A closer look at the fluctuation – dissipation theorem

unperturbed system H

$$\langle A \rangle = \int dr^N dp^N e^{-\beta H} A\left(r^N, p^N\right) / \int dr^N dp^N e^{-\beta H}$$

$$= Tr\left(e^{-\beta H} A\right) / Tr\left(e^{-\beta H}\right)$$

Now suppose at $t = 0$ system is not at equil.
assume system prepared by a field, f, that
couples to a variable, A

$$\Delta H = -fA$$

from $t = -\infty$ to 0, and then shut off the interaction

I.e., initial state is an equilibrium state with the field on.

$$F \propto e^{-\beta(H+\Delta H)}$$

$$\bar{A}(0) = Tr\left[e^{-\beta(H+\Delta H)} A\right] / \left[Tre^{-\beta(H+\Delta H)}\right] =$$ initial value of $\bar{A}(t)$

as time evolves $\overline{A}(t)$ changes as

$$\overline{A}(t) = Tr\left[e^{-\beta(H+\Delta H)}A(t)\right] / Tr\left[e^{-\beta(H+\Delta H)}\right]$$

$$\overline{A}(t) = Tr\left\{e^{-\beta H}\left(1-\beta\Delta H+\ldots\right)A(T)\right\} / Tre^{-\beta H}\left(1-\beta\Delta H+\ldots\right)$$

$$\overline{A}(t) = \langle A\rangle - \beta\left[\langle \Delta H A(t)\rangle - \langle A\rangle\langle \Delta H\rangle\right] + \vartheta\left(\left(\beta\Delta H\right)^2\right)$$

$$\Delta\overline{A}(t) = \beta f\left\langle \delta A(0)\delta A(t)\right\rangle$$

$$\Delta\overline{A}(0) = \beta f\left\langle \left(\delta A\right)^2\right\rangle$$

Response functions (generalized susceptibility)

$$\Delta\overline{A}(t) = \int_{-\infty}^{\infty} dt' \underbrace{\chi(t,t')} f(t') + \vartheta\left(f^2\right)$$

External perturbation *f(t)* couples to a variable *A*

χ is a property of equil. system

Write $A(t)$ as a Taylor series in $f(t')$

$$\sum_i \left[\frac{\partial \Delta \bar{A}(t)}{\partial f(t_i)} \right]_0 f(t_i)$$

sum over all points in time

↓ pass to continuous limit

$$\frac{\delta \Delta \bar{A}(t)}{\delta f(t')}$$

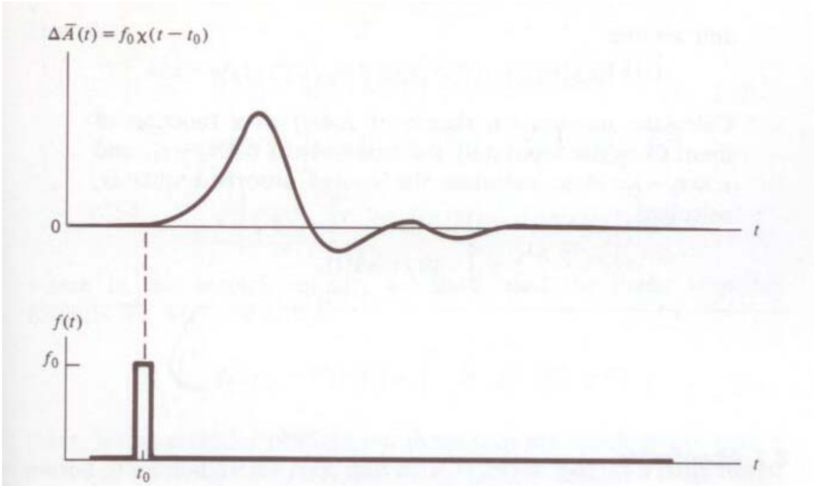
This is an example of a functional derivative

$\chi(t,t')$ rate of change of $\Delta \bar{A}(t)$ when system is perturbed at t'

$$\chi(t,t') = \chi(t-t')$$

$$\chi(t-t') = 0 \quad t-t' \le 0$$

causality



Consider

$$f(t) = \begin{cases} f & t < 0 \\ 0 & t \geq 0 \end{cases}$$

system prepared at equil. with *H - fA*

we have shown

$$\Delta \bar{A}(t) = \beta f \langle \delta A(0) \delta A(t) \rangle$$

$$\Delta\bar{A}(t) = f\int_{-\infty}^{0} dt'\chi(t-t')$$
$$= f\int_{t}^{\infty} d\tau\chi(\tau)$$

$$\tau = t - t'$$
$$d\tau = -dt'$$
$$t' = 0, \quad \tau = t$$
$$t' = \infty, \quad \tau = \infty$$

this implies that

$$\chi(t) = \begin{cases} -\beta\dfrac{d}{dt}\langle\delta A(0)\delta A(t)\rangle & t > 0 \\ 0 & t < 0 \end{cases}$$

Can show

$$abs(\omega) = \frac{\beta\omega^2|f|^2}{4}\int_0^t \langle\delta A(0)\delta A(t)\rangle\cos\omega t$$

suppose *A(t)* obeyed harmonic oscillator dynamics

$$\frac{d^2A}{dt^2} = -\omega_0^2 A(t), \quad \omega_0 = \text{ osc. frequency}$$

$$\langle \delta A(0)\,\delta A(t) \rangle = \langle \delta A \rangle^2 \cos \omega_0 t$$

fourier transfer $\rightarrow$ δ functions at $\pm\,\omega_0$

There is no mechanism of damping the correlations at large time in this example

More on the Langevin eq.

Consider an oscillator coupled to a bath

$$H = H_0 - xf + H_b\left(y_1, \ldots y_N\right)$$

force $f = \sum c_i y_i$

y_i are variables associated with the bath

i.e., *xf* is the coupling term

$$H_0 = \frac{m\dot{x}^2}{2} + V\left(x\right)$$

$$\frac{dH_0}{dt} = 0 \Rightarrow m\ddot{x} = dV/dx$$

Conserves energy

assume H_b is a collection of harmonic oscillators

response of isolated bath characterized by

$$c_b\left(t\right) = \left\langle \delta f\left(0\right)\delta f\left(t\right)\right\rangle_b = \underline{\sum_{iN} c_i c_j \left\langle \delta y_i\left(0\right)\delta y_i\left(t\right)\right\rangle_b}$$

↓

diagonal in normal modes

Harmonic bath has only linear response

$\chi(t)$ changes $f(t)$ from that of the isolated bath

$$f(t) = f_b(t) + \int_{-\infty}^{\infty} dt' \; \chi_b(t-t')\, x(t')$$

$$\chi_b(t-t') = \frac{-\beta dC_b(t-t')}{d(t-t')} \qquad t > t'$$

$$= 0 \qquad t < t'$$

$$m\ddot{x} = \underline{f_0\left[x(t)\right]} + \underline{f_b(t)} + \underline{\int_{-\infty}^{\infty} dt' \chi_b(t-t')\, x(t')}$$

$\uparrow$ fluctuating nonlocal in time

$$\frac{-dV}{dx}$$

osc. pot. $V(x)$
bath

$$\bar{V} = V - \beta C_b(0)\frac{x^2}{2}, \qquad \delta f(t) = f_b - \beta C_b(t)x(0)$$

$$m\ddot{x} = \bar{f}[x(t)] + \delta f - \beta\int_0^t dt' C_b(t-t')\dot{x}(t')$$

$f_b(t)$ is Gaussian with mean $\beta C_b(t)x(0)$ and variance $C_b(t-t')$

$\bar{V}(x)$ = potential mean force

$f_b(t)$ evolves into $\delta f(t)$ a Gaussian fluctuating force

friction is the result of the fluctuating force

When we first considered Brownian motion, we had $\overline{f} = 0$

no average force due to the fast relaxation of fluctuating force

$$\int_0^t dt' C_b(t')\, x(t-t') \approx \dot{x}(t) \int_0^\infty dt' C_b(t')$$

memory effects vanish

$$\to m\ddot{x} \approx f_b - \gamma v(t) \qquad \gamma = \beta \int_0^\infty \langle \delta f(t)\, \delta f(0) \rangle_b$$