Notes 2

Notes 2: Linear Response Theory
Green-Kubo Formalism
Section 1: Kubo Formula for Conductivity
Now Diffusion

- so far: Boltzmann Eqn. and H-Thm, Chapman-Enskog Expansion, Onsager Symmetry

Key calculation - Chapman-Enskog Theory

→ effectively linear response of f to thermodynamic forces

i.e. $\delta f = [\;] \cdot \nabla T$, etc.

→ now aim to study (generally) response to external perturbing field ⇒ how does f evolve?

→ how relate:

- δf response
- transport coefficient ?
- correlation function

i.e. classic:

~ consider a slowly varying, smooth electric field

then if $\rho(\Gamma, t)$ is Liouville Distribution

$$\delta\rho = \beta \int_{t_0}^{t} d\tau \; \underline{j}[-(t-\tau)] \cdot \underline{E}(\tau)\, \rho_0[-(t-\tau)]$$

i.e. linear response

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

conductivity

current correlation.

essence of Kubo formula:

transport coefficient:

= F.T. of correlation fctn.

i.e. $\omega \to 0$

$$\underline{\underline{\sigma}} = \frac{\beta}{V} \int_0^\infty d\tau \, \langle \underline{J}(0) \, \underline{J}(t) \rangle$$

Related:

$$D = \int_0^\infty d\tau \, \langle v(0) \, v(\tau) \rangle$$

$\downarrow$

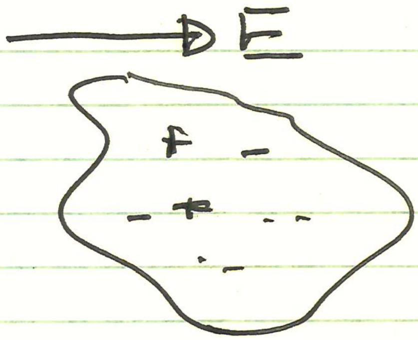
diffusion coefficient

i.e. $\Gamma = -D \nabla n$

$\to$ Leads to set of relations between
- response
- correlation
- transport
- susceptibility

→ Kubo Formulae – Conductivity (the Classic)

Consider:



→ system of charged particles (plasma)

→ $\underline{E}(t)$ applied

System described by:

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

Liouville Eqn. (Vlasov)

$$f = f_{eq} + \delta f$$

$$\delta f \sim \underline{E}$$

Obviously,

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

Poisson Bracket

$H = H_0 + H_1$ — Hamiltonian

$$H_0 = \sum_i \frac{p_i^2}{2m} + \underbrace{\sum_{\substack{ij \\ i<j}} \phi_{ij}}_{\text{Coulomb}}$$

$H_1 = \sum_i - z_i (\underline{r}_i \cdot E(t))$ — external field

$f = f_0 + f_1$

$f_0 = \frac{1}{Z} e^{-\beta H_0}$ (asserted → how?)

$$\partial_t (f_0 + f_1) + \{(f_0 + f_1), H_0 + H_1\} = 0$$

$$\cancel{\partial_t f_0} + \cancel{\{f_0, H_0\}} = 0$$

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

$$\partial_t f_1 + \mathcal{L} f_1 = -\{f_0, H_1\}$$

Liouville Opr.

$$\partial f_1 = \sum_i \frac{\partial f_1}{\partial x_i}\frac{\partial H_0}{\partial p_i} - \frac{\partial f_1}{\partial p_i}\frac{\partial H_0}{\partial x_i}$$

$$= \sum_i \frac{p_i}{m}\cdot\frac{\partial f_1}{\partial x_i} - \cancel{\frac{\partial H_0}{\partial x_i}\cdot\frac{\partial f_1}{\partial p_i}}$$

ok

$$\frac{\partial f_1}{\partial t} + \sum_i \frac{p_i}{m}\cdot\frac{\partial}{\partial x_i} f_1 = -\sum_i \left\{ \frac{\partial f_0}{\partial x_i}\cdot\frac{\partial H_1}{\partial p_i} - \frac{\partial f_0}{\partial p_i}\cdot\frac{\partial H_1}{\partial x_i} \right\}$$

$$\boxed{\partial_t f_1 + \mathcal{L} f_1 = -\{f_0, H_1\} = -\sum_i \frac{\partial f_0}{\partial x_i}\cdot\frac{\partial H_1}{\partial p_i}}$$

$$\mathcal{L} f_1 = \{f_1, H_0\}$$

$f_1(t_0) = 0$

so

$$f_1 = \cancel{e^{-(t-t_0)\mathcal{L}} f_1(t_0)} - \int_{t_0}^{t} e^{-(t-\tau)\mathcal{L}}\{f_0, H_1(\tau)\}\, d\tau$$

so

$$f = f_0 - \int_{t_0}^{t} d\tau\, e^{-(t-\tau)\mathcal{L}} \sum_i \left\{ \cancelto{0}{\frac{\partial f_0}{\partial \underline{x}_i} \cdot \frac{\partial H}{\partial \underline{p}_i}} - \frac{\partial H}{\partial \underline{x}_i} \cdot \frac{\partial}{\partial p_i} f_0 \right\}$$

$$= f_0 + \int_0^t d\tau\, e^{-(t-\tau)\mathcal{L}} \left[\sum_i Z_0 \underline{E}_i(\tau) \frac{\underline{p}_i}{m} f_0 \right] \beta$$

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

<u>Linear response</u>

(i.e. Linearized Vlasov)

N.B.: What is $e^{-(t-\tau)\mathcal{L}}$?

Now, can simplify:

$$A(\Gamma(t)) = e^{t\mathcal{L}} A(\Gamma)$$

$\mathcal{L}$ simply pushes particles / dep. on time. — time advancement operator.

ie A time-indep.

$$\frac{dA}{dt} = \mathcal{L} A = \sum_i \frac{\underline{p}_i}{m} \cdot \frac{\partial A}{\partial \underline{x}_i} + \sum_i \underline{F}_i \cdot \frac{\partial A}{\partial \underline{p}_i}$$

So

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

$H_0[\Gamma]$ const $\Rightarrow$ $f_0(\Gamma)$ const

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

Now see transport coefficient $\to \sigma$

so:

ensemble avg. (phase space density)

$$\langle \underline{J}(t) \rangle = \int d\Gamma\, \underline{J}(\Gamma)\, f(\Gamma, t)$$

ensemble avg. current

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

$$\int d\Gamma\, \underline{J}(\Gamma)\ \text{[redacted]}\ f_0 \left\{ 1 + \beta \int_{t_0}^{t} d\tau\, e^{-(t-\tau)L} \left[\underline{J}(\Gamma) \cdot \underline{E}(\tau) \right] \right\}$$

① ②

$$e^{iLt} f_0 = f_0 \quad \checkmark$$

① $\to 0 \Rightarrow$ no current without $\underline{E}$.

so

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

$$\int_{t_0}^{t} d\tau \rightarrow \int_{0}^{t-t_0} d\tau' \qquad \tau \to \tau' = t - \tau.$$

change variables

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

$\Rightarrow$

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

and re-write:

$$\boxed{\langle \underline{J}(t)\rangle = \beta \int_0^{t-t_0} d\tau\, \langle \underline{J}(\Gamma)\, \underline{J}(\Gamma(-\tau))\rangle \cdot \underline{E}(t-\tau)}$$

→ current.

$$\langle F\rangle \equiv \int d\Gamma\, f_0 F$$

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

$$\langle \underline{J}(t)\rangle = \beta \int_0^{t-t_0} d\tau\, e^{i\omega\tau} \langle \underline{J}(\Gamma)\, \underline{J}(\Gamma,-\tau)\rangle \cdot \underline{E}_0\, e^{-i\omega t}$$

$t_0 = 0$

$t \to \infty$

$$\underline{J}_e = \underline{\underline{\sigma}}(\omega)\cdot \underline{E}(t) = \frac{\langle J(t)\rangle}{V}$$

$$\underline{J}_e = \underline{\underline{\sigma}}(\omega) \cdot \underline{E}(t)$$

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

- Kubo / Green-Kubo Formula
- conductivity ~ F.T. of current correlation fctn.
- $\underline{\underline{\sigma}}(\omega)$ reflects system history
- relates transport coeff to linear response.
- similar, in philosophy, to Chapman - Enskog expansion
- generalizable!

- Buried bodies:

f_0 ?

$\int e^{t\delta} \rightarrow T_c$?

related

Origin of irreversibility.

$\Rightarrow$ QL

→ Diffusion via Kubo Formalism

μ, T $\tilde{f}$ random force

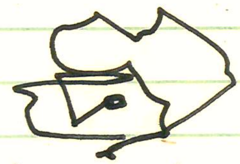
i.e. • test particle / Brownian

$$m\frac{d\underline{v}}{dt} = -\underbrace{\mu \underline{v}}_{\text{Stokes Drag}} + \tilde{\underline{f}}$$

$t \gg \mu^{-1}$

$$\Rightarrow \quad \frac{d\underline{x}}{dt} = \frac{\tilde{\underline{f}}}{\mu}$$

$$\delta \underline{x} = \int dt \, \frac{\tilde{f}}{\mu}$$



particle diffuses

$$\langle \delta x^2 \rangle = \frac{\langle \tilde{f}^2 \rangle}{\mu^2} \tau_{ac} t \rightarrow \frac{T}{\mu} t$$

$$\langle \delta \underline{x}^2 \rangle \sim D t$$

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

how show?

Now, consider a tagged test particle in equilibrium with a fluid of like particles. Seek follow tagged particle at $\underline{r}_1$

$\frac{d\eta}{V}$ norm backgnd

$$f(\Gamma, t=0) = \frac{V}{Z} e^{-\beta H_0} w(\underline{r}_i)$$

$$Z \equiv \int d\Gamma\, e^{-\beta H_0}$$

$$\int d\eta\, w(\underline{r}_i) = 1$$

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

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

$$\equiv \frac{V}{Z} e^{-t\mathcal{L}} e^{-\beta H_0} w(\underline{r}_i)$$

orbit propagator.

$w(\underline{r}_i) \to w.$ No pref. prob. r_i

$$f(\Gamma, t) = \frac{V}{Z} w\, e^{-t\mathcal{L}} e^{-\beta H_0}.$$

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

clearly,

$$\frac{\partial\rho}{\partial t} = D\nabla^2\rho \quad , \quad \rightarrow \text{need show.}$$

ρ satisfies diffn.

$$\rho(\underset{\sim}{r},t) = \int d\Gamma\, f(\Gamma,t)\, \delta(\underset{\sim}{r_1} - \underset{\sim}{r})$$

$$= \frac{V}{Z}\int d\Gamma\, e^{-t\mathcal{L}} e^{-\beta H_0}\, W\, \delta(\underset{\sim}{r_1} - \underset{\sim}{r})$$

$$= \frac{V}{Z}\int d\Gamma\, e^{-\beta H_0}\, W\, \delta(\underset{\sim}{r_1}(t) - \underset{\sim}{r})$$

Now, using Liouville Thm

$$e^{-t\mathcal{L}} e^{-\beta H_0} = e^{-\beta H_0}$$

eq'bm unchanged
test particle

$$\boxed{\rho(\underset{\sim}{r},t) = \frac{V}{Z}\int d\Gamma\, e^{-\beta H_0}\, W \delta(\underset{\sim}{r_1}(t) - r)}$$

Fourier analyzing,

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

$\Rightarrow$

$$\rho_{\underset{\sim}{k}}(t) = \frac{V}{Z}\int d\Gamma\, e^{-\beta H_0}\, W e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r_1}(t)}$$

re-write:

$$P_k(t) = \frac{V}{Z}\int d\Gamma\, e^{-ik\cdot r_1}\, w(r_1)\, e^{-\beta H_N}\, e^{-ik\cdot[r_1(t) - r_1]}$$

Further, $\begin{cases} w(r_1) \to \text{const. } W \\ \text{Nothing special about } r_1 \end{cases}$

$$P_k(t) = \frac{V}{Z}\int d\Gamma\, e^{-ik\cdot r_1}\, W e^{-\beta H_N}\, e^{-ik\cdot(r_1(t) - r_1)}$$

$$= \overbrace{V W e^{-ik\cdot r_1}}^{W_k}\, F(k,t) \equiv W_k F(k,t)$$

$$\boxed{F = \frac{1}{Z}\int d\Gamma\, e^{-\beta H_N}\, e^{-ik\cdot\Delta r_1}}$$

order scattering fctn.

$$F \underset{\text{small}}{\approx} \left\langle e^{ik\cdot\Delta r_1(t)} \right\rangle$$

($\langle\ \rangle \to$ ensemble)

$$\cong \left\langle 1 - \underbrace{\cancel{ik\cdot\Delta r_1(t)}}_{\text{odd, ensemble avg.}} - \frac{(k\cdot\Delta r_1)^2}{2} + \cdots \right\rangle$$

cumulant expansion.

$$\cong 1 - \frac{k^2}{2}\left\langle (\hat{k}\cdot\Delta r_1)^2 \right\rangle$$

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

x - direction

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

so

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

so

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

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

$$\boxed{\frac{\partial\rho}{\partial t} = D(t)\, \nabla^2\rho}$$

$$\Delta r = \int_0^t v$$

$$D(t) = \langle \Delta\dot{r}_{i,x}\, \Delta r_{i,x}\rangle$$

$$= \int_0^t \langle v_{i,x}(t)\, v_{i,x}(\tau)\rangle\, d\tau$$

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

x direction:

$$\boxed{F(k,t) \cong \exp\left[-\frac{k^2}{2}\langle(\Delta r_{i,x}(t))^2\rangle\right]}$$

so

$$\rho = V^{-1}\sum_{k} W_k F(k,t)\, e^{+ik\cdot r}$$

[inv-do trans.

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

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

$$\boxed{\frac{\partial\rho}{\partial t} \equiv D(t)\,\nabla^2\rho}$$

$$D(t) = \langle\Delta r_1\Delta\dot{r}_1\rangle$$

$$= \langle v_x\,\Delta r_{1x}\rangle$$

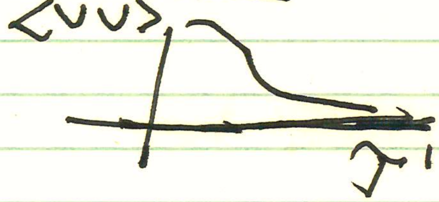
$$= \int_0^t \langle v_x(t)\,v_x(t)\rangle\, dt$$

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

if $t \gg \tau_c$

$\downarrow$

microscopic



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

and note:

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

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

$$= 2D(t)$$

$t \gg \tau_c$

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

$$\boxed{\langle \Delta r^2 \rangle = 2Dt}$$

Diffn "const" characterizes random walk.