Non-linear response

Going beyond linear response

- Perturbation strength larger
- Around equilibrium and nonequilibrium
- Response beyond regime of Kubo formula (or Nonequilibrium equivalent)
- General structure?
- Use dynamical ensembles

Extend the linear response

- Observable $\langle O(t)\rangle_\varepsilon - \langle O(t)\rangle_0 = \varepsilon\chi_1 + \varepsilon^2\chi_2 + \mathcal{O}(\varepsilon^3)$
- Second order susceptibility

$$\chi_2 = \frac{1}{2}\frac{d^2}{d\varepsilon^2}\langle O(t)\rangle_\varepsilon \Big|_{\varepsilon=0}$$

- Express χ_2 in terms of correlations in the unperturbed state ?
- Particularly relevant around equilibrium

Static, equilibrium

- System in equilibrium, energy $H_0(x)$, inverse temperature β
- Perturbation at $t = 0$ with additional potential $H(x) = H_0(x) - \varepsilon V(x)$
- After initial relaxation, new equilibrium with $\rho_\varepsilon(x) = \dfrac{e^{-\beta H(x)}}{\int dx \; e^{-\beta H(x)}}$
- Expectation $\langle O \rangle_\varepsilon = \sum_x O(x)\rho_\varepsilon(x)$
- Expand in ε

$$\chi_2 = \frac{\beta}{2}[\langle V^2 O \rangle_0 - \langle V^2 \rangle_0 \langle O \rangle_0 + 2\langle V^2 \rangle_0 \langle O \rangle_0 - 2\langle VO \rangle_0 \langle V \rangle_0]$$

Dynamical response

- Use dynamical ensembles
- Expected value of observable

$$\langle O(\omega)\rangle_\varepsilon = \sum_\omega P_\varepsilon(\omega)O(\omega) = \sum_\omega e^{-A_\varepsilon(\omega)}P_0(\omega)O(\omega)$$

- Second order response: second derivative wrt ε

$$\frac{d^2\langle O\rangle}{d\varepsilon^2} = -\langle A''(\omega)\,O(\omega)\rangle_\varepsilon + \langle A'^2(\omega)\,O(\omega)\rangle_\varepsilon$$

$$A = D - \frac{1}{2}S$$

- Decompose in terms of S and D
- Assume $S''_\varepsilon = 0$: entropy generated is linear in perturbation strength
- True in most physical scenarios (as seen in examples)
  — defines order of perturbation : eg, linear change in Hamiltonian
- General nonequilibrium second order response:

$$\frac{d^2}{d\varepsilon^2}\langle O(\omega)\rangle = -\langle D''O\rangle_\varepsilon + \langle (D')^2 O\rangle_\varepsilon + \frac{1}{4}\langle (S')^2 O\rangle_\varepsilon - \langle S'D'O\rangle_\varepsilon$$

- Around equilibrium?

Second order response around equilibrium

- Unperturbed state is equilibrium
- Response of state observable $\langle O(x_t) \rangle$
- Take $Y(\omega) = O(x_t) - O(x_0)$: anti-symmetric under time reversal

$$\frac{d^2}{d\varepsilon^2}\langle Y \rangle \Big|_0 = -\langle D'' Y \rangle_0 + \langle (D')^2 Y \rangle_0 + \frac{1}{4}\langle (S')^2 Y \rangle_0 - \langle S' D' Y \rangle_0$$

$$= -\langle S' D' [O(x_t) - O(x_0)] \rangle_0$$

$$\frac{d^2}{d\varepsilon^2}\langle O(x_t) \rangle \Big|_0 = -2\langle S' D' O(x_t) \rangle_0 \quad \Rightarrow \quad \chi_2 = -\langle S' D' O(x_t) \rangle_0$$

- Nonlinear fluctuation dissipation relation around equilibrium:

$$\langle O(x_t)\rangle_\varepsilon = \langle O(x_t)\rangle_0 + \varepsilon\langle S'O(x_t)\rangle_0 - \varepsilon^2\langle S'D'O(x_t)\rangle_0$$

- Only linear excesses appear
- Observable: current (anti-symmetric)

$$\langle J\rangle_\varepsilon = \frac{\varepsilon}{2}\langle S'J\rangle_0 - \frac{\varepsilon^2}{2}\langle S'D'J\rangle_0$$

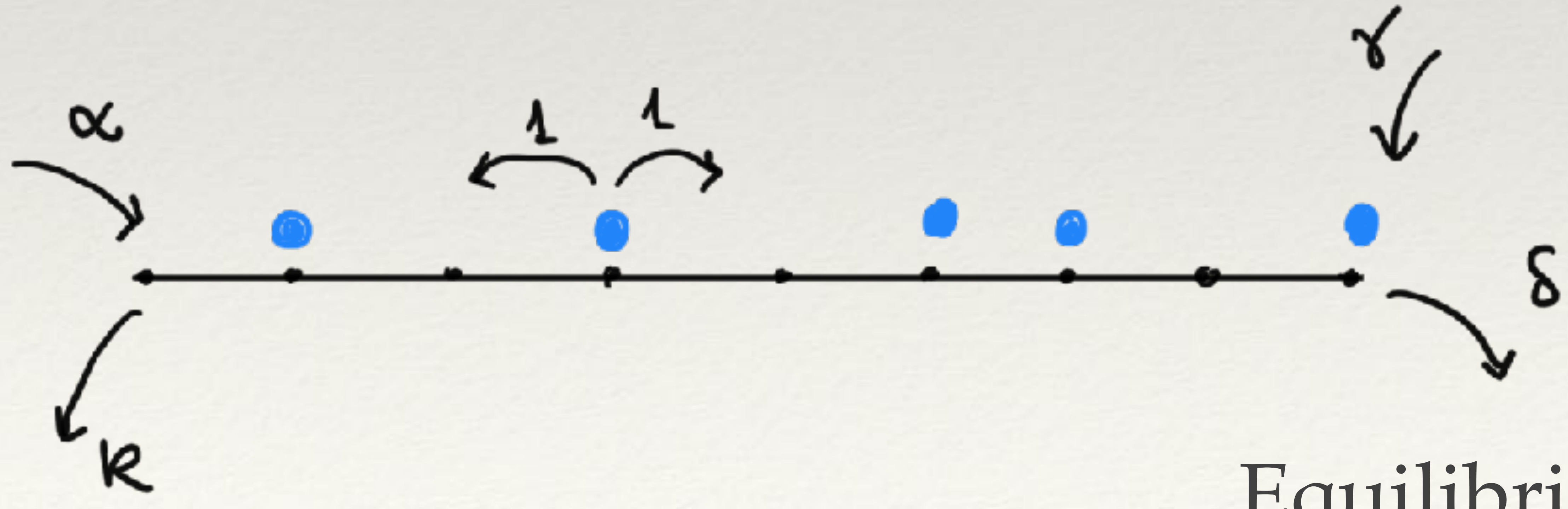
- Nonlinear extension of Green-Kubo relation

- Kinetic details (friction, coupling, dwelling times) enter explicitly even around equilibrium
- There is no “the” second order response, depends on the kinetic aspects
- Two perturbations which are thermodynamically same can give rise to different second order response
- Examples?

Boundary driven SEP

- Symmetric exclusion process on a 1D lattice: $s_i = 0,1; i = 1,2,\ldots L$
- Symmetric hopping at the bulk 10 <—> 01 with rate 1
- Particles enter and exit at the boundaries: reservoirs with same chemical potential $\mu_L = \mu_R$
- Perturbation: increase chemical potential of the left reservoir

$$\frac{\alpha}{\kappa} = e^{\beta\mu_L}$$



$$\frac{\gamma}{\delta} = e^{\beta\mu_R}$$

Equilibrium $\mu_L = \mu_R$

- Change in boundary drive: $\mu_L \to \mu_L + d\mu_L$ at the left reservoir
- Only terms involving jumps at the left boundary
- Entropy $S(\omega) = N_L^{\rightarrow} \log \frac{\alpha}{\kappa} + N_L^{\leftarrow} \log \frac{\kappa}{\alpha} = J_L^{in} \log \frac{\alpha}{\kappa} = J_L^{in} \beta \mu_L$

  $+\mu_L$ independent terms
- Net influx at the left boundary $J_L^{in} = N_L^{\rightarrow} - N_L^{\leftarrow}$
- Excess entropy $\left.\frac{dS(\omega)}{d\mu_L}\right|_{\mu_L=\mu_R} = \beta J_L^{in}$

- Frenesy $D(\omega) = -\frac{1}{2}(N_L^{\rightarrow} + N_L^{\leftarrow})\log \alpha\kappa + \alpha t_0 + \kappa t_1$ $+\mu_L$ independent terms
- t_0, t_1 time during which $s_1 = 0{,}1$ respectively
- Excess depends on the specific dependence of α, β on chemical potential
- Examples:
  I. $\alpha = e^{\beta\mu_L/2},\ \kappa = e^{-\beta\mu_L/2}$ (ie, $\alpha\kappa = 1$) ⇒ $D'(\omega) = \frac{\beta}{2}(\alpha t_0 - \kappa t_1)\Big|_{\mu_L=\mu_R}$
- II. $\alpha = e^{\beta\mu_L},\ \kappa = 1$ ⇒ $D'(\omega) = -\frac{\beta}{2}N + \beta\alpha t_0\Big|_{\mu_L=\mu_R}$

- Perturbations are thermodynamically identical: same change in chemical potential
- Differ in kinetic details: specific coupling to the reservoir
- Excess entropy same : linear response is identical
- Second order response of observables (density, current,…) are very different

Extrapolation

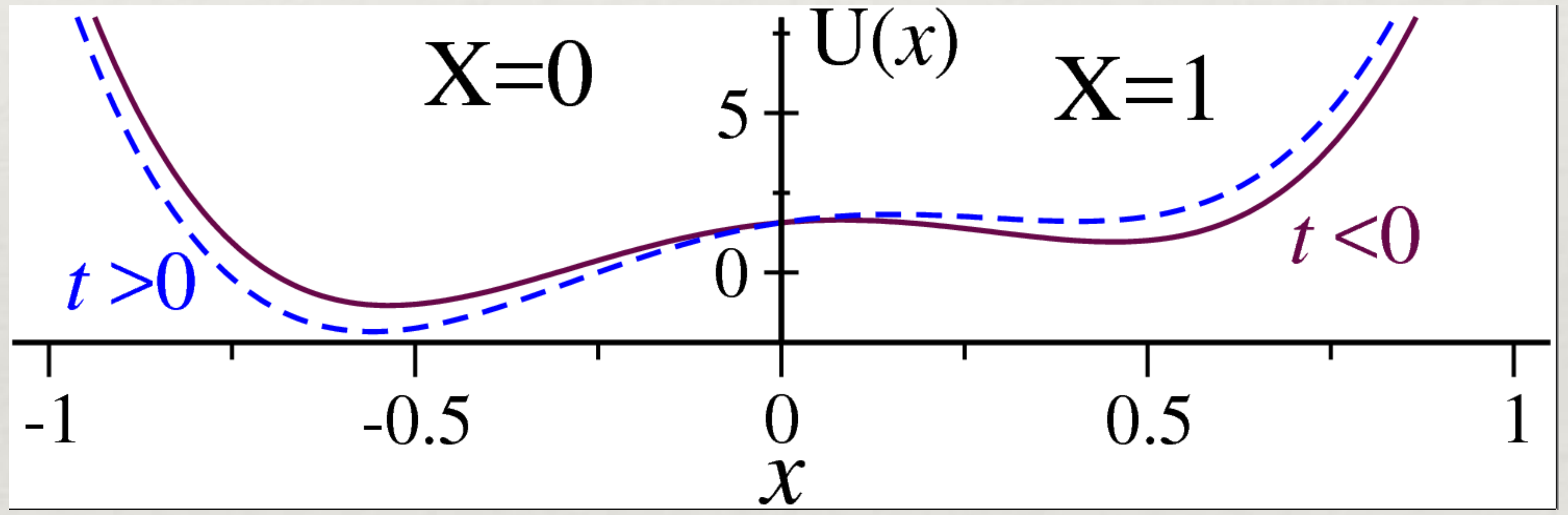
- Second order response depends only on linear excesses of entropy and frenesy

$$\chi_2 = -\langle S'D'O(x_t)\rangle_0$$

- Possibility of extrapolation: if we can measure the linear excesses with a small perturbation, second order response can be predicted
- Requires knowledge of all possible paths - not feasible in general
- Useful in a coarse-grainined picture where only a few (macroscopic) dof
- Eg - experiments where only some observables are accessible…

Extrapolation

- Coarse grained 'macro' states X in a complex system
- X=0,1,2...n-1 depending on the microscopic configuration
- Examples: n=2
  - Particle in a double well potential



  - Classical Ising model

$$X = \Theta(m)$$

magnetization

Paths in the macro-space

- Path [ij;t] connecting states X=i (t=0) and X=j (time t)
- Probability $P_{ij}(t) = \int_{ij} d\omega \; p(\omega)$ ⟵ Microscopic
- Action

$$\mathscr{A}_{ij} \equiv -\log \frac{P_{ij}}{P_{ij}^{\text{eq}}} = \log \left[\frac{1}{P_{ij}^{\text{eq}}} \int_{ij} d\omega \; p_{\text{eq}}(\omega) e^{-a(\omega)} \right].$$

- Decompose $\mathscr{A}_{ij} = \mathscr{D}_{ij} - \frac{1}{2}\mathscr{S}_{ij}$
- Entropy and freneisy in coarse-grained path space

Equilibrium: time-reversible

$$P_{ij}^{\text{eq}}(t) = P_{ji}^{\text{eq}}(t)$$

Ref: Phys. Rev. Lett 120,180604 (2018)

- Observable in coarse grained space $O(X_t)$
- Second order response formula for coarse-grained observable

$$\langle O(X_t)\rangle = \sum_{ij} P_{ij} O(j) = \langle O(X)\rangle^{\rm eq} + \varepsilon \sum_{ij} \mathcal{S}'_{ij} P^{\rm eq}_{ij} O(j)$$
$$- \varepsilon^2 \sum_{ij} \mathcal{S}'_{ij} \mathcal{D}'_{ij} P^{\rm eq}_{ij} O(j) + \frac{\varepsilon^2}{2} \sum_{ij} \mathcal{S}''_{ij} P^{\rm eq}_{ij} O(j).$$

- Excesses

$$\mathcal{S}'_{ij} \equiv \mathcal{A}'_{ji} - \mathcal{A}'_{ij} = \frac{1}{P^{\rm eq}_{ij}} \int_{ij} {\rm d}\omega\ p_{\rm eq}(\omega) s'(\omega),$$
$$\mathcal{D}'_{ij} \equiv \frac{1}{2}\left(\mathcal{A}'_{ij} + \mathcal{A}'_{ji}\right) = \frac{1}{P^{\rm eq}_{ij}} \int_{ij} {\rm d}\omega\ p_{\rm eq}(\omega) d'(\omega),$$
$$\mathcal{S}''_{ij} \equiv \left(\mathcal{A}''_{ji} - \mathcal{A}''_{ij}\right) = 2\mathcal{D}'_{ij}\mathcal{S}'_{ij} - \frac{2}{P^{\rm eq}_{ij}} \int_{ij} {\rm d}\omega\ p_{\rm eq}(\omega) d' s'.$$

→ Non-zero in general

$$\mathcal{S}_{ij} = -\mathcal{S}_{ji}$$
$$\mathcal{D}_{ij} = \mathcal{D}_{ji}$$

- Consider perturbations acting on the coarse-grained variable X only
- Example: potential $V(X)$
- Microscopic entropy same for all macro-paths

$$\int_{ij} \mathrm{d}\omega\ p_{\mathrm{eq}}(\omega) d' s' = \mathcal{S}'_{ij} \int_{ij} \mathrm{d}\omega\ p_{\mathrm{eq}}(\omega) d' = \mathcal{S}'_{ij}\mathcal{D}'_{ij}P^{\mathrm{eq}}_{ij}. \quad \Rightarrow \quad \mathcal{S}'' = 0$$

- Response formula reduces to:

$$\langle O(X_t)\rangle = \langle O(X)\rangle^{\mathrm{eq}} + \varepsilon \sum_{ij} \mathcal{S}'_{ij} P^{\mathrm{eq}}_{ij} O(j) - \varepsilon^2 \sum_{ij} \mathcal{S}'_{ij}\mathcal{D}'_{ij} P^{\mathrm{eq}}_{ij} O(j).$$

- For n=2 and O=X

$$\chi_2^{\mathrm{eq}} = -\mathcal{S}'_{01}\mathcal{D}'_{01}P^{\mathrm{eq}}_{01}$$

Extrapolation scheme

- Measure macroscopic S' and D' from near equilirium (linear regime) experiments

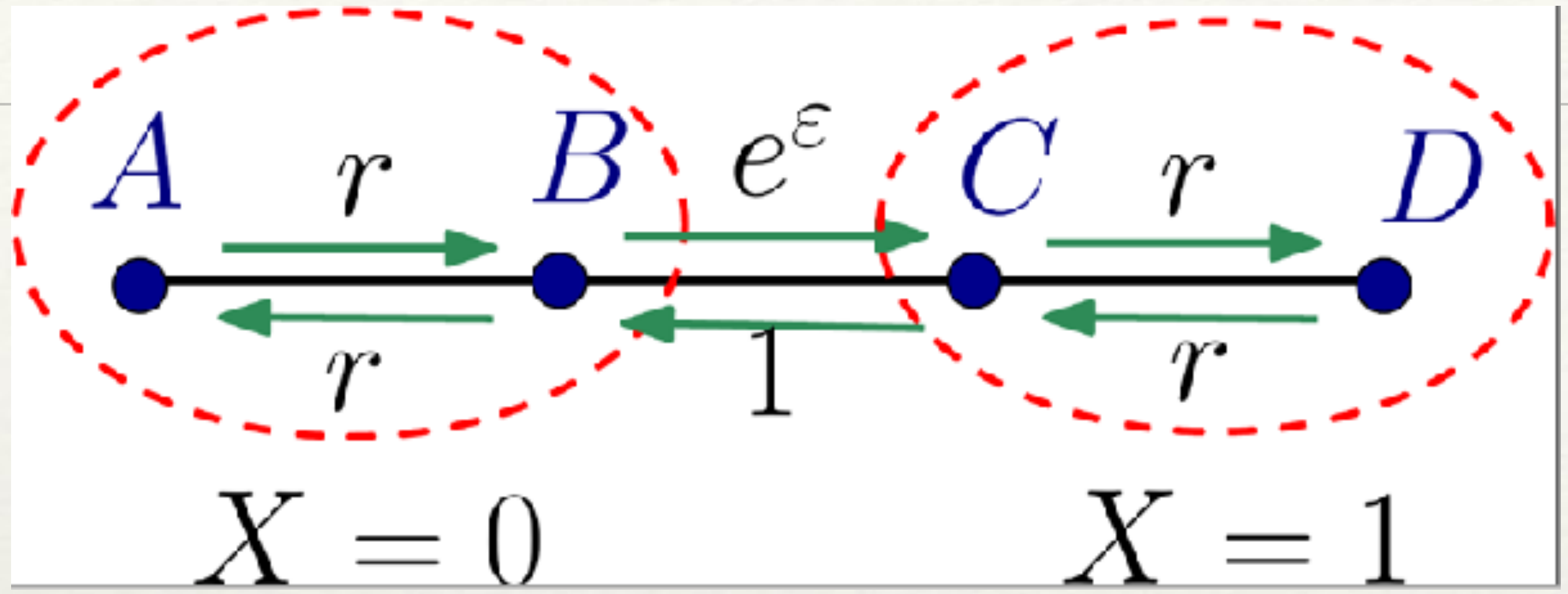
$$\mathcal{S}'_{ij} = \frac{1}{\varepsilon} \log \frac{P^{\varepsilon}_{ij}}{P^{\varepsilon}_{ji}} \qquad \mathcal{D}'_{ij} = \frac{1}{2\varepsilon}[-\log P^{\varepsilon}_{ij} P^{\varepsilon}_{ji} + 2 \log P^{\text{eq}}_{ij}]$$

- Use these to predict far away from equilibrium (second order) reponse

- No detail about system required!
  - Price: an extra nonequilibrium experiment

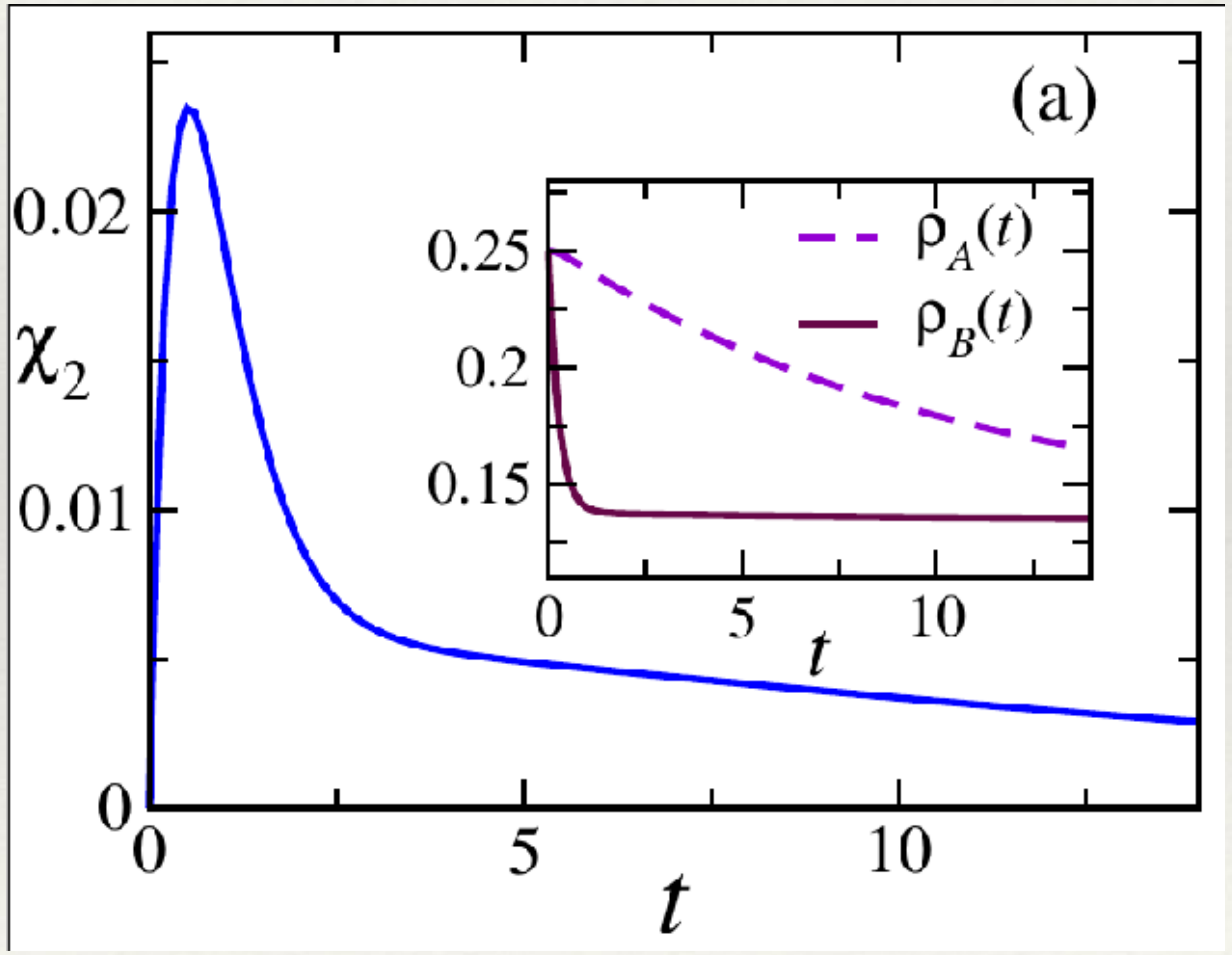
Assumption: perturbation in X

Example I: 4-state jump process



Observable $\langle X \rangle - \langle X \rangle_0 = \varepsilon \chi_1 + \varepsilon^2 \chi_2$

- Perturbation: change in rate B—> C (coupled to X)
- Analytically solvable
- Response calculated directly and using equilibrium prediction: identical



Does not rely on fast equilibration of integrated degrees!

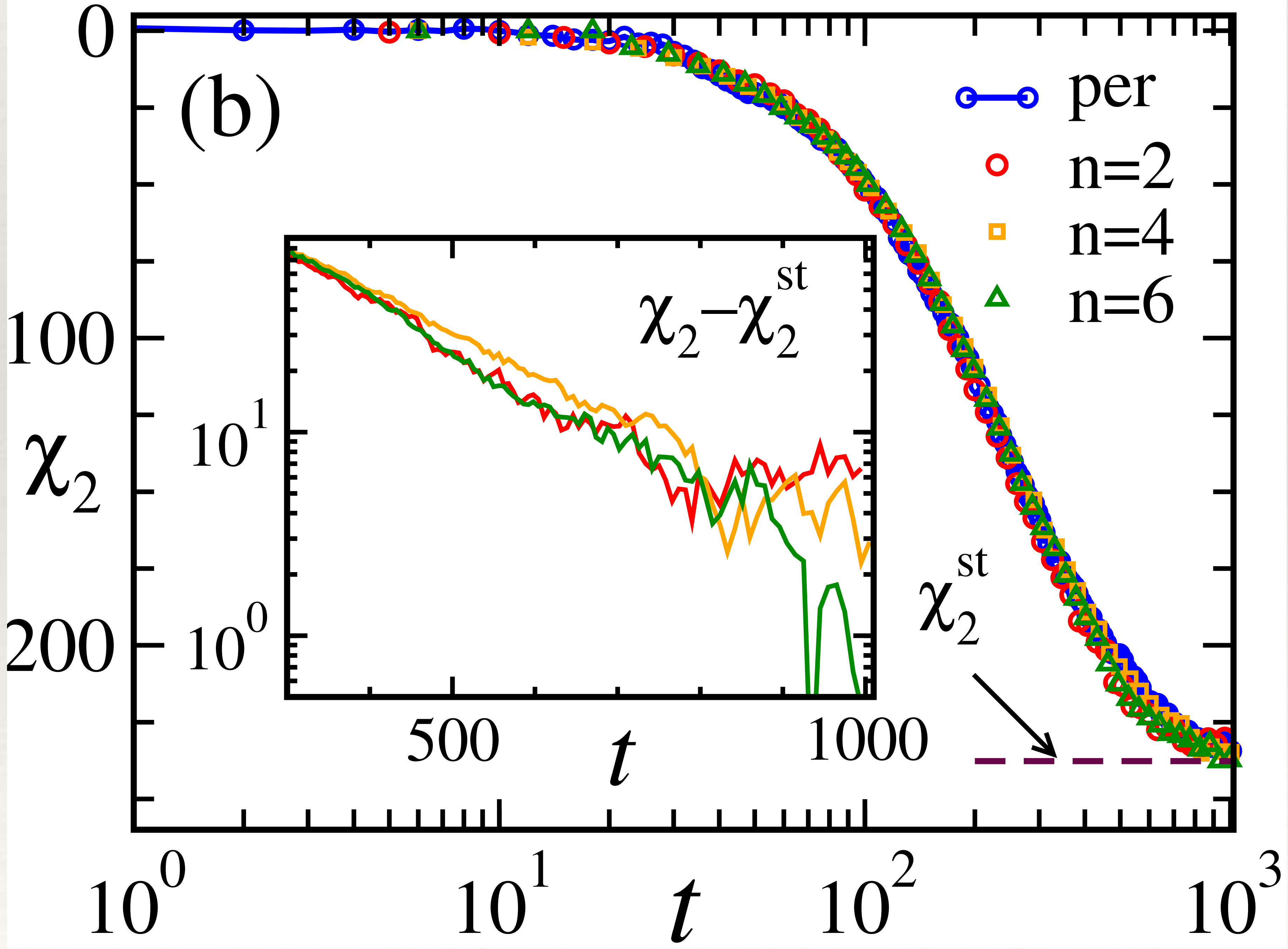
Example II: 2d Ising model

- Near-critical Ising model
- Perturbation: change in magnetic field
- Coarse-grained observable $X = \Theta(\sum_i s_i)$
- Perturbation not in X-space

$$H = -\sum_{ij} s_i s_j - (h+\varepsilon)\sum_i s_i$$

$$\langle X\rangle - \langle X\rangle_0 = \varepsilon\chi_1 + \varepsilon^2\chi_2$$

- Excess entropy and dynamical activity determined at $\varepsilon = 0.0005$
- Compared to direct measurement at $\varepsilon = 0.003$
- No system details needed



T=2.45

Perturbation is not in X, still works quite well...fast convergence

- Prediction of second order response of coarse-grained observable
- Two sets of experiment needed: equilibrium and close-to-equilibrium
- No knowledge about dynamics needed
- Easily applicable for complex systems
- Example: Colloid moving in viscoelastic medium

Overview

- Linear response theory around equilibrium
- Response in nonequilibrium : dynamical ensembles
- Entropic and frenetic components
- Nonlinear response
- Untouched questions
  - Thermal response - same formalism, but some additional nuances
  - Nonequilibrium baths
  - Time-dependent rates