Fluctuation relations and nonequilibrium thermodynamics – VII

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Stochastic non-equilibrium systems
Motivations

- “Simple” lattice systems
- Steady states depend on initial state, boundary conditions, and internal parameters
- Bulk and boundary perturbations may induce phase transition in steady state and dynamic behaviour
- Heat conduction, diffusion, sand pile models, avalanches, ....
Random walk on 1d-lattice

\[ P_l(t) \] probability that the particle is at site \( l \) at time \( t \)

\[
\frac{dP_l(t)}{dt} = W_+ P_{l-1} + W_- P_{l+1} - (W_+ + W_-) P_l = J_{l-1/2} - J_{l+1/2}
\]

\[
J_{l+1/2} = W_+ P_l - W_- P_{l+1}; \quad J_{l-1/2} = W_+ P_{l-1} - W_- P_l
\]
the asymmetric simple exclusion process (ASEP)

\[ n_l = 0, 1 \text{ occupation number, } \rho_l(t) \equiv \langle n_l(t) \rangle \]

\[
\frac{d\rho_l(t)}{dt} = \langle J_{l-1/2} - J_{l+1/2} \rangle
\]

\[
J_{l+1/2} = W_+ n_l (1 - n_{l+1}) - W_- n_{l+1} (1 - n_l)
\]

\[
J_{l-1/2} = W_+ n_{l-1} (1 - n_l) - W_- n_l (1 - n_{l-1})
\]
ASEP: mean field approximation

\[ \langle n_l(t) n_{l \pm 1}(t) \rangle = \langle n_l(t) \rangle \langle n_{l \pm 1}(t) \rangle = \rho_l(t) \rho_{l \pm 1}(t) \]

\[
\frac{d\rho_l(t)}{dt} = W_+ \rho_{l-1}(1 - \rho_l) + W_- \rho_{l+1}(1 - \rho_l) - W_+ \rho_l(1 - \rho_{l+1}) - W_- \rho_l(1 - \rho_{l-1})
\]

\[
\frac{d\rho_0(t)}{dt} = \alpha(1 - \rho_0) + W_- \rho_1(1 - \rho_0) - \gamma \rho_0 - W_+ \rho_0(1 - \rho_1)
\]

\[
\frac{d\rho_N(t)}{dt} = \delta(1 - \rho_N) + W_+ \rho_{N-1}(1 - \rho_N) - \beta \rho_N - W_- \rho_N(1 - \rho_{N-1})
\]

\[ a = L/N, \; x = la, \; \nu = a(W_+ - W_-), \; \mu = a^2(W_+ + W_-)/2 \]

\[
\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left( \mu \frac{\partial \rho}{\partial x} - \nu \rho (1 - \rho) \right)
\]
ASEP: mean field approximation II

Steady state: $\partial_t \rho = 0$

Boundary conditions

\[
0 = \alpha(1 - \rho_0) + W_- \rho_1(1 - \rho_0) - \gamma \rho_0 - W_+ \rho_0(1 - \rho_1)
\]

\[
0 = \delta(1 - \rho_N) + W_+ \rho_{N-1}(1 - \rho_N) - \beta \rho_N - W_- \rho_N(1 - \rho_{N-1})
\]

\[
\rho(0) = \frac{W_+ - W_- + \alpha + \gamma - \sqrt{(\alpha - \gamma - W_+ + W_-)^2 + 4\alpha\gamma}}{2(W_+ - W_-)}
\]

\[
\rho(L) = \frac{W_+ - W_- - \beta - \delta + \sqrt{\beta - \delta - W_+ + W_-)^2 + 4\beta\delta}}{2(W_+ - W_-)}
\]
$N = 100, W_+ = 1, W_- = 0.75, \rho_A = 0.75, \rho_B = 0.25,$
Phase diagram

A: low density phase, B: high density phase, C: high current phase

Schütz and Domany, 1993
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Fluctuation theorems can be interpreted as giving connections between the probability of entropy-generating trajectories with respect to that of entropy-annihilating trajectories.
Heat Fluctuation: Motivations

- The concept of entropy is usually associated with probability distributions (ensembles) via Gibbs’ formula.

- In nonequilibrium systems one can consistently define the entropy production along a single trajectory, *Crooks PRE 1999, 2000; Qian PRE 2001; Seifert PRL 2005.*

- Fluctuation theorems can be interpreted as giving connections between the probability of entropy-generating trajectories with respect to that of entropy-annihilating trajectories.

- The entropy flow along a given trajectory is experimentally accessible, *Tietz et al. PRL 2006*
A stochastic system is described by a Markovian dynamics

\[
\frac{dp_i(t)}{dt} = \sum_{j \neq i} \left[ W_{ij}(t)p_j(t) - W_{ji}(t)p_i(t) \right]
\]

Path \( \omega \): \( \omega(t) = i_k \) if \( t_k \leq t < t_{k+1} \), \( k = 0, 1, \ldots, M \),
\( t_{M+1} = t_f \)

Time-reversed path \( \tilde{\omega} \): \( \tilde{\omega}(t) = i_k \) if \( \tilde{t}_{k+1} \leq t < \tilde{t}_k \),
\( \tilde{t} = t_0 + t_f - t \)

\( \mathcal{P}(\omega), \tilde{\mathcal{P}}(\tilde{\omega}) \): probability of the forward and of the time-reversed path (conditioned by their initial states)

\[
Q(\omega) = -\ln \left( \frac{\mathcal{P}(\omega)}{\tilde{\mathcal{P}}(\tilde{\omega})} \right) = -\sum_{k=1}^{M} \ln \left( \frac{W_{i_k i_{k-1}^{-1}}(t_k)}{W_{i_{k-1}^{-1} i_k}(t_k)} \right).
\]
Entropy flow and entropy production

Gibbs entropy of the system \( S(t) = -\sum_i p_i(t) \ln p_i(t), \quad (k_B = 1). \)

\[
\frac{dS}{dt} = - \sum_{i \neq j} W_{ij} p_j \ln \left( \frac{W_{ji} p_i}{W_{ij} p_j} \right) - \sum_{i \neq j} W_{ij} p_j \ln \frac{W_{ij}}{W_{ji}}.
\]

- The first sum is non-negative (\( \ln x \leq x - 1 \)): entropy production rate
- The second sum defines the entropy \( S_f \) flowing into the reservoir
- \( \langle Q \rangle_t \) : average of \( Q(\omega) \), over all possible paths up to time \( t \)
- \( d \langle Q \rangle_t / dt = dS_f / dt \)
\[ Q(\omega) \text{ as heat exchange} \]

\[ Q(\omega) = -\ln \left( \frac{\mathcal{P}(\omega)}{\bar{\mathcal{P}}(\bar{\omega})} \right) = -\sum_{k=1}^{M} \ln \left[ \frac{W_{i_k i_{k-1}}(t_k)}{W_{i_{k-1} i_k}(t_k)} \right]. \]

If the detailed balance conditions hold for the transition rates \( W_{ij}(t) \), and an energy \( E_i(t) \) is associated to the system states

\[ W_{ji}(t)/W_{ij}(t) = \exp \left\{ \left[ E_i(t) - E_j(t) \right] / T \right\} \]

\( T \ln \left[ W_{ji}(t)/W_{ij}(t) \right] \) represents the heat exchanged with the reservoir in the jump from state \( j \) to state \( i \).

\( Q(\omega) \) is the heat exchanged with the reservoir along the trajectory \( \omega \).
Joint probability distribution $\phi_i(Q, t)$, that the system is found at time $t$ in state $i$, having exchanged a total entropy flow $Q$

$\Delta s_{ij} = \log [W_{ji}(t)/W_{ij}(t)]:$ entropy which flows into the reservoir in the jump $j \rightarrow i$

$$\phi_i(Q, t + \tau) \simeq \phi_i(Q, t) + \tau \sum_{j \neq i} W_{ij} \phi_j(Q - \Delta s_{ij}, t) - W_{ji} \phi_i(Q, t)$$

$$= \phi_i(Q, t) + \tau \sum_{j \neq i} \left\{ W_{ij} \left[ \sum_{n=0}^{\infty} \frac{(-\Delta s_{ij})^n}{n!} \frac{\partial^n \phi_j(Q,t)}{\partial Q^n} \right] - W_{ji} \phi_i(Q, t) \right\},$$

Differential equation for $\phi_i(Q, t)$:

$$\frac{\partial \phi_i(Q, t)}{\partial t} = \sum_{j \neq i} \left\{ W_{ij} \left[ \sum_{n=0}^{\infty} \frac{(-\Delta s_{ij})^n}{n!} \frac{\partial^n \phi_j(Q,t)}{\partial Q^n} \right] - W_{ji} \phi_i(Q, t) \right\}.$$
\[
\psi_i(\lambda, t) = \int dQ \ e^{\lambda Q} \phi_i(Q, t),
\]
\[
\frac{\partial \psi_i(\lambda, t)}{\partial t} = \sum_{j \neq i} \left[ W_{ij} \left( \frac{W_{ji}}{W_{ij}} \right)^\lambda \psi_j(\lambda, t) - W_{ji} \psi_i(\lambda, t) \right]
\]
\[
= \sum_j H_{ij}(\lambda) \psi_j(\lambda, t).
\]


\( g(\lambda) \) M.E. of \( H_{ij}(\lambda) \), in the limit \( t \to \infty \), \( \psi(\lambda, t) = \exp \left[ tg(\lambda) \right] \)

\[
\phi(Q, t) = \int \frac{d\lambda}{2\pi i} e^{-\lambda Q} \psi(\lambda, t) \propto e^{t g(\lambda^*) - \lambda^* Q}
\]

\( \lambda^* \) saddle point value implicitly defined by \( \partial g/\partial \lambda |_{\lambda^*} = Q/t \).
Perron–Frobenius theorem

Let $M$, an $n \times n$ matrix with positive entries $m_{ij} > 0$. Then the following statements hold:

- There is a positive real eigenvalue $\alpha^*$ of $M$ such that $|\alpha_i| < \alpha^*$.
- The eigenvalue $\alpha^*$ is simple.
- $v_R$ right eigenvector: $M \cdot v_R = \alpha^* v_R$, with $v_R^i > 0$.
- Eigenvalue estimate: $\min_i \sum_j M_{ij} \leq \alpha^* \leq \max_i \sum_j M_{ij}$.
Maximum eigenvalue

\[ \dot{\psi}(\lambda, t) = H(\lambda)\psi(\lambda, t) \quad \Rightarrow \quad \psi(\lambda, t) = e^{H(\lambda)t}\psi(\lambda, t = 0) \]

\[ \psi(\lambda, t = 0) = \sum_i c_i \psi_i \quad \Rightarrow \quad \psi(\lambda, t) = \sum_i c_i \psi_i e^{\alpha_i(\lambda)t} \]

\[ \psi(\lambda, t \rightarrow \infty) \propto \psi_{\text{max}} e^{g(\lambda)t} \]

\[ \psi(\lambda, t) = \int dQ e^{\lambda Q} \Phi(Q) = \sum_j \int dQ e^{\lambda Q} \phi_j(Q, t) \]

\[ = \sum_j \psi_j(\lambda, t) \quad t \rightarrow \infty \quad e^{g(\lambda)t} \]
Gallavotti–Cohen relation

\[ H_{ij}(\lambda) = W_{ij} \left( \frac{W_{ji}}{W_{ij}} \right)^\lambda \]
\[ \frac{H(1 - \lambda)}{H^T(\lambda)} \]
\[ \phi(Q, t) = \int \frac{d\lambda}{2\pi i} e^{-\lambda Q} \psi(\lambda, t) \propto e^{t g(\lambda^*) - \lambda^* Q}; \quad \partial g / \partial \lambda |_{\lambda^*} = Q/t \]
\[ e^{-Q} \phi(-Q, t) = e^{-Q} \int \frac{d\lambda}{2\pi i} e^{\lambda Q} \psi(\lambda, t) = - \int \frac{d\lambda'}{2\pi i} e^{-\lambda' Q} \psi(1 - \lambda', t) \]
\[ \propto e^{t g(\lambda^*) - \lambda^* Q} \quad \lambda' = 1 - \lambda \]

\[ \phi(Q, t) / \phi(-Q, t) = e^{-Q}, \text{ for, } t \to \infty \]
Comparison with experiments


- Two-state system: an optically driven defect center in diamond
- If excited by a red light laser, the defect exhibits fluorescence.
- By superimposing a green light laser, the rate of transition from the non-fluorescent to the fluorescent state ($W_+$) and from the fluorescent to the non-fluorescent state ($W_-$), turn out to depend linearly on the laser's intensity.
Comparison with experiments

the experimental set-up

\[ W_- = (21.8 \text{ ms})^{-1}, \quad W_+(t) = W_0 [1 + \gamma \sin(2\pi t/t_m)], \]

\[ W_0 = (15.6 \text{ ms})^{-1}, \quad \gamma = 0.46, \quad t_m = 50 \text{ ms}. \]

entropy flux measured, over 2000 trajectories of
time-length \(20 t_m\).

Solve the equation for \(\psi_+, \psi_-\),
and compute

\[ \phi(q, t) \propto \exp \left[ t g(\lambda^*) - \lambda^* Q \right], \]

where

\[ g(\lambda) = \frac{1}{t} \log \left[ \psi_+(\lambda, t) + \psi_-(\lambda, t) \right] \]

in the limit \(t \to \infty\).
Large systems

- $N$ equations for the $\phi_i(Q)$ or the $\psi_i(\lambda)$: the direct approach becomes rapidly impracticable, as the system phase space size increases.

- Evaluation of $\phi(Q)$ by direct simulation of the stochastic process described by the master equation: highly difficult task, since one is interested in the tails of the distribution (rare events).

- Solution: sample trajectories in the weighted ensemble $P(\omega_t) \exp[\lambda Q(\omega_t)]$ rather than successions of single states in the unbiased ensemble.
Since \( \psi(\lambda, t) = \int D\omega_t \, \mathcal{P}(\omega_t) \, e^{\lambda Q(\omega_t)} \)
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We have

\[
\frac{\partial \psi(\lambda, t)}{\partial \lambda} = \int D\omega_t Q(\omega_t) \mathcal{P}(\omega_t) e^{\lambda Q(\omega_t)} = \langle Q \rangle_\lambda \psi(\lambda, t)
\]
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\]

\( \langle \ldots \rangle_{\lambda} \) is the average in the weighted ensemble

\( \mathcal{P}(\omega_t) \exp[\lambda Q(\omega_t)] / \psi(\lambda, t) \)
**Biased trajectories**

- Since \( \psi(\lambda, t) = \int D\omega_t \, P(\omega_t) \, e^{\lambda Q(\omega_t)} \)

- We have
  \[
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  \]

- \( \langle \ldots \rangle_\lambda \) is the average in the weighted ensemble \( P(\omega_t) \exp[\lambda Q(\omega_t)] / \psi(\lambda, t) \)

- \( \psi(\lambda, t) = Z_\lambda \) is the “partition function” of this ensemble,
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The solution reads: \( \psi(\lambda, t) = \exp \left[ \int_0^\lambda d\lambda' \langle Q \rangle_{\lambda'} \right] \)
Biased trajectories

Since \( \psi(\lambda, t) = \int \mathcal{D} \omega_t \, \mathcal{P}(\omega_t) \, e^{\lambda Q(\omega_t)} \)

We have
\[
\frac{\partial \psi(\lambda, t)}{\partial \lambda} = \int \mathcal{D} \omega_t \, Q(\omega_t) \mathcal{P}(\omega_t) \, e^{\lambda Q(\omega_t)} = \langle Q \rangle_{\lambda} \psi(\lambda, t)
\]

\( \langle \ldots \rangle_{\lambda} \) is the average in the weighted ensemble
\( \mathcal{P}(\omega_t) \exp [\lambda Q(\omega_t)] / \psi(\lambda, t) \)

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The solution reads:
\[
\psi(\lambda, t) = \exp \left[ \int_{0}^{\lambda} d\lambda' \, \langle Q \rangle_{\lambda'} \right]
\]

\[
\langle Q \rangle_{\lambda} = \frac{\int \mathcal{D} \omega_t \, (Q(\omega_t)/\Pi(\omega_t))\Pi(\omega_t)\mathcal{P}(\omega_t)e^{\lambda Q(\omega_t)}}{\int \mathcal{D} \omega_t \, (1/\Pi(\omega_t))\Pi(\omega_t)\mathcal{P}(\omega_t)e^{\lambda Q(\omega_t)}} = \frac{\langle Q/\Pi \rangle_{\lambda, \Pi}}{\langle 1/\Pi \rangle_{\lambda, \Pi}}
\]

\( \langle \ldots \rangle_{\lambda, \Pi} \) is the average in the \( \mathcal{P}(\omega_t)\Pi(\omega_t) \exp [\lambda Q(\omega_t)] \) ensemble
Probability of a given path $\omega$: $\mathcal{P}(\omega) = K_{i_N, i_{N-1}} K_{i_N, i_{N-2}} \ldots K_{i_1, i_0} p_{i_0}^0$

transition probabilities $K_{ij} = \tau W_{ij}$, and $K_{ii} = 1 - \sum_j (\neq i) K_{ji}$

Define the new transition probabilities $\tilde{K}_{ij} = \tau W_{ij} (W_{ji} / W_{ij})^\lambda$, and $\tilde{K}_{ii} = 1 - \sum_j (\neq i) \tilde{K}_{ji}$

$\Pi(\omega) = \prod_{k=1}^M \Pi_{i_k, i_{k-1}}(t_k)$ with

$$\Pi_{ij}(t) = \begin{cases} 1, & \text{if } i \neq j; \\ \tilde{K}_{jj}(t) / K_{jj}(t), & \text{if } i = j. \end{cases}$$

$\mathcal{P}(\omega)\Pi(\omega) \exp[\lambda Q(\omega)] = \tilde{K}_{i_N, i_{N-1}} \tilde{K}_{i_N, i_{N-2}} \ldots \tilde{K}_{i_1, i_0} p_{i_0}^0$,

Evaluate $\langle Q \rangle_\lambda = \frac{\langle Q / \Pi \rangle_\lambda, \Pi}{\langle 1 / \Pi \rangle_\lambda, \Pi}$
the asymmetric simple exclusion process (ASEP)

By taking $\rho_A > \rho_B$ and $W_+ > W_-$, one observes a net particle current from the left to the right reservoir. $L = 100$, $W_+ = 1$, $W_- = 0.75$, $\rho_A = 0.75$, $\rho_B = 0.25$, maximum current phase

\[ \psi(\lambda, t) = \exp \left[ \int_{0}^{\lambda} d\lambda' \langle Q \rangle_{\lambda'} \right] \]

\[ g(\lambda) = \frac{1}{t} \log [\psi(\lambda, t)] \text{ in the long } t \text{ limit.} \]
Comparison with simulations

entropy flow per time unit $q = Q/t$, corresponding to 1000 unbiased trajectories.

$$f(q) = \log [\phi(q)]$$ and $$f(q) + q$$ exhibit the symmetry required by the Gallavotti-Cohen relation

$$\phi(Q)/\phi(-Q) = \exp(Q)$$

Typical trajectories

current $J(\lambda)$ of particles that, in the steady state of weighted ensembles, jump to the right (positive current) or to the left (negative current), in the unit time. Measured as biased trajectories are generated
the parameter $\lambda$, which is the thermodynamic conjugate of $q$, selects dynamical trajectories in the same way as an external field selects states in an ordinary statistical ensemble

$$f(q) \equiv g(\lambda^*) - \lambda^* q = \lim_{t \to \infty} \frac{1}{t} \log \phi(Q, t).$$

the functions $g(\lambda)$ and $f(q)$ are Legendre transform of each other, and can be then interpreted in terms of path thermodynamics: $g(\lambda)$ can be viewed as a path Gibbs free energy, while $f(q)$ is the corresponding Helmholtz free energy.

The Totally Asymmetric Exclusion Process (TASEP)

At any given time step $t$, a given particle moves to the right with probability $\alpha$ if the target site is empty.

Configuration $C = (n_i)$, $n_i \in \{0, 1\}$, $i = 1, L$, periodic b.c.

Current $J$:

$$J_{C'C} = \begin{cases} 1, & \text{if one particle jumps to the right;} \\ 0, & \text{if nothing happens.} \end{cases}$$

We wish to evaluate

$$e^{\Lambda(\lambda)} = \langle \exp \left( \lambda \sum_t J_{t+1} c_t \right) \rangle$$
The large-deviation function

\[ \text{Prob}[C_0, C_1, \ldots, C_T] = U_{C_T} C_{T-1} \cdots U_{C_2} C_1 \cdot U_{C_1} C_0 \]

\[ e^{\Lambda(\lambda)} = \sum_{C_1, \ldots, C_T} \tilde{U}_{C_T} C_{T-1} \cdots \tilde{U}_{C_1} C_0 = \sum_{C_T} \left[ \tilde{U}^T \right]_{C_T} C_0 \]

where

\[ \tilde{U}_{C'C} := e^{\lambda J_{C'C}} U_{C'C} \]

Define

\[ K_C := \sum_{C'} \tilde{U}_{C'C}, \quad U_{C'C} \equiv \tilde{U}_{C'C} K_C^{-1} \]

\[ e^{\Lambda(\lambda)} = \sum_{C_2, \ldots, C_T} U'_{C_T} C_{T-1} K_{C_{T-1}} \cdots U'_{C_1} C_0 K_{C_0} \]
The simulation steps

A cloning step:

\[ P_c(t + 1/2) = K_c P_c(t) \]

\( G \) clones of \( C \):

\[ G = \begin{cases} 
[K_c] + 1, & \text{with probability } K_c - [K_c]; \\
[K_c], & \text{otherwise}
\end{cases} \]
The simulation steps

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[K_c], & \text{otherwise}
\end{cases} \]

- A shift step:

\[ P_{c'}(t + 1) = \sum_{c} U'_{c',c} P_c(t + 1/2) \]
The simulation steps

- A cloning step:

\[ P_c(t + 1/2) = K_c P_c(t) \]

\( G \) clones of \( C \):

\[ G = \begin{cases} [K_c] + 1, & \text{with probability } K_c - [K_c]; \\ [K_c], & \text{otherwise} \end{cases} \]

- A shift step:

\[ P_{c'}(t + 1) = \sum_c U'_{c'c} P_c(t + 1/2) \]

- Overall cloning step with an adjustable rate:

\[ M_t = N/(N + G) \] (the same for all configurations)
For long times

\[ -\lim_{t \to \infty} \frac{1}{t} \ln[M_T \cdots M_2 \cdot M_1] = \lim_{t \to \infty} \frac{\Lambda(\lambda)}{t} = \sigma(\lambda) \]
The configurations

Space-time diagram for a ring of $N = 100$ sites, $\lambda = -50$ and density 0.5

Note the logarithmic scale on the $y$-axis
Moving shock waves

Space-time diagram for a ring of $N = 100$ sites, $\lambda = -30$ and density $0.3$
Biased dynamics is effective to reconstruct entropy flow distributions of systems with many states.
Discussion

- Biased dynamics is effective to reconstruct entropy flow distributions of systems with many states.
- Entropy distributions can be used to reconstruct thermodynamic equilibrium quantities.
Biased dynamics is effective to reconstruct entropy flow distributions of systems with many states.

Entropy distributions can be used to reconstruct thermodynamic equilibrium quantities.

Gene regulation networks, signal processing networks, molecular motors with many states.


