Linear response theory (LRT):

- generally concerned w/ response of a system to small perturbations

example: Ohm's Law

$$\vec{J} = \sigma \vec{E}$$

response (current)

transport coefficient

external perturbation / applied force

Notice that the response ($\vec{J}$) is linear in the perturbation ($\vec{E}$).

A central idea of LRT is that the transport coefficient is determined by the fluctuations of the system <u>in equilibrium</u>.

This idea traces back to Onsager's Regression Hypothesis (1931), & even earlier in a few specific cases (Einstein-Smoluchowski relation; Johnson-Nyquist noise, 1920's)

The fullest expression of this idea is given by the Fluctuation-Dissipation Theorem — really a collection of results

Callen & Welton, Green, Kubo & others

(1950's, 60's)

My aim here is to give a brief summary of LRT.

Lars Onsager,

"Reciprocal relations in irreversible processes"

I. Phys. Rev. 37, 405 (1931)

II. Phys. Rev. 38, 2265 (1931)

→ Nobel Prize (Chem., 1968)

regression hypothesis:

"... we shall assume that the average regression of fluctuations will obey the same laws as the corresponding macroscopic irreversible processes." (II, 1st page)

~ decay of correlations in equilibrium determines the relaxation of small perturbations away from equilibrium.

derive & illustrate Regr'n. Hyp. for overdamped Brownian particle.

$$\dot{x} = -\frac{1}{\gamma}\frac{\partial V_0(x)}{\partial x} + \tilde{v}(t) \qquad \langle \tilde{v}_0 \tilde{v}_t \rangle = 2D\,\delta(t)$$

$$1/\gamma = \beta D$$

assume $\langle x \rangle_0^{eq} = 0$

Setup: $V(x,t) = \begin{cases} V_0(x) - \epsilon x, & t \leq 0 \\ V_0(x), & t > 0 \end{cases}$

$$\therefore \quad f(x,0) = \frac{1}{Z_\epsilon} e^{-\beta V_0(x) + \beta \epsilon x}$$

$$t>0: \quad f(x,t) = \int dx'\, K(x,t|x',0)\, f(x',0)$$

Evaluate $\langle x \rangle_t \equiv \int dx\, x\, f(x,t)$ to $O(\epsilon)$

$$Z_\epsilon \simeq \int dx\, e^{-\beta V_0(x)}(1 + \beta \epsilon x)$$

$$= Z_0 \left(1 + \beta \epsilon \langle x \rangle_0^{eq}\right) = Z_0$$

$$\pi(x) \equiv \frac{1}{Z_0} e^{-\beta V_0(x)}$$

$$\langle x\rangle_t = \int dx \int dx' \left[K(x,t|x',0)\ \frac{1}{Z_\epsilon}\, e^{-\beta V_0 + \beta\epsilon x'} \right] x$$

$$\simeq \int dx \int dx' \left[K(x,t|x',0)\ (1+\beta\epsilon x')\ \pi(x') \right] x$$

$$= \int dx\ x \overbrace{\int dx'\ K(x,t|x',0)\,\pi(x')}^{\pi(x)} \longleftarrow 0$$

$$+\ \beta\epsilon \int dx \int dx'\ x\ K(x,t|x',0)\ x'\,\pi(x')$$

$$= \beta\epsilon\, \langle x_0\, x_t\rangle^{eq} = \beta\epsilon\, C_x(t)$$

Note: $\langle x\rangle_0 = \beta\epsilon \langle x^2\rangle^{eq} = \beta\epsilon\, C_x(0)$

$$\boxed{\frac{\langle x\rangle_t}{\langle x\rangle_0} = \frac{C_x(t)}{C_x(0)}}$$

regression hypothesis

"macroscopic"
relaxation
to equilibrium

microscopic
fluctuations
in equilibrium

derived here for a specific model,
but in fact quite general.

Fluctuation-Dissipation Theorem (FDT) in terms of response functions.

Setup: • start in equil ($t<0$)

• perturb, $\alpha(t) A(x)$ $(t \geq 0)$

• observe $\langle B \rangle_{t>0}$, $B = B(x,p)$

Brownian particle w/ inertia

$$\mathcal{H}_0(x,p) \quad , \quad \pi = \frac{1}{Z_0} e^{-\beta \mathcal{H}_0}$$

$$A(x) \quad , \quad B(x,p)$$

assume $\langle B \rangle_{eq} = 0$

$$\mathcal{H}(x,p,t>0) = \mathcal{H}_0(x,p) - \epsilon\,\alpha(t)\, A(x)$$

↑ formal "smallness parameter"

$f(x,p,t)$:

$$\frac{\partial f}{\partial t} = \{\mathcal{H}_0, f\} + D_p \frac{\partial}{\partial p}\left[\pi \frac{\partial}{\partial p} \frac{f}{\pi}\right] - \epsilon\,\alpha(t)\{A, f\}$$

$$= \hat{\mathcal{L}}_0 f - \epsilon\,\alpha(t)\{A, f\}$$

expand: $f = f_0 + \epsilon f_1 + \cdots$

ϵ^0 : $\dfrac{\partial f_0}{\partial t} = \hat{\mathcal{L}}_0 f_0 \implies f_0(x,p,t) = \pi(x,p)$

$$\epsilon^1: \quad \frac{\partial f_1}{\partial t} = \hat{\mathcal{L}}_0 f_1 - \alpha(t)\{A, f_0\}$$

$$= \hat{\mathcal{L}}_0 f_1 - \alpha(t)\ \{A(x), \pi(x,p)\}$$

$$= \hat{\mathcal{L}}_0 f_1 - \alpha(t)\ \frac{\partial A}{\partial x}\frac{\partial \pi}{\partial p} \qquad \pi \propto e^{-\beta\left[\frac{p^2}{2m} + V_0(x)\right]}$$

$$= \hat{\mathcal{L}}_0 f_1 + \alpha(t)\ \beta\, \underbrace{\frac{\partial A}{\partial x}\frac{p}{m}}\, \pi$$

$$\frac{\partial A}{\partial x}(x)\cdot\frac{p}{m} = \frac{\partial A}{\partial x}\cdot\frac{dx}{dt} \equiv \dot{A}(x,p)$$

So: $$\frac{\partial f_1}{\partial t} - \hat{\mathcal{L}}_0 f_1 = \alpha(t)\ \beta\ \dot{A}(x,p)\,\pi(x,p)$$

This is a 1st-order inhomogeneous diff. eqn, whose solution is:

$$f_1(x,p,t) = \int_0^t ds\, \alpha(s)\, \beta\, e^{(t-s)\hat{\mathcal{L}}_0}\, \dot{A}(x,p)\,\pi(x,p)$$

$$= \int_0^t ds\, \alpha(s)\, \beta \int dx' \int dp'\ K_0(x,p,t-s\,|\,x',p',0)\, \dot{A}(x',p')\,\pi(x',p')$$

$$\langle B\rangle_t = \int dx \int dp\ B(x,p)\, f(x,t)$$

$\leftarrow \pi + \epsilon f_1$

$$= \epsilon \int dx \int dp\ B(x,p)\, f_1(x,t) \qquad \langle B\rangle_{eq} = 0$$

$$= \epsilon \int_0^t ds\, \alpha(s)\, \beta \int d\Gamma \int d\Gamma'\, B(\Gamma)\, K(\Gamma, t-s\,|\,\Gamma', 0)\,\dot{A}(\Gamma')\,\pi(\Gamma')$$

$\Gamma = (x,p)$, etc.

$$= \epsilon \int_0^t ds\, \alpha(s)\, \beta\, \langle \dot{A}(\Gamma_0)\, B(\Gamma_{t-s})\rangle$$

$$\langle B \rangle_t = \epsilon \int_0^t ds\, \alpha(s)\, \beta \langle \dot{A}(\Gamma_0) B(\Gamma_{t-s}) \rangle$$

$$\equiv \epsilon \int_0^t ds\, \alpha(s)\, R_{AB}(t-s)$$

$$\boxed{R_{AB}(t) = \beta \langle \dot{A}_0 B_t \rangle}$$

response function

response of observable B
to perturbation A, after time t

Now consider many particles:

$$\Gamma = (\vec{r}_1, \cdots, \vec{r}_N ; \vec{p}_1, \cdots, \vec{p}_N)$$

N particles in box, volume V.

$$\mathcal{H}_0(\Gamma) = \sum_i \frac{p_i^2}{2m_i} + \sum_{i<j} \phi_{ij}$$ ← pairwise interactions

$$\mathcal{H}(\Gamma, t) = \mathcal{H}_0(\Gamma) - \sum_i q_i \vec{E}(t) \cdot \vec{r}_i$$

$$\begin{cases} \epsilon \vec{\alpha}(t) = \vec{E}(t) \\ \vec{A} = \sum_i q_i \vec{r}_i \end{cases}$$

$$f = f_0 + \epsilon f_1$$

$$f_0 = \pi = \frac{1}{Z_0} e^{-\beta \mathcal{H}_0}$$

$$f_1 = \beta \int_0^t ds\, \vec{E}(s) \cdot e^{(t-s)\hat{\mathcal{L}}_0} \vec{A}(\Gamma)\, \pi(\Gamma)$$

$$\dot{\vec{A}} = \sum_i q_i \vec{v}_i \equiv \vec{J}$$, total electric current

$$\langle \vec{J} \rangle_t = \int d\Gamma\, \vec{J}(\Gamma)(f_0 + f_1)$$

$$= \beta \int_0^t ds \int d\Gamma \int d\Gamma'\, \vec{J}(\Gamma)\, e^{(t-s)\hat{\mathcal{L}}_0} \vec{J}(\Gamma') \cdot \vec{E}(s)\, \pi(\Gamma')$$

$$= \beta \int_0^t ds\, \langle \vec{J}(\Gamma_t) \underbrace{\vec{J}(\Gamma_s) \rangle \cdot \vec{E}(s)}_{\text{dot product}}$$

Note: $\langle \vec{j}(\Gamma_t)\vec{j}(\Gamma_s)\rangle$ is a tensor:

$$\begin{pmatrix} \dot{j}_x \dot{j}_x & \dot{j}_x \dot{j}_y & \dot{j}_x \dot{j}_z \\ \dot{j}_y \dot{j}_x & \dot{j}_y \dot{j}_y & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix}$$

depends on $t-s \equiv \tau$

$$\langle \vec{j}\rangle_t = \beta \int_0^t d\tau \, \langle \vec{j}(\Gamma_\tau)\vec{j}(\Gamma_0)\rangle \cdot \vec{E}(t-\tau)$$

Let $\vec{E}(t) = \vec{E}_0 e^{i\omega t}$ ← real part

$$\langle \vec{j}\rangle_t = \underbrace{\beta \int_0^t d\tau \, e^{-i\omega\tau} \langle \vec{j}_\tau \vec{j}_0\rangle}_{} \cdot \underbrace{\vec{E}_0 e^{i\omega t}}_{\vec{E}(t)}$$

for $t\to\infty$ this is the F.T. of the auto-correl'n tensor

$$\langle \vec{j}\rangle \longrightarrow \beta \left[\int_0^\infty d\tau \, e^{-i\omega\tau} \langle \vec{j}_\tau \vec{j}_0\rangle\right] \cdot \vec{E}_0 e^{i\omega t}$$

current density $= \vec{J} = \vec{j}/V$

An oscillating field produces an oscillating current:

$$\vec{E}(t) = \vec{E}_0 e^{i\omega t} \Longrightarrow \vec{J}(t) = \vec{J}(\omega) e^{i\omega t}$$

$$\vec{J}(\omega) = \sigma(\omega)\vec{E}_0$$

electrical conductivity tensor

Combining results, we finally get: equil. flucts.

$$\boxed{\sigma(\omega) = \frac{\beta}{V} \int_0^\infty d\tau \; e^{-i\omega\tau} \langle \vec{J}_\tau \vec{J}_0 \rangle}$$

Green-Kubo formula for electrical conductivity

There are other examples of fluct.-dissip'n. results that give transport coeffs. in terms of equil. correl. fns.

(viscosity, thermal conductivity, frequency-dependent magnetic susceptibility, ...)

Brief Summary of Lin. Resp. Results

Onsager's regression hypothesis:

$$\frac{\langle x\rangle_t}{\langle x\rangle_0} = \frac{C_x(t)}{C_x(0)}$$

← μ-scopic fluct. in equil.

M-scopic relax'n to equil.

linear response fn: $\mathcal{H}_0 - \epsilon\,\alpha(t)\,A(x)$

$$\begin{cases} \langle B\rangle_t = \epsilon \int_0^t ds\ \alpha(s)\, R_{AB}(t-s) \\ R_{AB}(t) = \beta \langle \dot{A}_0 B_t\rangle^{eq.} \end{cases}$$

~~Kubo~~ Green – Kubo formula

$$\begin{cases} \vec{E}(t) = \vec{E}_0 e^{i\omega t} \implies \vec{J}(t) = \vec{J}_\omega e^{i\omega t} \\ \vec{J}_\omega = \sigma(\omega)\,\vec{E}_0 \\ \sigma(\omega) = \frac{\beta}{V}\int_0^\infty d\tau\, e^{-i\omega\tau}\langle \vec{j}_\tau \vec{j}_0\rangle \end{cases}$$

↑ tensor

(Note: if no magn. fields are present, then the tensor $\sigma(\omega)$ is symmetric. This is an example of the Onsager reciprocal relations.)

Intuition for G-K formula: analogy w/ tuning in to a radio station ...

In equil. the current $\vec{j}(t)$ fluctuates ~ random superposition of various freqs. By applying weak oscillatory external field $\vec{E}(t)$, we "tune in" to a particular frequency ... resonance.