Thermodynamic macroscopic observable X

time evolution (fluctuation driven)

stochastic noise

Langevin eq. $\tilde{\gamma} \frac{dX}{dt} = F(X) + \hat{\eta}(t)$

(no "mass" term → "overdamped" Langevin eq.)

generalized friction coefficient

thermodynamic force

$\langle \hat{\eta}(t) \rangle = 0 \qquad \langle \hat{\eta}(t)\,\hat{\eta}(t') \rangle = \hat{\Gamma}\,\delta(t-t')$

uncorrelated noise $(t \neq t')$ ⇒ $X(t)$ varies on time scale much larger than microscopic noise correlation time

Fokker-Planck

$$\frac{\partial \rho(X,t)}{\partial t} = - \frac{\partial J(X,t)}{\partial X} \qquad (d=1)$$

generalized current $J(X,t) = \underbrace{v(X)\,\rho(X,t)}\; - \boxed{\frac{\hat{\Gamma}}{2\tilde{\gamma}^2}\frac{\partial \rho(X,t)}{\partial X}}$

$$v(X) = \frac{F(X)}{\tilde{\gamma}} = -\frac{1}{\tilde{\gamma}}\frac{\partial U(X)}{\partial X}$$

generalized drift velocity

$U(X)$ thermodynamic potential

U is minimum for $X = X^*$ (equilibrium value)

$U(X^*) = F(V,T)$ (Helmholtz free energy)

At equilibrium $P(x) = C \exp\left(-\frac{U(x)}{T}\right)$

$\boxed{\text{local}}$ $\quad J = 0$ $\quad \boxed{\tilde{\Gamma} = 2\tilde{\gamma} T}$ Einstein relation $(k_B = 1)$

$$\to \quad v(x) = -\frac{2T}{\tilde{\Gamma}} \frac{\partial U(x)}{\partial x}$$

Taylor expansion for $U(x)$ around x^*

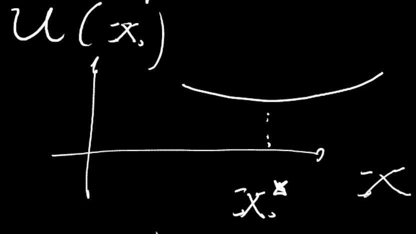
$$U(x) = F(V,T) + \frac{1}{2} \frac{\partial^2 U}{\partial x^2}\Big|_{x=x^*} (x - x^*)^2 + \dots$$

$$\frac{\partial x}{\partial t} = -\frac{2T}{\tilde{\Gamma}} \frac{\partial U}{\partial x} + \frac{\tilde{\eta}(t)}{\tilde{\gamma}}$$ Langevin (non-linear)

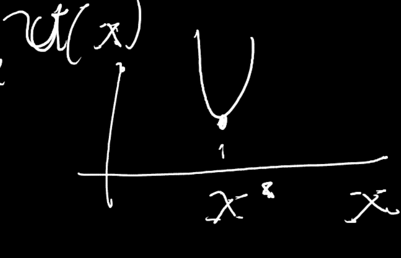
$$\simeq -\frac{2T}{\tilde{\Gamma}} \chi_x^{-1} (x - x^*) + \tilde{\eta}(t)/\tilde{\gamma}$$ (linear)

$$\boxed{\chi_x = \frac{1}{\frac{d^2 U(x)}{d^2 x}\Big|_{x=x^*}}}$$ thermal (static) susceptibility

$\chi_x \gg 1 \to$ restoring force small



$\chi_x \ll 1 \to$ restoring force large



LINEAR RESPONSE THEORY

① microscopic dynamics (Hamilton equations)

(2) statistical mechanics (Boltzmann-Gibbs ensemble)

(1) N particles (d dimension)

positions $q_i(t)$ momenta $p_i(t)$ $i = 1, \dots, dN$

Hamilton function $\mathcal{H}(q_i, p_i) = E$ (energy is conserved)

Hamilton equations:
$$\begin{cases} dq_i/dt = \dfrac{\partial \mathcal{H}}{\partial p_i} \\ dp_i/dt = -\partial \mathcal{H}/\partial q_i \end{cases}$$

deterministic dynamics

(microscopic reversibility & time reversal invariance) $\to$ forward/backward trajectories determined by initial conditions

(2) Statistical mechanics

$$\pi(q_i, p_i) = \frac{1}{Z} \exp(-\beta \mathcal{H}(q_i, p_i))$$

B-G ensemble

$\beta = 1/T$

$$Z = \int_\nu d\nu \exp(-\beta \mathcal{H}) = \exp(-\beta F(V, T))$$

Canonical partition function

$$d\nu = \frac{1}{N!} \prod_{i=1}^{dN} \left(\frac{dq_i \, dp_i}{2\pi\hbar} \right)$$

phase space volume element

Perturbed Hamiltonian: $\mathcal{H}' = \mathcal{H} - hX$

perturbation $\underbrace{h}X$

perturbation field $\to$ coupled to macroscopic observable $X(q_i, p_i)$

h, X are conjugate thermodynamic variables
(h intensive, X extensive; like PV, TE, μN)

$$Z_h = \int_{d\gamma} \exp(-\beta \mathcal{H}') = \exp(-\beta F_h)$$

perturbed partition function — perturbed free energy

$$\frac{\partial F_h}{\partial h} = -\langle X \rangle \; ; \; \boxed{\chi_X = \frac{\partial \langle X \rangle}{\partial h}} = -\frac{\partial^2 F_h}{\partial h^2}$$

$$F_h \longrightarrow U(X) \quad \left(= \frac{1}{\frac{\partial^2 U(X)}{\partial x}} \right)$$

Legendre Transform

$$\& \quad \underline{\chi_X = \beta\left[\langle X^2 \rangle - \langle X \rangle^2\right]}$$

Example: magnetic susceptibility

$H \; M$ — macroscopic magnetization

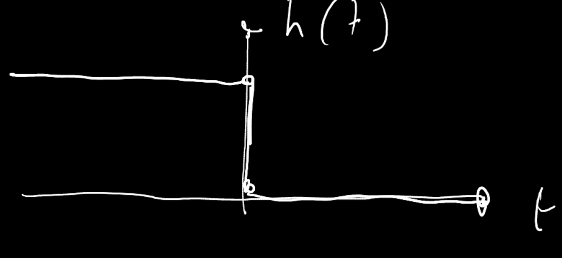
$$\chi = \frac{\partial M}{\partial H} = -\frac{\partial^2 F}{\partial H^2} = \beta\left[\langle M^2 \rangle - \langle M \rangle^2\right]$$

$$\mathcal{H}' = \mathcal{H} - HM$$

H = magnetic field

So far: equilibrium shifted by perturbing fields

Now: response to out-of-equilibrium <u>small</u> perturbation



$$h(t) = \begin{cases} h & -\infty < t < 0 \\ 0 & t > 0 \end{cases}$$

At $t=0$ system is out-of-equilibrium $\mathcal{H}' = \mathcal{H} - h X$

relaxation to equilibrium for $t>0$

at $t=0$ $\quad \langle X \rangle_h \sim$ eq. average for $\mathcal{H}'$

for $t>0$ $\quad X(t)$ relaxes to $\langle X \rangle_0$

non eq. quantity

eq. average for $\mathcal{H}$

$$\langle X(t) \rangle = \underbrace{\frac{1}{Z_h} \int_\Omega d\Omega \exp(-\beta \mathcal{H}')}\, X(t)$$

out-of-equilibrium average

Boltzmann Gibbs ensemble for initial conditions

$q_i(0), p_i(0)$

$$X(t) = X(q_i(t), p_i(t))$$

solving Hamilton equation with initial conditions $q_i(0), p_i(0)$

Linear response to SMALL perturbations

$$h \ll 1 \; ; \quad \exp(\beta h X) \simeq 1 + \beta h X$$

$$\langle X(t) \rangle = \frac{\int_{d\Omega} d\Omega \exp(-\beta \mathcal{H}(q_i, p_i)) (1 + \beta h X(0)) \, X(t) / Z_0}{\int_\Omega d\Omega \exp(-\beta \mathcal{H}(q_i, p_i)) (1 + \beta h X(0)) / Z_0}$$

Z_0 = unperturbed partition function

$$\langle X(t) \rangle = \frac{\langle (1 + \beta h X(0)) X(t) \rangle_0}{\langle 1 + \beta h X(0) \rangle_0}$$

$\langle \cdot \rangle_0$: eq. averages (at equilibrium time translation invariance)

$\langle X(t) \rangle_0 = \langle X \rangle_0$

$$\boxed{\langle X(t) \rangle - \langle X \rangle_0 = \beta h \left[\langle X(t) X(0) \rangle_0 - \langle X \rangle_0^2 \right]}$$

(Fluctuation - dissipation relation

non-equilibrium relaxation → dissipation (entropy production)

eq. fluctuations autocorrelation function

both decay in the same way!