$$\cancel{-\{f_1, H_1\}} \;\; \text{h.o.}$$

So

$$\partial_t \delta f + \underbrace{\mathcal{L}_0}_{\{\delta f,\, H_0\}} \delta f = -\{f_0, H_1\}$$

$\rightarrow$ Liouville operator (unperturbed)

$\mathcal{L}_0$ vs $\mathcal{L}$!

meaning ! timescale

so

$$\boxed{\delta f = e^{-(t-t_0)\mathcal{L}_0}\delta f(t_0) - \int_{t_0}^{t} d\tau\, e^{-(t-\tau)\mathcal{L}_0}\{f_0, H_1(\tau)\}}$$

So, expanding the P.B.:

no f dep.

$$f = f_0 - \int_{t_0}^{t} d\tau\, e^{-(t-\tau)\mathcal{L}_0} \sum_i \left\{ \frac{\partial f_0}{\partial x_i} \cdot \cancel{\frac{\partial H_1}{\partial p_i}} - \frac{\partial f_0}{\partial p_i} \cdot \frac{\partial H_1}{\partial x_i} \right\}$$

$$= f_0 + \int_0^{t} d\tau\, e^{-(t-\tau)\mathcal{L}_0} \left[\sum_i q_i \underline{E}(\tau) \cdot \frac{\underline{p}_i}{m} f_0 \right] \beta$$

$$\boxed{f = f_0 + \int_0^{t} d\tau\, e^{-(t-\tau)\mathcal{L}_0} f_0\, \beta\, \underbrace{\underline{J}}_{\text{current}} \cdot \underline{E}(\tau)}$$

is linear response

current

$$\sum_i q_i \frac{\underline{p}_i}{m}$$

Now, what is $e^{-(t-\tau)\mathcal{L}_0}$?

→ $\mathcal{L}_0$ simply pushes the particles in (d-o-f) time.

⇒ advances along orbits (unperturbed)

i.e. if A time independent

$$A = A(p_i, x_i)$$

$$\frac{dA}{dt} = \sum_i \left[\frac{dx_i}{dt} \cdot \frac{\partial A}{\partial x_i} + \frac{dp_i}{dt} \cdot \frac{\partial A}{\partial p_i} \right]$$

$$= \sum_i \left[\frac{p_i}{m} \cdot \frac{\partial A}{\partial x_i} + \dot{p}_i \cdot \frac{\partial A}{\partial p_i} \right] = \mathcal{L} A$$

so

$$A(\Gamma(t)) = e^{t\mathcal{L}} A(\Gamma) \qquad \left(\text{i.e. } \frac{d}{dt} \text{ this}\right)$$

orbit propagator

Then:

$$f = f_0 + \int_0^t d\tau \; f_0(t-\tau)\, \beta \, \underline{J}(t-\tau) \cdot \underline{E}(\tau)$$

$$\boxed{f = f_0 + \int_0^t d\tau \; f_0(-(t-\tau))\, \beta\, \underline{J}(-(t-\tau)) \cdot \underline{E}(\tau)}$$

Now: – $H_0[\Gamma]$ const. $\quad$ $\Gamma \equiv$ phase space variables.

so – f_0 const $\left(\sim \frac{\exp\left[-\beta H_0\right]}{Z}\right)$

$\Rightarrow$

$$\boxed{f = f_0(\Gamma)\left[1 + \beta\int_{t_0}^{t} d\tau\ \underline{E}(\tau)\cdot \underline{J}(-(t-\tau))\right]}$$

δf

Since seek conductivity σ, ensemble average:
↳ phase space

$$\langle \underline{J}(t)\rangle = \int d\Gamma\ \underbrace{\underline{J}(\Gamma)}_{\sum_i q v_i} f(\Gamma, t)$$

so

$$\langle \underline{J}(t)\rangle = \int d\Gamma\ \underline{J}(\Gamma)\left[f_0 + \delta f\right]$$

$$\langle \underline{J}(t)\rangle = \int d\Gamma\, \underline{J}(\Gamma) f_0 \left\{ \overset{①}{1} \cdot \right. \left. + \beta \int_{t_0}^{t} d\tau\, \overset{②}{e^{-(t-\tau)\mathcal{L}}} \left[\underline{J}(\Gamma)\cdot \underline{E}(\tau) \right] \right\}$$

$$e^{\mathcal{L}t} f_0 = f$$

$① \to 0$, w/o $\underline{E}$ (no $\underline{E}$, no current)

$$\langle \underline{J}(t)\rangle = \int d\Gamma\, \underline{J}(\Gamma) f_0\, \beta \int_{t_0}^{t} d\tau\, e^{-(t-\tau)\mathcal{L}}\, \underline{J}(\Gamma)\cdot \underline{E}(\tau)$$

$$\int_{t_0}^{t} d\tau \to \int_0^{t-t_0} d\tau' , \quad \tau \to \tau' = t-\tau$$

so changing variables

$$\langle \underline{J}(t)\rangle = \beta \int d\Gamma\, f_0\, \underline{J}(\Gamma) \int_0^{t-t_0} d\tau'\, e^{-\tau'\mathcal{L}} \left[\underline{E}(t-\tau')\cdot \underline{J}(\Gamma) \right]$$

and re-write:

$$\langle \underline{J}(t) \rangle = \beta \int d\Gamma\, f_0\, \underline{J}(\Gamma) \int_0^{t-t_0} d\tau'\, e^{-\tau' \mathcal{L}_0} \left[\underline{E}(t-\tau') \cdot \underline{J}(\Gamma) \right]$$

$$= \beta \int d\Gamma\, f_0 \int_0^{t-t_0} d\tau' \left(\underline{J}(\Gamma)\, e^{-\tau' \mathcal{L}_0}\, \underline{E}(t-\tau') \cdot \underline{J}(\Gamma) \right)$$

$$= \beta \int_0^{t-t_0} d\tau' \int d\Gamma\, f_0 \left(\underline{J}(\Gamma)\, \underline{J}(\Gamma(-\tau')) \right) \underline{E}(t-\tau')$$

<u>but</u>

$$\boxed{\int d\Gamma\, f_0 \left(\underline{J}(\Gamma)\, \underline{J}(\Gamma(-\tau')) \right) = \langle \underline{J}(\Gamma)\, \underline{J}\, (\Gamma(-\tau')) \rangle}$$

(brackets)

→ Note this is <u>equilibrium</u> fluctuation correlation function.

→ computed with f_0, $e^{\mathcal{L}t}$ etc.

<u>so</u>

$$\boxed{\langle \underline{J}(t) \rangle = \beta \int_0^{t-t_0} d\tau' \, \langle \underline{J}(\Gamma)\, \underline{J}\, (\Gamma(-\tau')) \rangle \cdot \underline{E}(t-\tau')}$$

→ gives current (mean), in terms
in terms equilibrium correlation
fctn.

Now;

$$\underline{E}(t) = \underline{E}_0 e^{-i\omega t}$$

$$\langle \underline{J}(t) \rangle = \beta \int_0^{t-t_0} d\tau' \, e^{i\omega\tau'} \langle \underline{J}(0)\, \underline{J}(\Gamma, -\tau') \rangle \underline{E}_0 e^{-i\omega t}$$

$t_0 = 0$

$t \to \infty$

$$\underset{\substack{\text{electrical}\\ \text{current}\\ \text{density}}}{\underline{J}_e} = \frac{\langle \underline{J}(t) \rangle}{V} = \underline{\underline{\sigma}}(\omega) \cdot \underline{E}(t)$$

where:

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

→ Kubo / Green-Kubo Formula.

→ Conductivity ~ F.T. of current correlation Fctn.

→ $\underline{\sigma}(\omega)$ reflects system history.

→ relates transport coefficient to linear response.

→ fundamental → at level of Liouville's Thm / Eqn.

→ generalizable

Transport coeff ⟺ Correlation of Flux.

A bit more:

$$\langle \underline{J}(\Gamma)\, \underline{J}(\Gamma(t))\rangle = \frac{1}{Z}\int d\Gamma\, e^{-\beta H_0} \sum_{i,j} q_i\, q_j\, v_i(0)\, v_j(t)$$

Now, from structure $\mathcal{L}$,

$$\left.\begin{array}{l} \underline{v} \rightarrow -\underline{v} \\ t \rightarrow -t \end{array}\right\} \text{ leaves } e^{t\mathcal{L}} \text{ invariant.}$$

as $\underline{v} \to -\underline{v}$ symmetric

$$\langle \underline{J}(\Gamma)\, \underline{J}(\Gamma(t)) \rangle = \langle J(\Gamma)\, J(\Gamma(-t)) \rangle$$

Comments:

→ f_0 ? → un-perturbed Liouville

→ $\int e^{t\mathcal{L}}$ → τ_c ? what is correlation time ? How calculate ?

→ What makes it irreversible ?

Where does entropy production enter ? → $\mathcal{L}_0$.

→ General, But formal

→ Can extend to QM case. (coming).

→ Diffusion via Kubo Formalism.

Recall: $D = \int_0^\infty d\tau \, \langle \tilde{v}(0)\, \tilde{v}(\tau) \rangle$

$$\frac{d}{dt} \langle x^2 \rangle = 2D$$

How show?

Now,

- consider a tagged test particle in equilibrium with a fluid of like particles.

- seek follow 'tagged' particle at $\underline{r}_1$

so

$$f(\Gamma, t=0) = \underbrace{\frac{V}{Z}}_{\text{norm}} \, \underbrace{e^{-\beta H_N}}_{\text{backgnd.}} \, W(\underline{r}_1)$$

↳ weight.

$$Z = \int d\Gamma \, e^{-\beta H_N} \quad , \quad \int d\underline{r}_1 \, W(\underline{r}_1) = 1$$

as $(\partial_t + \mathcal{L}) f = 0$

$$f(\Gamma, t) = e^{-t\mathcal{L}} f(\Gamma, t=0)$$

$$= \frac{V}{Z} e^{-t\mathcal{L}} e^{-\beta H_N} w(\underline{r}_1)$$

$w(\underline{r}_1) \to w$ no preferred prob. for $\underline{r}_1$

$$f(\Gamma, t) \equiv \frac{V}{Z} w e^{-t\mathcal{L}} e^{-\beta H_N}$$

Seek: $\rho(\underline{r}, t)$ = prob. tagged particle at $\underline{r}$, at t.

Clearly,

$$\partial_t \rho = D \nabla^2 \rho$$

but need show.

so

$$\rho(\underline{r}, t) = \int d\Gamma\, f(\Gamma, t)\, \delta(\underline{r} - \underline{r}_1)$$

$$\rho(\underline{r}, t) = \int d\Gamma\, \frac{V}{Z}\, e^{-t\mathcal{L}} e^{-\beta H_N} w\, \delta(\underline{r}_1 - \underline{r})$$

$$= \frac{V}{Z} \int d\Gamma\, e^{-\beta H_N} w\, \delta(\underline{r}_1(t) - \underline{r})$$

Using Liouville thm:

$$e^{-t\mathcal{L}} e^{-\beta H_N} = e^{-\beta H_N}$$

equilibrium unchanged by test particle. (Recall $N-1$ vs N ...)

$$\rho(\underline{r}, t) = \frac{V}{Z} \int d\Gamma\, e^{-\beta H_N} w\, \delta(\underline{r}_1(t) - \underline{r})$$

so Fourier analyzing:

$$\rho(\underline{r}, t) = \frac{1}{V} \sum_{\underline{k}} e^{i\underline{k}\cdot\underline{r}} \rho_{\underline{k}}(t)$$

$$\Rightarrow \boxed{\rho_{\underline{k}}(t) = \frac{V}{Z} \int d\Gamma\, e^{-\beta H_N} w\, e^{-i\underline{k}\cdot\underline{r}_1(t)}}$$

re-writing:

$$P_{\underline{k}}(t) = \frac{V}{Z}\int d\Gamma\, e^{-i\underline{k}\cdot\underline{r}_1}\, w(\underline{r}_1)\, e^{-i\underline{k}\cdot[\underline{r}_1(t)-\underline{r}_1]}$$

Now: $w \to$ const / nothing special about $\underline{r}_1$

$$P_{\underline{k}}(t) = \frac{V}{Z}\int d\Gamma\, e^{-i\underline{k}\cdot\underline{r}_1}\, w\, e^{-\beta H_N}\, e^{-i\underline{k}\cdot\Delta\underline{r}_1}$$

$$\Delta\underline{r}_1 = \underline{r}_1(t) - \underline{r}_1$$

$$\boxed{\begin{aligned} P_k(t) &= V\underbrace{\left[w e^{-i\underline{k}\cdot\underline{r}_1}\right]}_{w(\underline{k})}\ \underbrace{F(\underline{k},t)}_{\text{orbit scattering function}} \\ F &= \frac{1}{Z}\int d\Gamma\, e^{-\beta H_N}\, e^{-i\underline{k}\cdot\Delta\underline{r}_1} \end{aligned}}$$

or $\quad F = \langle e^{ik\cdot\Delta\underline{r}_1(t)}\rangle \quad$ ensemble avg. over equilibrium.

Now, a cumulant expansion: (as previous)

$$F = \langle e^{i\underline{k}\cdot\Delta\underline{r}_i(t)} \rangle$$

$$\cong \langle 1 - \cancel{i\underline{k}\cdot\Delta\underline{r}_i(t)} - \frac{(\underline{k}\cdot\Delta\underline{r}_i)^2}{2} + \dots \rangle$$

no drift
ensemble avg
$\to 0$

$$\cong 1 - \frac{k^2}{2}\langle(\hat{k}\cdot\Delta\underline{r}_i)^2\rangle$$

$$\boxed{F \cong \exp\left[-\frac{k^2}{2}\langle(\hat{k}\cdot\Delta\underline{r}_i(t))^2\rangle\right]}$$

for simplicity, k in x direction,

$$F(\underline{k}, t) = \exp\left[-\frac{k^2}{2}\langle\Delta r_{jx}(t)\rangle^2\right].$$

So

$$\rho = \frac{1}{V} \sum_{\underline{k}} w_{\underline{k}} \, F(\underline{k},t) \, e^{i\underline{k}\cdot\underline{r}} \qquad \text{(inversion)}$$

$$\frac{\partial \rho}{\partial t} = -\langle \Delta \underline{r}_{1,x} \Delta \dot{r}_{1,x} \rangle \frac{1}{V} \sum_{\underline{k}} k^2 w_{\underline{k}} F(\underline{k},t) \, e^{i\underline{k}\cdot\underline{r}}$$

$$= \langle \Delta \underline{r}_{1,x} \Delta \dot{\underline{r}}_{1,x} \rangle \nabla^2 \rho$$

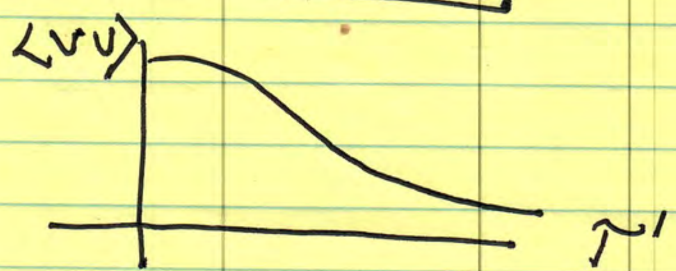
So

$$\boxed{\begin{aligned} \frac{\partial \rho}{\partial t} &= D(t) \nabla^2 \rho \\ D(t) &= \langle \Delta r_1 \Delta \dot{r}_1 \rangle \\ &= \langle v_x \Delta r_{1x} \rangle \end{aligned}}$$

$$\boxed{\begin{aligned} D(t) &= \int_0^t \langle v_x(t) \, v_x(\tau) \rangle \, d\tau \\ &= \int_0^t \langle v_{x,1}(t) \, v_{x,1}(\tau) \rangle \, d\tau \end{aligned}}$$

$$\boxed{\begin{aligned} D(t) &= \int_0^t \langle v_{i,x}(0)\, v_{i,x}(\tau - t) \rangle \, d\tau \\ &= \int_0^t \langle v(0)\, v(\tau') \rangle \, d\tau' \end{aligned}}$$

if $t \gg \underbrace{T_{ac}}_{\text{micro}}$



$$\boxed{D(t) \to D = \int_0^\infty d\tau \, \langle v(0)\, v(\tau) \rangle}$$

and,

$$\frac{d}{dt} \langle \Delta r(t)^2 \rangle = \frac{d}{dt} \int_0^t dt_1 \int_0^t dt_2 \, \langle v(t_1)\, v(t_2) \rangle$$

$$= 2 \int_0^t \langle v(0)\, v(\tau) \rangle \, d\tau$$

$$= 2 D(t)$$

$t \gg \tau_{ac}$

$$\boxed{\begin{aligned} \frac{d}{dt}\langle \Delta r^2 \rangle &= 2D \\ \langle \Delta r^2 \rangle &= 2Dt \end{aligned}}$$

- diffusion const characterizes random walk.

- Note:

→ autocorrelation time τ_{ac}
(scattering field)

→ decorrelation / scattering time for mode k

$$e^{-k^2\langle\Delta r^2\rangle} \to e^{-k^2 D t}$$

$$\tau_c = (k^2 D)^{-1}$$

(time to scatter)

mode k

obviously $\tau_{ac} \ll \tau_c$.

Next: Generalization!