NONEQUILIBRIUM RESPONSE - I

RECAP

- Linear response in equilibrium
- Fluctuation-dissipation theorem (Kubo formula)

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

- Correlation of observable with entropy generated by the perturbation - thermodynamic in nature

NONEQUILIBRIUM

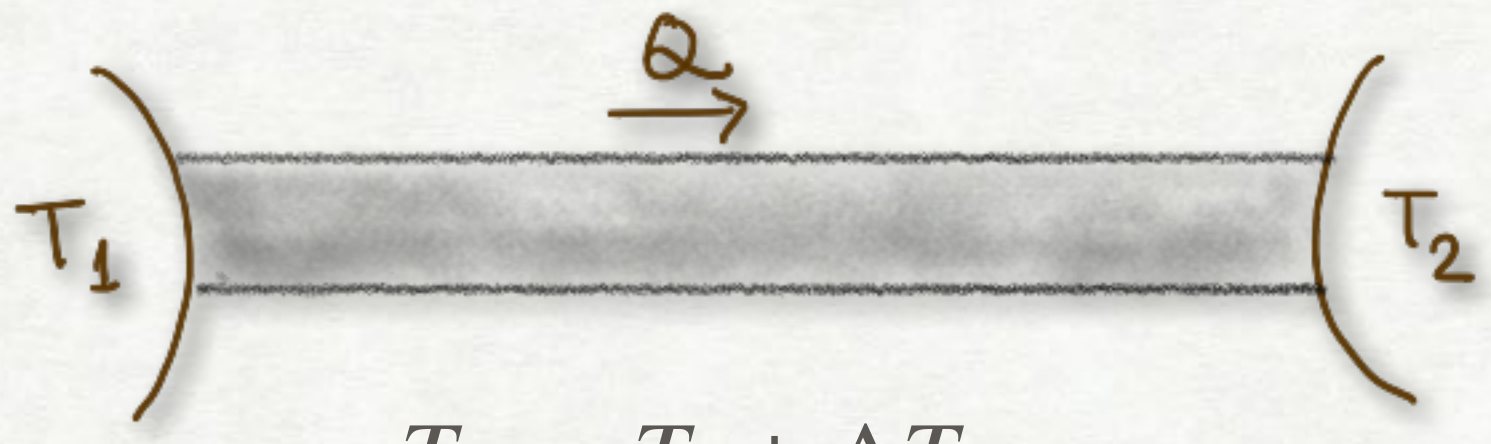
- Ubiquitous in nature, at all length scales
- Often defined by dynamical rules and not Hamiltonian description
- No generalised framework, even for stationary distribution
- Various scenarios:
    - Externally driven, in a nonequilibrium stationary state (NESS)
    - Relaxing to equilibrium (dynamics is detailed balanced)
    - Time-dependent force

NONEQUILIBRIUM LINEAR RESPONSE

- Adding perturbation to a system which is out of equilibrium
- Perturbation: (i) (small) change in existing nonequilibrium drive
  (ii) introduction of additional (small) drive
- Change in observable - prediction?
- Unifying formalism?
- How is it different than equilibrium response?

- Examples:

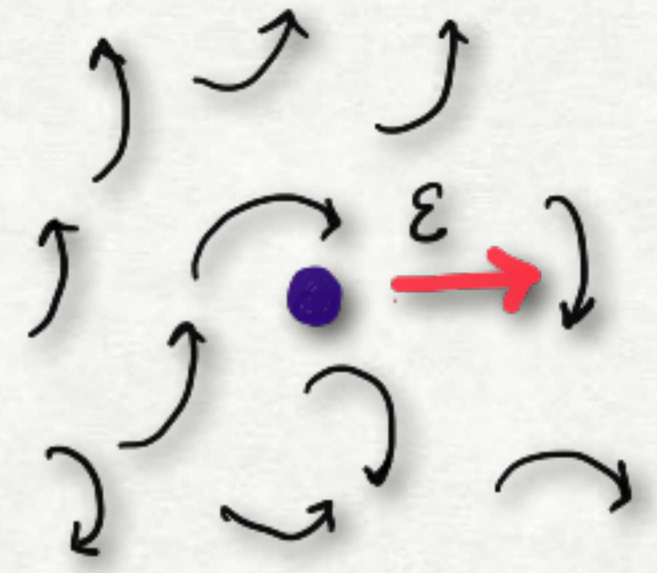
- Conducting rod in contact with two thermal reservoirs



$T_1 \to T_1 + \Delta T$

  - How does the thermal current change when temperature gradient is changed?

- Particle moving in a nonconservative force field



  - How does the velocity change when an additional force is added?

FORMAL EXTENSION OF KUBO-FORMULA

- Possible for perturbations around nonequilibrium stationary state (NESS)
- Use the generator approach
- Agarwal - Kubo formula: for $L = L_0 + \varepsilon h_s L_1$

$$\langle O(t)\rangle_\varepsilon - \langle O\rangle_0 = \varepsilon \int_0^t ds\ h_s\ R(t,s) \qquad R(t,s) = \left\langle \frac{L_1^\dagger \rho_0(s)}{\rho_0(s)}\ O(t) \right\rangle_0$$

Averaged over the unperturbed NESS

- Evolution of expectation value of the observable

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

- Initial distribution is not equilibrium, but stationary: $e^{L_0^\dagger t}\rho_0(x) = \rho_0(x)$

- Susceptibility

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

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

$$\Rightarrow \quad R(t,s) = \left\langle \frac{L_1^\dagger \rho_0(s)}{\rho_0(s)}\, O(t) \right\rangle_0$$

- Correlation of the observable with $L_1^\dagger \rho_0(x)/\rho_0(x)$ in the unperturbed NESS

- No practical utility : stationary state weights are not known in general (unlike equilibrium)

- Use a different approach …

- Path integral formalism using dynamical ensembles

DYNAMICAL ENSEMBLES

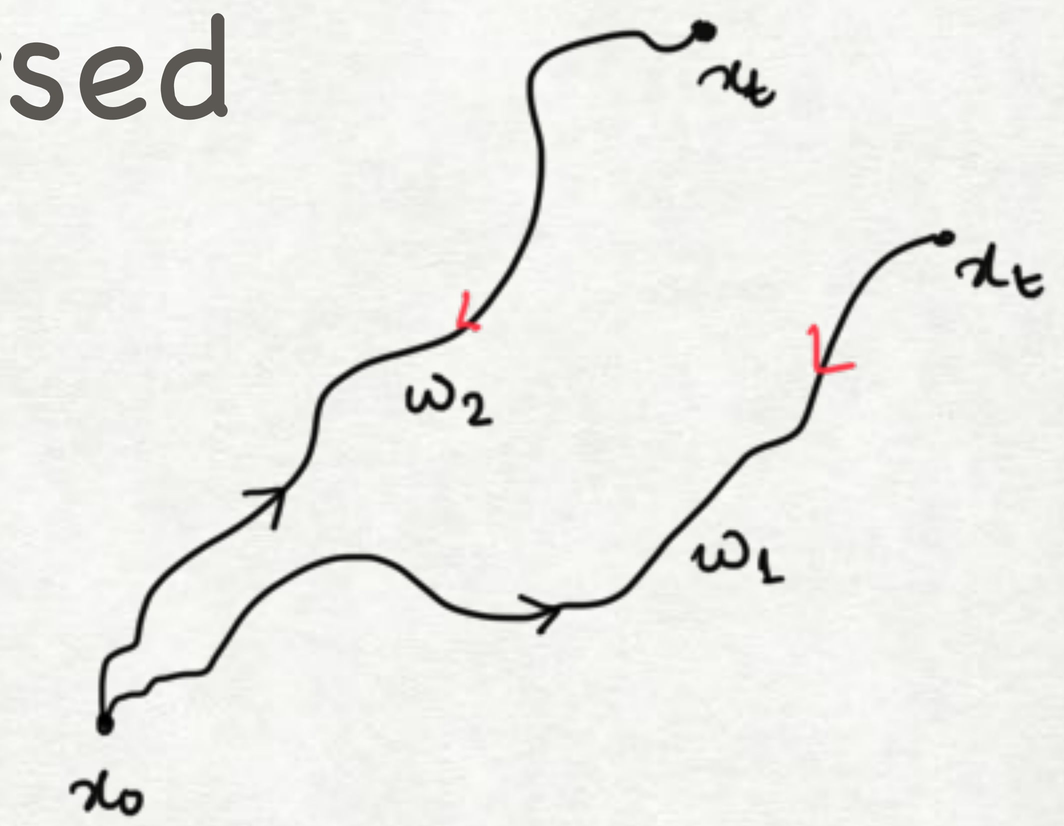
- Trajectory based approach
- System configuration x: position, velocity, collective dof, discrete state
- Evolution: stochastic Markov process (Jump rates, Langevin equation,...)
- Each trajectory $\omega = \{x_s; 0 \leq s \leq t\}$ has a probability $P(\omega)$
- Normalization $\sum_\omega P(\omega) = 1$ (sum over all possible trajectories)
- Observable (can depend on the trajectory)

$$\boxed{\langle O(\omega) \rangle = \sum_\omega O(\omega)\, P(\omega)}$$

TIME REVERSAL

- Trajectory reversed in time $\theta\omega = \{x_{t-s}; 0 \leq s \leq t\}$
- Velocities reverse sign also (kinematic reversal)
- If any time-dependent protocol, that is also reversed
- Equilibrium: time-reversal invariant

$$P(\omega) = P(\theta\omega)$$



- Not true in general : time-reversal symmetry is broken in nonequilibrium

ACTION

- Useful to define an ‘action’ with respect to a reference process

Example: Onsager-Machlup (1953)

$$P(\omega) = e^{-A(\omega)} P_0(\omega)$$

- Reference process must be defined in the same trajectory space

- Assume same initial distribution $\rho(x_0)$ for the original process and the reference process

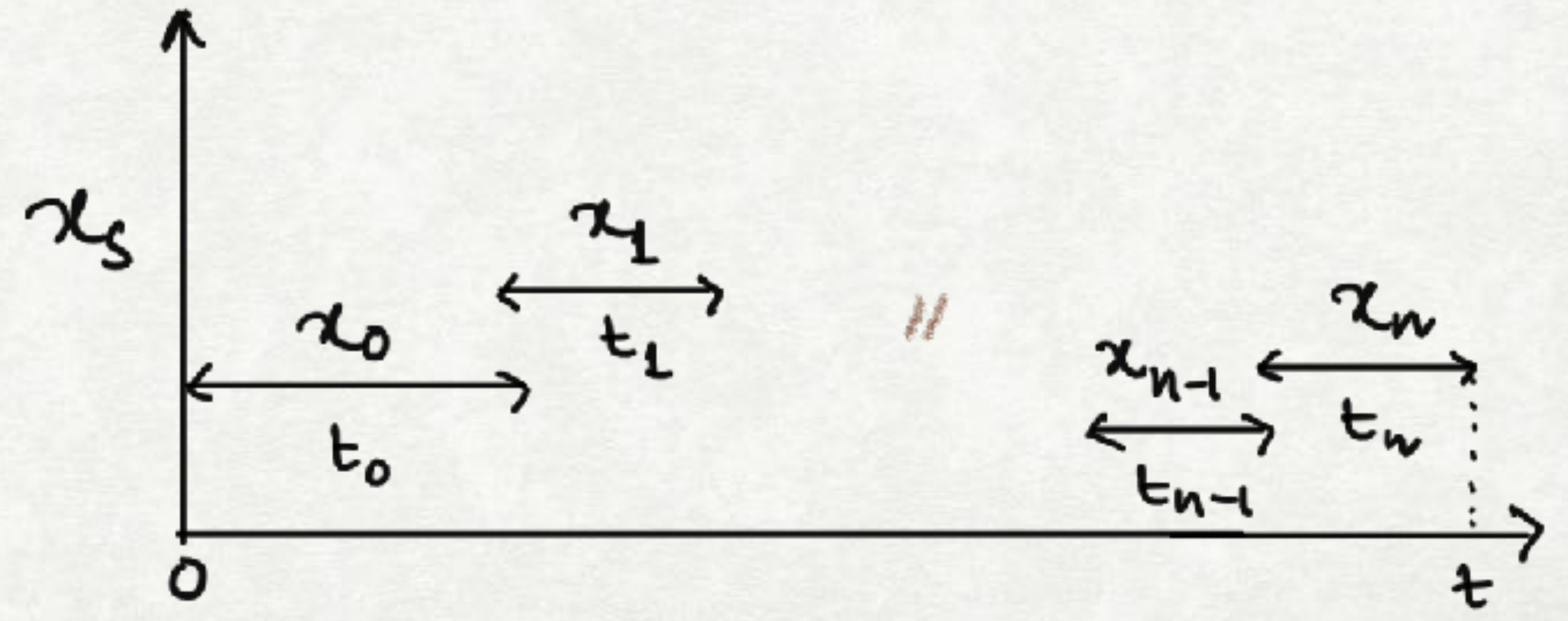
- Each trajectory is then associated with an action (independent of initial distribution)

$$A(\omega) = -\log \frac{P(\omega)}{P_0(\omega)}$$

Radon-Nikodym derivative

ILLUSTRATION: MARKOV JUMP PROCESS

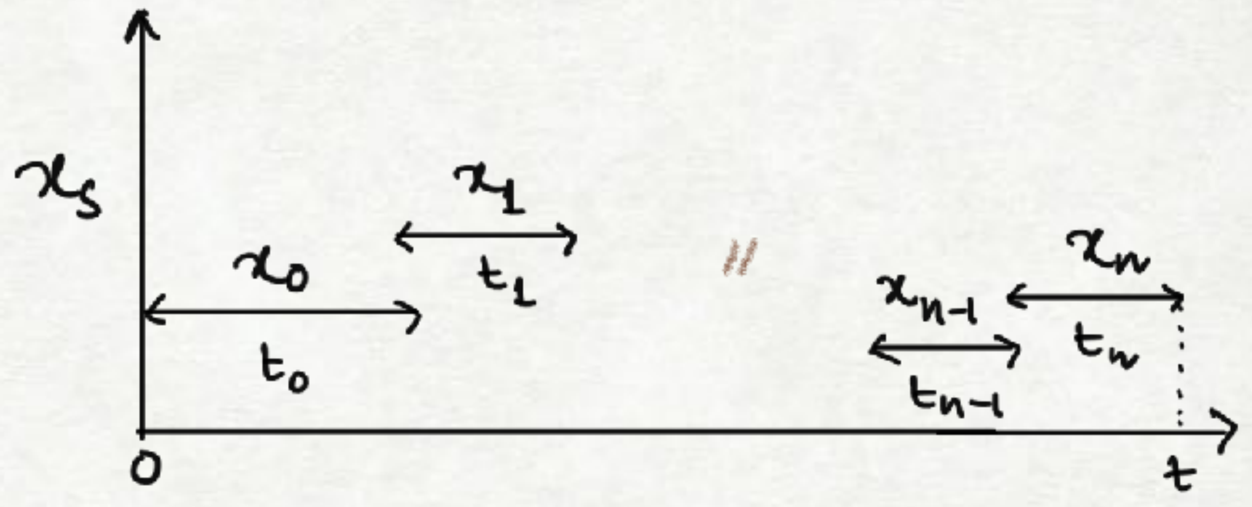
- Jump rate $k(x,y)$ from $x \to y$: probability of jump $k(x,y)\ dt$
- Escape rate $\lambda(x) = \sum_y k(x,y)$
- During $[0,t]$ trajectory $\omega = \{(x_0,t_0),(x_1,t_1),\ldots(x_n,t_n)\}$
- n-jumps, at intervals $\{t_i\}$
- Final configuration $x_n \equiv x_t$ and $\sum_{i=0}^{n} t_i = t$



- Probability of this trajectory $\omega = \{(x_0, t_0), (x_1, t_1), \ldots (x_n, t_n)\}$

$$P(\omega) \propto \rho(x_0) e^{-\lambda(x_0)t_0} \, k(x_0, x_1) e^{-\lambda(x_1)t_1} \, k(x_1, x_2) \ldots e^{-\lambda(x_n)t_n}$$

- Combining



$$P(\omega) \propto \rho(x_0) \prod_{i=0}^{n-1} k(x_i, x_{i+1}) e^{-\int_0^t \lambda(x_s) ds}$$

- Reference process: rate $k_0(x, y)$

$$P_0(\omega) \propto \rho(x_0) \prod_{i=0}^{n-1} k_0(x_i, x_{i+1}) e^{-\int_0^t \lambda_0(x_s) ds}$$

Same initial distribution

- Action wrt the reference process

$$A(\omega) = -\log \frac{P(\omega)}{P_0(\omega)}$$

$$= -\log \prod_i \frac{k(x_i, x_{i+1})}{k_0(x_i, x_{i+1})} + \int_0^t ds\ [\lambda(x_s) - \lambda_0(x_s)]$$

- Assumption for simplicity, $k_0(x, y) = 1$ for all nonzero $k(x, y)$

- No loss of generality - does not change any physical result (can be proven)

$$\boxed{A(\omega) = -\sum_i \log k(x_i, x_{i+1}) + \int_0^t ds\ [\lambda(x_s) - \lambda_0(x_s)]}$$

ACTION: TIME REVERSAL

- Time-reversed trajectory $\theta\omega = \{(x_n, t_n), (x_{n-1}, t_{n-1}), \ldots (x_0, t_0)\}$

- Probability

$$P(\theta\omega) \propto \rho(x_n) e^{-\lambda(x_n)t_n} \, k(x_n, x_{n-1}) \ldots k(x_1, x_0) e^{-\lambda(x_0)t_0}$$

- Similar form for $P_0(\theta\omega)$

- Action for the reversed path

$$A(\theta\omega) = -\log \prod_i \frac{k(x_{i+1}, x_i)}{k_0(x_{i+1}, x_i)} + \int_0^t ds \, [\lambda(x_s) - \lambda_0(x_s)]$$

ACTION: DECOMPOSITION

Decompose according to time-reversal symmetry

$$\boxed{A(\omega) = D(\omega) - \frac{1}{2} S(\omega)}$$

Time reversal: $\omega \to \theta\omega$

$$\boxed{\begin{aligned} D(\theta\omega) &= D(\omega) \\ S(\theta\omega) &= -S(\omega) \end{aligned}} \Rightarrow \boxed{\begin{aligned} S(\omega) &= A(\theta\omega) - A(\omega) \\ D(\omega) &= \frac{1}{2}\left[A(\theta\omega) + A(\omega)\right] \end{aligned}}$$

What are these quantities?

- Time anti-symmetric part $S(\omega)$: Entropy generated along the trajectory (local detailed balance)

- Time symmetric part $D(\omega)$: Frenesy [measure of `(dynamical) activity']

- Reference process defines a reference level - all quantities are in excess wrt it : physical results independent of choice of reference

JUMP PROCESS

$$A(\omega) = -\sum_i \log k(x_i, x_{i+1}) + \int_0^t ds\ [\lambda(x_s) - \lambda_0(x_s)]$$

- Entropy flux

$$S(\omega) = \sum_i \log \frac{k(x_i, x_{i+1})}{k(x_{i+1}, x_i)}$$

- Ratio of forward and backward jump rates, sum over all jumps

- Frenesy

$$D(\omega) = -\frac{1}{2}\sum_i \log k(x_i, x_{i+1})k(x_{i+1}, x_i) + \int_0^t ds\ [\lambda(x_s) - \lambda_0(x_s)]$$

Still assuming $k_0(x, y) = 1$,
defining reference level

TIME-ANTISYMETRIC TERM: ENTROPY

- Stationary nonequilibrium process
- Violation of time-reversal symmetry

$$\frac{P(\omega)}{P(\theta\omega)} = \frac{e^{-A(\omega)}\, P_0(\omega)}{e^{-A(\theta\omega)}\, P_0(\theta\omega)}$$

Still assuming $k_0(x, y) = 1$, defining reference level

- Identify with entropy

$$\log \frac{P(\omega)}{P(\theta\omega)} = S(\omega) + \underbrace{\log \rho(x_0) - \log \rho(x_t)}$$

Total entropy change of the universe

Entropy generated along the trajectory, released in the environment

Change in entropy of the system (Shanon-like sense)

- Time anti-symmetric part of action: entropy generated along the path
- Physical reason : Local detailed balance

Katz, Lebowitz, Spohn 1983

- Interaction with each reservoir happens in a (locally) detailed balanced way
- Weak coupling with reservoirs which are in equilibrium at all times
- If more than one, reservoirs are well separated (no interaction among themselves)
- For exchanges with the reservoir $\dfrac{k(x,y)}{k(y,x)} = \exp \Delta S$

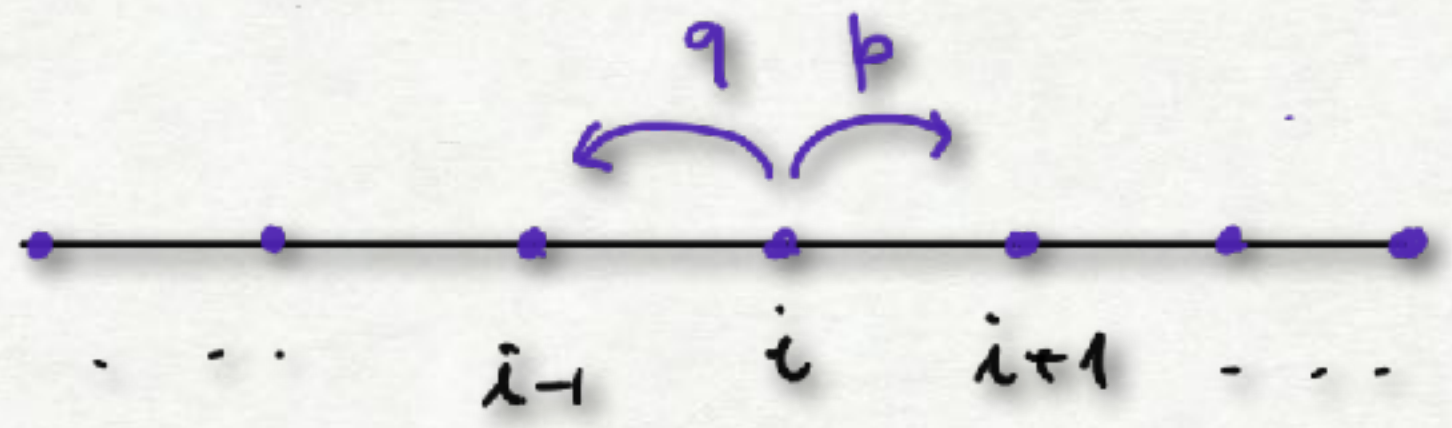
Does not hold if reservoirs are out of equilibrium

FRENESY

$$D(\omega) = -\frac{1}{2}\sum_i \log k(x_i, x_{i+1})k(x_{i+1}, x_i) + \int_0^t ds\ [\lambda(x_s) - \lambda_0(x_s)]$$

- Symmetric under time reversal
- Two components: jumps (traffic/dynamical activity) and escape rates
- Physical quantities: time-symmetric currents, dwelling times,…
- Kinetic (nonthermodynamic) information
- Crucial for nonequilibrium response

EXAMPLE: RANDOM WALK



- Biased random walk on 1D periodic lattice
- Driving field ε, jump rates $p(\varepsilon)$, $q(\varepsilon)$
- Local detailed balance $p/q = e^{\beta\varepsilon}$, does not specify the rates completely
- Trajectory $\omega = \{(x_0, t_0), (x_1, t_1), \ldots (x_n, t_n)\}$
- Number of jumps N_R, N_L, current $J = N_R - N_L$

Reference process: p=q=1

- Entropy flux

$$S(\omega) = \sum_i \log \frac{k(x_i, x_{i+1})}{k(x_{i+1}, x_i)} = (N_R - N_L)\log \frac{p}{q} = \beta\varepsilon\ J$$

- Frenesy

$$D(\omega) = -\frac{1}{2}\sum_i \log k(x_i, x_{i+1})k(x_{i+1}, x_i) + \int_0^t ds\ [\lambda(x_s) - \lambda_0(x_s)]$$

$$= -\frac{1}{2}(N_R + N_L)\log pq + (p + q - 2)t$$