Fluctuations and Response
In nonequilibrium

Plan of the course

- Introduction
- Equilibrium linear response
- Path-integral formalism
- Nonequilibrium linear response
- Nonlinear response
- Coarsegrained picture

What is response?

- Response: reaction of a system to external stimulus
- Examples:
  - External mechanical force/ potential to a particle : mobility
  - Electric field to charged particle : current
  - Magnetic field to spins : magnetization
  - Temperature gradient : heat/ thermal conductivity
  - Shear : momentum current

- Systems in contact with environment (energy/particle exchange)
- Fluctuations : response is not deterministic
- Statistical prediction?
- Various examples:
    - Fourier law (Thermal conductivity)
    - Curie Law (Magnetization)
    - Einstein relation (diffusion)

Response theory: unifying formalism

General question

- System prepared in some initial condition (equilibrium/nonequilibrium)
- Perturbation added at time t=0, strength ε (dimensionless)
- Response : change in expectation of observable O
- Small perturbation:
  expect linear change $\langle O(t)\rangle_\varepsilon - \langle O\rangle_0 = \varepsilon\,\chi(t)$

Susceptibility

★ Goal of linear response theory : predict the susceptibility

- Various scenarios:
  - Initial condition : Equilibrium/ Nonequilibrium
  - Perturbation: time-dependent/constant
  - Relaxation to equilibrium
- Response depends on the protocol/observable/initial condition

Linear response around Equilibrium

- System in equilibrium at temperature T
- Configuration x (position, velocity, collection of dof…)
- Energy : Hamiltonian $H_0(x)$

(Z_0 :Partition function)

- Gibbs-Boltzmann distribution $\rho_0(x) = \dfrac{1}{Z_0}\exp[-\beta H_0(x)]$ $(\beta = T^{-1}, k_B = 1)$
- Adding a small potential perturbation $H(x, s) = H_0(x) - \varepsilon h_s V(x)$ for $s \geq 0$
- Response?

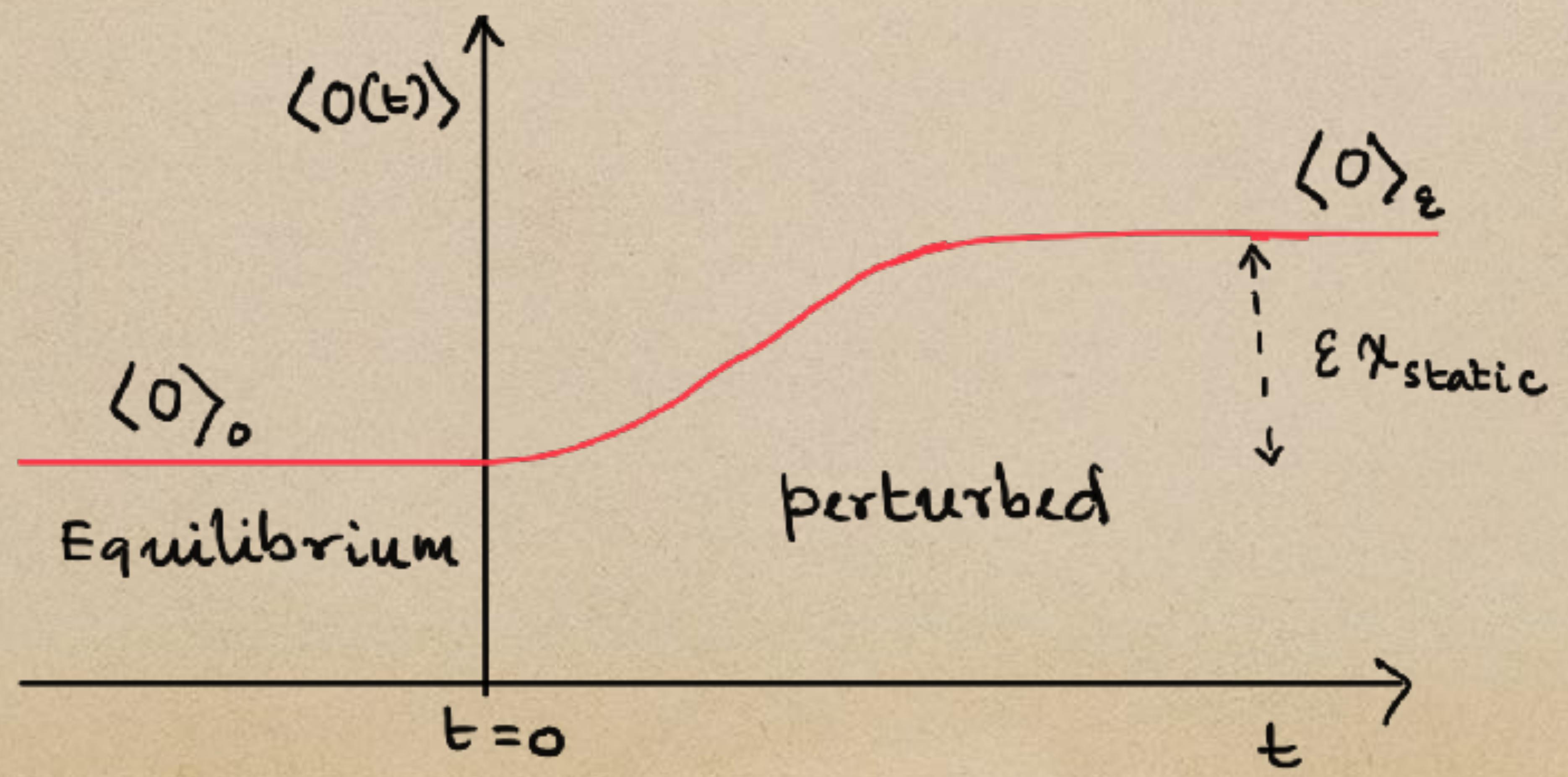
Equilibrium Response (Static)

- Time independent perturbation switched on at t=0

$$H(x) = H_0(x) - \varepsilon V(x)$$

- Observable $O(t) \equiv O(x_t)$

- For t <=0: $\langle O \rangle_0 = \sum_x \rho_0(x) O(x)$



- Response after a long time

$$\chi_{static} = \lim_{t \to \infty} \frac{1}{\varepsilon} \left[\langle O(t) \rangle_\varepsilon - \langle O \rangle_0 \right]$$

- After an initial relaxation phase system reaches new equilibrium (assuming normalizable)

$$\rho_\varepsilon(x) = \frac{e^{-\beta H(x)}}{\int dx\ e^{-\beta H(x)}}$$

- Expected value $\langle O \rangle_\varepsilon = \sum_x O(x) \rho_\varepsilon(x)$

- Expand in ε: $\langle O \rangle_\varepsilon = \langle O \rangle_0 + \varepsilon\beta[\langle VO \rangle_0 - \langle V \rangle_0 \langle O \rangle_0] + \mathcal{O}(\varepsilon^2)$

$$\chi_{\text{static}} = \beta \left[\langle VO \rangle_0 - \langle V \rangle_0 \langle O \rangle_0 \right]$$

Response to perturbation is related to correlation in the unperturbed state

Example I

- Ising Model at temperature T

$$H = -J\sum_{ij} s_i s_j - h\sum_i s_i$$

Perturbation

Magnetization $M = \sum_i s_i$

- In the paramagnetic phase $\langle M \rangle_0 = 0$
- Induced total magnetization $\langle M \rangle_h = \beta h \langle M^2 \rangle_0$ Curie Law
- Local magnetisation $\langle s_k \rangle_h = \beta h \sum_j \langle s_k s_j \rangle_0$

Example II

- Particle in a confining potential U(x): $H_0 = \frac{1}{2}mv^2 + U(x)$
- Perturb with V(x): $H = H_0 - \varepsilon V(x)$
- Change in average position $\langle x \rangle_\varepsilon = \varepsilon[\langle xV(x) \rangle_0 - \langle x \rangle_0 \langle V(x) \rangle_0]$
- Change in average velocity $\langle v \rangle_\varepsilon = \varepsilon[\langle vV(x) \rangle_0 - \langle v \rangle_0 \langle V(x) \rangle_0] = 0$

Equilibrium response (Dynamic)

- How does $\langle O(t) \rangle_\varepsilon$ change with time for constant perturbation?
- Response to time-dependent perturbation ?
- Response at time t expected to depend on the perturbation protocol up to time t
- May not have static limit …

Time-evolution of the system is needed …

Onsager's Regression Hypothesis

"The relaxation of macroscopic nonequilibrium disturbances is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium system"

L. Onsager, 1931

- Connects nonequilibrium relaxation with equilibrium fluctuations
- Predecessor of fluctuation dissipation theorem
- Applications: diffusion, ...

We will use the more modern formalism...adding perturbation at t=0

Fluctuation dissipation theorem

- Consider a (time-dependent) perturbation added at time t=0
- Response of some observable at time t

$$H(x,s) = H_0(x) - \varepsilon h_s V(x)$$

$$\langle O(t) \rangle_\varepsilon - \langle O \rangle_0 = \varepsilon \int_0^t ds\ h_s\ R(t,s)$$

- Response function

$$R(t,s) = \beta \frac{d}{ds} \langle V(s) O(t) \rangle_0$$

Temporal correlation in equilibrium

Callen & Welton 1951

Kubo 1957

...contd

- Relates dissipation when driven (lhs) with fluctuations in equilibrium(rhs)
- Originally derived for Hamiltonian dynamics
- Much wider validity
- Simplification for time-independent perturbation

$$\langle O(t)\rangle_\varepsilon - \langle O\rangle_0 = \varepsilon\beta \int_0^t ds\ \frac{d}{ds}\langle V(s)O(t)\rangle_0$$
$$= \varepsilon\beta\langle [V(t) - V(0)]O(t)\rangle_0$$

- Can be expressed in other forms:

- Stationary equilibrium —> time-translation invariance:

$$\langle V(s)O(t)\rangle_0 = \langle V(0)O(t-s)\rangle_0$$

- Response function depends on the time-difference only

  $R(t,s) = R(t-s)$

- Can be recast as $R(t,s) = -\beta \frac{d}{dt}\langle V(s)O(t)\rangle_0$

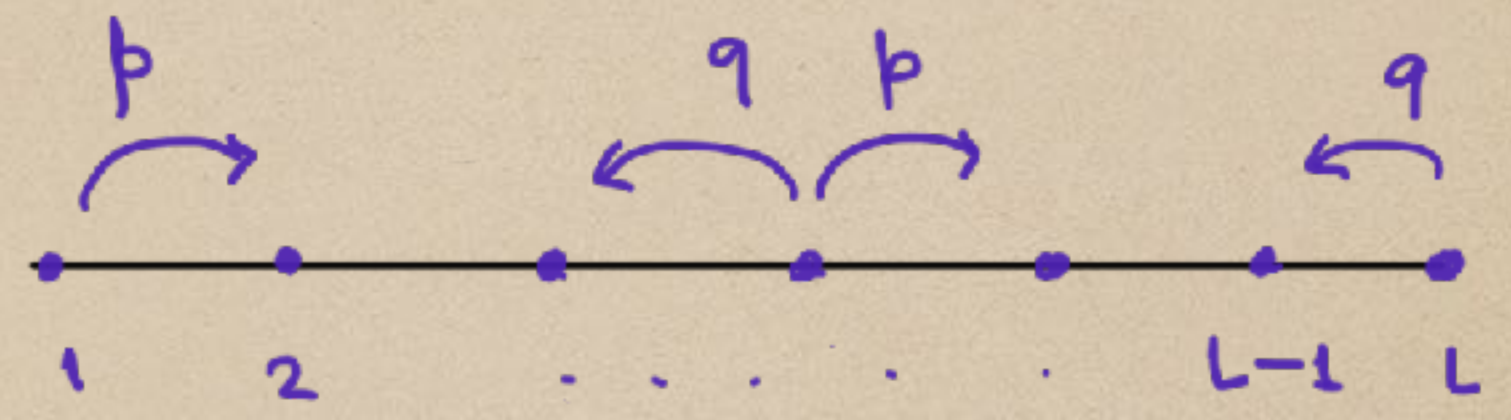
$$R(\tau) = -\beta \frac{d}{d\tau}\langle V(0)O(\tau)\rangle_0$$

- To apply to specific systems - dynamics needed
- Illustration with some examples : Stochastic Markov process
  - Random walk on a 1-d lattice: jump process
  - Particle in thermal bath: diffusion

Stochastic dynamics ...

1. Random walk (continuous time)

- Particle on a 1d lattice; position x=1,2…L
- Jump rate k(x,x+1)=p, k(x,x-1)=q



- Equilibrium: p=q, no potential and all positions are equally likely
- Perturbation at t=0 with linear potential $-\varepsilon V(x) = -\varepsilon x$
- Rates : from detailed balance condition $p = qe^{\beta\varepsilon}$

- Observable : O=x
- Linear response $\langle x_t \rangle_\varepsilon = \langle x_0 \rangle_0 + \varepsilon\beta \langle (x_t - x_0) x_t \rangle_0$
- Recast in terms of displacement $J = x_t - x_0$ (time-integrated current)

$$\langle J(t) \rangle_\varepsilon = \frac{\varepsilon\beta}{2} \langle J(t)^2 \rangle_0$$

(Notice the 1/2)

Example of Green-Kubo relation

II. Particle in a heat bath

- Dynamics of a particle in contact with a reservoir of temperature T
- Force from bath particles: **dissipation** and **noise**
- Langevin equation

$$\ddot{x} = -U'(x) - \gamma \dot{x} + \sqrt{2\gamma T}\ \eta_t$$

$k_B = 1$ throughout

- White noise $\langle \eta_t \rangle = 0, \quad \langle \eta_t \eta_{t'} \rangle = \delta(t - t')$
- Dissipation and noise amplitude become related for equilibriation (Einstein relation)

- Equilibrium distribution $\rho_{\text{eq}}(x, v) \propto \exp -\beta \left[U(x) + \frac{v^2}{2} \right]$

- Perturb at t=0 with linear potential V(x)=x : constant force

$$\ddot{x} = -U'(x) - \gamma\dot{x} + \sqrt{2\gamma T}\ \eta_t + \varepsilon$$

- Change in average velocity $\langle v(t) \rangle = \langle \dot{x}(t) \rangle$ (zero in equilibrium) to linear order ε

$$\langle v(t) \rangle_\varepsilon = \varepsilon\beta \int_0^t ds\ \frac{d}{ds} \langle x(s)v(t) \rangle_0$$

$$= \varepsilon\beta \int_0^t ds\ \langle v(s)v(t) \rangle_0$$

Special case: free particle

Langevin equation

$$\dot{x} = v$$

$$\dot{v} = -\gamma v + \sqrt{2\gamma T}\,\eta + \varepsilon$$

White noise

$$\langle \eta(t) \rangle = 0$$

$$\langle \eta(t)\,\eta(t') \rangle = \delta(t-t')$$

Linear equation: Formal solution

$$v(t) = v_0\, e^{-\gamma t} + \int_0^t e^{-\gamma(t-s)} \left[\sqrt{2\gamma T}\,\eta(s) + \varepsilon\right] ds$$

$$\langle v(t) \rangle_\varepsilon = \langle v_0 \rangle\, e^{-\gamma t} + \varepsilon \int_0^t e^{-\gamma(t-s)}\, ds$$

$\langle v_0 \rangle \to 0$ (eqlm)

$\Rightarrow$

$$\langle v(t) \rangle_\varepsilon = \frac{\varepsilon}{\gamma}\left(1 - e^{-\gamma t}\right)$$

- Rhs- autocorrelation

$$v(t) = v(0)\, e^{-\gamma t} + \sqrt{2\gamma T} \int_0^t d\tau\, e^{-\gamma(t-\tau)}\, \eta(\tau)$$

- Take expectation in equilibrium

$$\langle v(s) v(t) \rangle = \langle v(0)^2 \rangle\, e^{-\gamma(t+s)}$$

$\langle v(0)^2 \rangle \to T$ (eqlm)

$$+ 2\gamma T \int_0^t d\tau \int_0^s d\tau'\, e^{-\gamma(t-\tau)}\, e^{-\gamma(s-\tau')} \langle \eta(\tau) \eta(\tau') \rangle$$

$\langle \eta(\tau) \eta(\tau') \rangle \to \delta(\tau-\tau')$

$$= T\, e^{-\gamma(t-s)}$$

$$\Rightarrow \int_0^t ds\, \langle v(s) v(t) \rangle = \frac{T}{\gamma} \left(1 - e^{-\gamma t}\right) = \frac{1}{\beta \varepsilon} \langle v(t) \rangle_\varepsilon$$

Einstein relation

- Mobility μ: change in velocity due to force $\lim_{t\to\infty} \langle v(t)\rangle = \frac{1}{\gamma}\varepsilon \equiv \mu\varepsilon$
- In equilibrium position diffuses: at late times $\langle x^2(t)\rangle \simeq 2Dt$
- Diffusion constant $D = \lim_{t\to\infty} \frac{1}{2t}\langle x^2(t)\rangle$

$$\langle x^2(t)\rangle = \int_0^t ds \int_0^t ds' \, \langle v(s)v(s')\rangle$$

$$\Rightarrow \quad \boxed{D = \frac{T}{\gamma} = \mu T}$$

Einstein relation

Relates fluctuation D with dissipation γ

Overdamped diffusion

- Large damping, acceleration negligible

$$\gamma \dot{x} = -U'(x) + \sqrt{2\gamma T}\ \eta_t + \varepsilon$$

- Equilibrium distribution $\rho_{\mathrm{eq}}(x) \propto e^{-\beta U(x)}$

- Change in average position

$$\langle x(t) - x(0) \rangle_\varepsilon = \frac{\varepsilon\beta}{2} \langle [x(t) - x(0)]^2 \rangle_0$$

Same as in the random walk case…

Derivation of FDT

- Various possible ways
- We will use generator approach
- Time evolution of probability: Master equation/Fokker-Planck

$$\frac{d}{dt}\rho(x,t) = L^\dagger \rho(x,t)$$

- Forward generator $L^\dagger$ (matrix/differential operator)
- Example: overdamped diffusion in 1d

$$\dot{x} = -\mu U'(x) + \sqrt{2\mu T}\ \eta_t$$

$$L^\dagger \rho = \mu \frac{d}{dx}\left[U'(x)\rho\right] + \mu T \frac{d^2\rho}{dx^2}$$

Mobility $\mu = 1/\gamma$

- Formal solution $\rho(x,t) = e^{L^\dagger t}\rho(x,0)$ (assuming time-independent)
- Observable $\langle O(t)\rangle = \int dx\ O(x)\ \rho(x,t) = \int dx\ O(x) e^{L^\dagger t}\rho(x,0)$

$$= \int dx\ \rho(x,0)\ (e^{Lt}O(x))$$

$$= \langle e^{Lt}O(x)\rangle$$

Average over initial $\rho(x,0)$

- L is adjoint of the Fokker-Planck operator: Backward generator
- Overdamped diffusion $LO = -\mu U'(x)\frac{dO}{dx} + \mu T\frac{d^2O}{dx^2}$

- Perturbation $U(x) \to U(x) - \varepsilon h_t V(x)$ ⇒ $L = L_0 + \varepsilon h_s L_1$
- Example: Overdamped diffusion $L_1 O = \mu V'(x) \dfrac{dO}{dx}$
- Switched on at t=0: observable evolution

$$\langle O(t) \rangle = \left\langle \exp\left[L_0 t + \varepsilon \int_0^t ds\, h_s\, L_1 \right] O(x) \right\rangle$$

[Average over initial distribution $\rho_0(x)$]

- Expand in ε (Dyson expansion)

$$\langle O(t) \rangle_\varepsilon = \langle O(t) \rangle_0 + \varepsilon \int_0^t ds\, h_s \int dx\, \rho_0(x)\, e^{sL_0}\, L_1\, e^{L_0(t-s)}\, O(x)$$

Linear response

- Initial state: stationary equilibrium $L_0^\dagger\, \rho_0 = 0 \;\Rightarrow\; e^{L_0^\dagger\, t}\rho_0(x) = \rho_0(x)$

- Change in the observable

$$\chi = \int_0^t ds\, h_s \int dx\, \rho_0(x)\, L_1\, e^{L_0(t-s)}\, O(x)$$

$$= \int_0^t ds\, h_s \int dx\, \left(L_1^+\, \rho_0(x)\right) e^{L_0(t-s)}\, O(x)$$

- Equilibrium $\rho_0(x) \propto e^{-\beta U(x)}$
- Overdamped diffusion

$$L_1^\dagger \rho_0(x) = -\frac{\mu}{Z}\frac{d}{dx}\left(\frac{dV}{dx}e^{-\beta U(x)}\right) = -\beta\rho_0(x)\ L_0 V(x)$$

- Response $\chi(t) = -\int_0^t ds\ h_s \langle L_0 V(s) O(t)\rangle_0 = \int_0^t ds\ h_s \frac{d}{ds}\langle V(s) O(t)\rangle_0$

$$\langle L_0 V(s) O(t)\rangle_0 = \langle L_0 V(t) O(s)\rangle_0 = \frac{d}{dt}\langle V(t) O(s)\rangle_0 = \frac{d}{dt}\langle V(s) O(t)\rangle_0$$

Time-reversal invariance

Thermodynamic interpretation

- Look back at Kubo formula

$$\langle O(t)\rangle_\varepsilon - \langle O\rangle_0 = \varepsilon \int_0^t ds\ h_s\ \frac{d}{ds}\langle V(s)O(t)\rangle_0$$

- Partial integration :

$$\langle O(t)\rangle_\varepsilon - \langle O\rangle_0 = \varepsilon \left\langle \left[\underline{V(x_t)h_t - V(x_0)h_0} - \underline{\int_0^t ds\ \dot{h}_s V(x_s)}\right] O(t) \right\rangle_0$$

(Along a trajectory)

Change in energy

Work done by the perturbation

- Entropy generated along a trajectory

$$V(x_t)h_t - V(x_0)h_0 - \int_0^t ds\ \dot{h}_s V(x_s)$$

- Linear response: Correlation of observable with entropy generated by the perturbation - measured in equilibrium

- Thermodynamic ...

- Equilibrium linear response for state observables is entropic, ie, thermodynamic
- Non-thermodynamic aspects are irrelevant
- Becomes crucial when moving beyond
  - nonequilibrium
  - nonlinear
  - General path observables