Fluctuation relations and nonequilibrium thermodynamics – VI

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Towards nonequilibrium thermodynamics?

Fluctuation theorem

Transition probabilities depending on a parameter μ:

$$\sum_{x'} W_{xx'}(\mu) p^{\mathrm{ss}}(x', \mu) = p^{\mathrm{ss}}(x, \mu)$$

$W_{xx'}(0)$ satisfies detailed balance

$$\begin{aligned}
\Delta S_{xx'} &= \ln \frac{W_{xx'}}{W_{x'x}} \\
\Psi(x, \lambda, t+1) &= \sum_{x'} W_{xx'} \left(\frac{W_{xx'}}{\widehat{W}_{x'x}} \right)^{\lambda} \Psi(x', \lambda, t) \\
\Psi(x, \lambda, t) &\sim \mathrm{e}^{-t\psi(\lambda)} \\
\psi_{\mu}(-\lambda) &= \psi_{\mu}(\lambda - 1)
\end{aligned}$$

Steady states near equilibrium

Entropy production vanishes as $\mu \to 0$

$$\Delta S_{xx'} = \mu J_{xx'} + \mathrm{o}(\mu)$$

Generating function of the fluctuations of J:

$$\begin{aligned}
\pi_\mu(\lambda) &= -\lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \ln \left\langle \mathrm{e}^{\lambda \int_0^{\mathcal{T}} \mathrm{d}t\ J(t)} \right\rangle^{\mathrm{ss}} \\
\pi_\mu(\lambda) &\simeq \psi_\mu\left(\frac{\lambda}{\mu}\right) \\
\langle J \rangle^{\mathrm{eq}} &= 0 \quad \Leftrightarrow \quad \pi_\mu(\lambda) = \frac{1}{2} a\lambda^2 + b\lambda\mu + \text{higher orders} \\
\psi_\mu\left(-\frac{\lambda}{\mu}\right) &= \psi_\mu\left(\frac{\lambda}{\mu} - 1\right) \quad \Leftrightarrow \quad \pi_\mu(-\lambda) = \pi_\mu(\lambda - \mu)
\end{aligned}$$

Fluctuation theorem vs. FDR

$$\pi_\mu(\lambda) = \frac{1}{2} a\,\lambda(\lambda - \mu)$$

Fluctuation-dissipation relation (FDR): for $\lambda, \mu \to 0$,

$$\boxed{\frac{\partial^2 \pi}{\partial\lambda\,\partial\mu} = \frac{1}{2}\frac{\partial^2 \pi}{\partial \lambda^2}}$$

Green-Kubo formula:

$$\lim_{\mu\to 0} \frac{\partial \left\langle J \right\rangle^{\mathrm{ss}}}{\partial \mu} = \lim_{\mathcal{T}\to\infty} \frac{1}{2\mathcal{T}} \int_0^{\mathcal{T}} \mathrm{d}t\,\mathrm{d}t' \left\langle J(t) J(t') \right\rangle^{\mathrm{eq}}$$

Onsager's reciprocity

$$\mu = (\mu_i) \qquad J = (J_i)$$

$$\begin{aligned} L_{ij} &= \lim_{\mu \to 0} \frac{\partial \langle J_i \rangle^{\mathrm{ss}}}{\partial \mu_j} \\ &= \lim_{\mathcal{T} \to \infty} \frac{1}{2\mathcal{T}} \int_0^{\mathcal{T}} \mathrm{d}t \, \mathrm{d}t' \, \langle J_i(t) J_j(t') \rangle^{\mathrm{eq}} \\ &= L_{ji} \end{aligned}$$

The fluctuation theorem can be considered as the extension to nonequilibrium steady states of the FDR and Onsager's reciprocity relations

Gallavotti, 1996

Equilibrium thermodynamics: Postulates

0th law: Stable thermodynamic states are characterized by E, (X_i)

1st law: There is a 1-form (heat) $\not{d}Q$ such that

$$\not{d}Q = \mathrm{d}E - \sum_i f_i \, \mathrm{d}X_i$$

and transformations with $\not{d}Q = 0$ are realizable (reversible adiabatics)

2nd law: In any neighborhood of a given state there are states which *cannot* be reached by reversible adiabatic processes

Carathéodory's theorem

There is an integrating factor $1/T$ such that

$$\not{\mathrm{d}}Q/T = \mathrm{d}S$$

where S is a state function *Carathéodory, 1909*

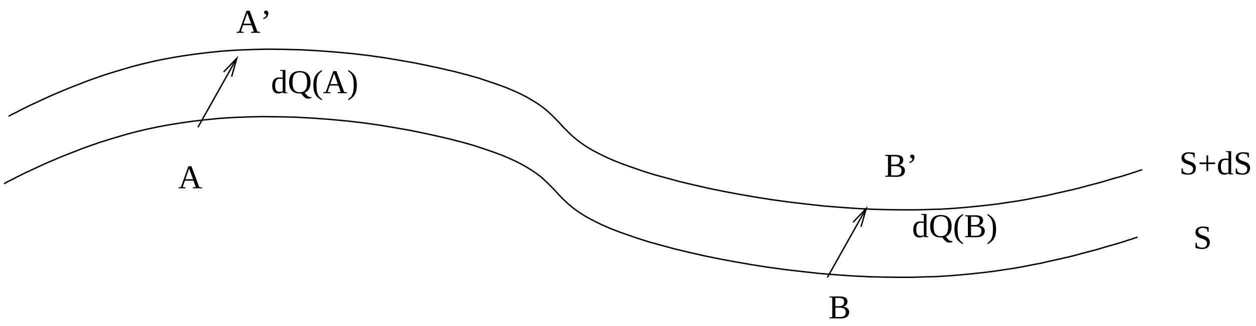
- *Proof:* Let $A \sim B$ if one can go $A \longrightarrow B$ with $\not{\mathrm{d}}Q = 0$
- $A \sim B$ is an equivalence relation:

$$A \sim A \qquad A \sim B \Rightarrow B \sim A \qquad A \sim B \,\&\, B \sim C \Rightarrow A \sim C$$

- $\exists S(X)$ such that if $A \sim B$, $S(A) = S(B)$ and $\mathrm{d}S = 0 \;\Leftrightarrow \not{\mathrm{d}}Q = 0$

Entropy and temperature

- If $A \sim A'$ & $B \sim B'$, $S(A') - S(A) = S(B') - S(B)$



- Thus if T is defined such that $\not{d}Q(A \longrightarrow B)/\not{d}Q(A' \longrightarrow B') = T(A)/T(B)$ we have $\mathrm{d}S = \not{d}Q/T$

Nonequilibrium thermodynamics

Oono and Paniconi, 1998

- Equilibrium (e) variables: E, X_i (extensive)
- The nonequilibrium state is characterized by *additional* nonequilibrium (n) variables Y_i
- $(X_i, Y_i) = (Z_i)$

Slow processes in equilibrium vs. nonequilibrium:

- Equilibrium: $\dot{S}^{\mathrm{tot}} \propto \Delta t^{-2} \quad \Rightarrow \quad \Delta S^{\mathrm{tot}} \propto \Delta t^{-1}$
- Nonequilibrium: $\dot{S}^{\mathrm{tot}} \simeq$ const. $\quad \Rightarrow \quad \Delta S \simeq \Delta t$ and $\Delta(\Delta S) \simeq$ const
- Quasisteady process:

$$\Delta S^{\mathrm{tot}} - \Delta S^{\mathrm{hk}} = \Delta S^{\mathrm{ex}} \text{ is minimal}$$

- "Adiabatic" process: $\Delta \dot{S}^{\mathrm{ex}} = 0$

Postulates

S0: Steady states are characterized by the extensive variables $(E, Z_i) = (E, X_i, Z_i)$

S1: There is a form $\not{d}Q^{\mathrm{ex}} = \mathrm{d}E - \sum_i h_i \, \mathrm{d}Z_i$, and $\not{d}Q^{\mathrm{ex}}$ is realizable (“adiabatic” processes)

S2: In any neighborhood of a state, there are states which *cannot be reached* by quasisteady “adiabatic” processes

Generalized Kelvin postulate:

S2T: A process converting work into excess heat is not inversible

Nonequilibrium entropy

- There is Σ and θ such that $\not{d}Q^{\mathrm{ex}} = \theta\,\mathrm{d}\Sigma$
- Thus

$$\mathrm{d}E = \theta\,\mathrm{d}\Sigma + \sum_i f_i\,\mathrm{d}X_i + \sum_i g_i\,\mathrm{d}Y_i$$

  where E is the total energy of the system, and Σ the "entropy"

By **S2T**, a spontaneous change satisfies $\Delta\Sigma > \not{d}Q^{\mathrm{ex}}/\theta$

Stability criterium: a state is stable if for all neighboring states one has

$$\mathrm{d}\Sigma \leq \not{d}Q^{\mathrm{ex}}/\theta = \theta^{-1}\left[\mathrm{d}E - \sum_i \left(f_i\,\mathrm{d}X_i + g_i\,\mathrm{d}Y_i\right)\right]$$

Stability

$$\Omega_{ij} = \left(\frac{\partial h_i}{\partial Z_j}\right)_{Z'_j}$$

$$\sum \Omega_{ij}\xi_i\xi_j \geq 0 \qquad \forall \xi = (\xi_i)$$

Generalized Le Chatelier-Braun principle: the change in an extensive quantity can only become larger (in absolute value) if one holds fixed *intensive* quantities rather than *extensive* ones

Thus, e.g.:

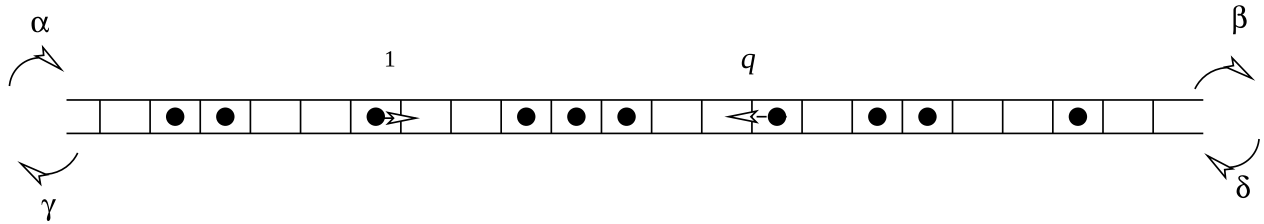
$$\left(\frac{\partial h_i}{\partial Z_i}\right)_{Z_j} \leq \left(\frac{\partial h_i}{\partial Z_i}\right)_{g_j} \qquad \forall i, j$$

Comments

- There have been several attempts to define a nonequilibrium entropy: Gibbs, coarse-grained entropy, Jou, etc.
- The usefulness of an entropy concept is related to its connections with energetic concepts ($\not{d}Q$)
- Operational definition is problematic
- The probability interpretation of the entropy should *follow* rather than be postulated

Examples of steady states

The Asymmetric Exclusion Process:



Probability of a microstate:

$$
\begin{aligned}
\tau_i &= 0,1 \qquad i=1,\ldots,L \\
\mathrm{Prob}(\tau_1,\ldots,\tau_L) &= \frac{\langle +|\, X_1 X_2 \cdots X_L \,|-\rangle}{\langle +|\,(D+E)^L\,|-\rangle} \\
X_i &= \tau_i D + (1-\tau_i) E \\
DE - qED &= D + E \\
\langle +|\,(\alpha E - \gamma D) &= \langle +| \\
(\beta D - \delta\, E)\,|-\rangle &= |-\rangle
\end{aligned}
$$

The large-deviation function

Coarse-grained density: $n = L/\ell$ boxes of size ℓ

$$\begin{aligned} \rho &= (\rho_1, \ldots, \rho_n) \\ \ell \rho_k &= \sum_{i=k\ell+1}^{(k+1)\ell} \tau_i \\ \mathrm{Prob}(\rho_1, \ldots, \rho_n) &\propto \mathrm{e}^{-L\, F(\rho_1, \ldots, \rho_L)} \end{aligned}$$

E.g., if $q = 0$ (TASEP):

$$\begin{aligned} B(\rho_i, p_i) &= D(\rho_i \| p_i) \\ F(\rho) &= \inf_{0<y<1} \left\{ \int_0^y \mathrm{d}x \left(B(\rho(x), \rho_a) + \log \frac{\rho_a(1-\rho_a)}{\langle J \rangle} \right) \right. \\ &\quad \left. \int_y^1 \mathrm{d}x \left(B(\rho(x), \rho_b) + \log \frac{\rho_b(1-\rho_b)}{\langle J \rangle} \right) \right\} \end{aligned}$$

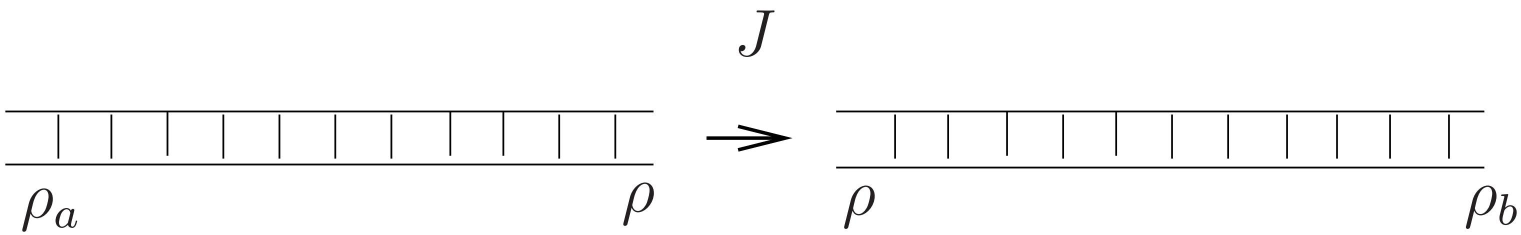
Sometimes nonconvex!

B. Derrida, J. L. Lebowitz, E. R. Speer, 2002

The additivity principle

- $F_L(J, \rho_a, \rho_b)$: large-deviation function of the *current* J with b.c. ρ_a on the left, ρ_b on the right
- For large $\mathcal{T}$, the current is the same on the left- and right-hand side of the system

$$\mathrm{Prob}_{L_1+L_2}(J, \rho_a, \rho_b) = \max_{\rho} \left(\mathrm{Prob}_{L_1}(L, \rho_a, \rho)\mathrm{Prob}_{L_2}(J, \rho, \rho_b)\right)$$



- In terms of the large-deviation function:

$$F_{L_1+L_2}(J, \rho_a, \rho_b) = \inf_{\rho} \left[F_{L_1}(J, \rho_a, \rho) + F_{L_2}(J, \rho, \rho_b)\right]$$

The Hatano-Sasa relation

$$\left\langle \mathrm{e}^{-[\Delta \mathcal{S}^{\mathrm{ex}} + \Delta S]} \right\rangle_0^{\mathrm{ss}} = 1$$

By Jensen's inequality

$$\langle \Delta \mathcal{S}^{\mathrm{ex}} \rangle + \Delta \langle S \rangle \geq 0$$

A “nonequilibrium” form of the 2nd law for the change in steady states

Note that the *excess* entropy appears in the inequality

Entropy production in the steady state

Detailed fluctuation relation:

$$\frac{\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}]}{\mathcal{P}[\boldsymbol{x}]} = \mathrm{e}^{-\Delta\mathcal{S}^{\mathrm{tot}}[\boldsymbol{x}]}$$

Driving force $\propto \mu$:

$$\lim_{\mu\to 0} p^{\mathrm{ss}}(x,\mu) = p^{\mathrm{eq}}(x,\mu)$$

Average entropy production:

$$\begin{aligned} \sigma(\mu) &= \lim_{\mathcal{T}\to\infty} \frac{1}{T} \left\langle \mathcal{S}[\boldsymbol{x}] \right\rangle^{\mathrm{ss}} \\ \sigma(0) &= 0 \end{aligned}$$

Approximate expression for the steady-state distribution

Komatsu and Nakagawa, 2007

Define the excess entropy:

$$\mathcal{S}^{\mathrm{ex}}[\boldsymbol{x}] = \mathcal{S}[\boldsymbol{x}] - \left\langle \dot{\mathcal{S}} \right\rangle^{\mathrm{ss}} \mathcal{T} = \mathcal{S}[\boldsymbol{x}] - \sigma(\mu)\, \mathcal{T}$$

Then the steady-state distribution is given by

$$\begin{aligned} p^{\mathrm{ss}}(x,\mu) &\propto \mathrm{e}^{\Phi(x,\mu)+\mathrm{O}(\mu^3)} \\ \Phi(x,\mu) &= \lim_{\mathcal{T}\to\infty} \frac{1}{2} \left[\left\langle \delta(x(\mathcal{T}) - x) \mathcal{S}^{\mathrm{ex}}[\boldsymbol{x}] \right\rangle^{\mathrm{ss}} \right. \\ &\qquad \left. - \left\langle \delta(x(0) - \widehat{x}) \mathcal{S}^{\mathrm{ex}}[\boldsymbol{x}] \right\rangle^{\mathrm{ss}} \right] \end{aligned}$$

Derivation I

Detailed fluctuation theorem:

$$\frac{\mathcal{P}_\mu[\boldsymbol{x} \mid x(0)]}{\widehat{\mathcal{P}}_\mu[\widehat{\boldsymbol{x}} \mid \widehat{x}(0)]} = \mathrm{e}^{\Delta\mathcal{S}^{\mathrm{tot}}[\boldsymbol{x}]}$$

Define $p^{\mathrm{ss}}(x,\mu)$, $p^{\mathrm{eq}}(x) = p^{\mathrm{ss}}(x,\mu{=}0)$

$$\begin{aligned}
\mathcal{P}^{\mathrm{ss}}[\boldsymbol{x}] &= \mathcal{P}_\mu[\boldsymbol{x} \mid x(0)]\, p^{\mathrm{ss}}(x(0),\mu) \\
\mathcal{P}^{\mathrm{eq}}[\boldsymbol{x}] &= \mathcal{P}_0[\boldsymbol{x} \mid x(0)]\, p^{\mathrm{eq}}(x(0)) \\
\mathcal{P}^{\mathrm{es}}[\boldsymbol{x}] &= \mathcal{P}_\mu \boldsymbol{x} \mid x(0)]\, p^{\mathrm{eq}}(x(0)) \\
p^{\mathrm{es}}(x,\mu,t) &= \sum_{\boldsymbol{x}} \delta_{x(t),x} \mathcal{P}_\mu \boldsymbol{x} \mid x(0)]\, p^{\mathrm{eq}}(x(0))
\end{aligned}$$

$$\begin{aligned}
\frac{\mathcal{P}^{\mathrm{es}}[\boldsymbol{x}]}{\mathcal{P}^{\mathrm{es}}[\widehat{\boldsymbol{x}}]} &= \mathrm{e}^{\mathcal{S}^{(1)}[\boldsymbol{x}]} \\
\mathcal{S}^{(1)}[\boldsymbol{x}] &= \mathcal{S}^{\mathrm{tot}}[\boldsymbol{x}] + \beta\,[H(x(\mathcal{T})) - H(x(0)))] = \mathrm{O}(|\mu|) \\
\mathcal{S}^{(1)}[\widehat{\boldsymbol{x}}] &= -\mathcal{S}^{(1)}[\boldsymbol{x}]
\end{aligned}$$

Derivation II

Thus for any functional $\mathcal{X}[\boldsymbol{x}]$ and define $\mathcal{S}^{\mathrm{ex}} = \mathcal{S} - \left\langle \dot{S} \right\rangle^{\mathrm{ss}} \mathcal{T}$

$$\langle \mathcal{X}[\boldsymbol{x}] \rangle^{\mathrm{es}} = \left\langle \mathcal{X}[\widehat{\boldsymbol{x}}]\, \mathrm{e}^{-\mathcal{S}^{(1)}[\boldsymbol{x}]} \right\rangle$$

Choose $\mathcal{X}[\boldsymbol{x}] = \delta_{x(\mathcal{T}),x}\, \mathrm{e}^{-\mathcal{S}^{(1)}/2}$ and define $\mathcal{S}^{\mathrm{ex}} = \mathcal{S} - \left\langle \dot{S} \right\rangle \mathcal{T}$

$$\begin{aligned}
p^{\mathrm{es}}(x, \mu, \mathcal{T}) &= p^{\mathrm{eq}}(\widehat{x}) \frac{\left\langle \delta_{x(0),\widehat{x}}\, \mathrm{e}^{-\mathcal{S}^{(1)}/2} \right\rangle^{\mathrm{es}}}{\left\langle \delta_{x(\mathcal{T}),x}\, \mathrm{e}^{-\mathcal{S}^{(1)}/2} \right\rangle^{\mathrm{es}}} \\
&= p^{\mathrm{eq}}(x)\, \exp\left[\frac{1}{2} \left(\left\langle \delta_{x(t),x} \mathcal{S}^{(1)} \right\rangle^{\mathrm{es}} - \left\langle \delta_{x(0),\widehat{x}} \mathcal{S}^{(1)} \right\rangle^{\mathrm{es}} + \mathrm{O}(\mu^3) \right) \right]^{\mathrm{a}} \\
&\xrightarrow{\mathcal{T}\to\infty} p^{\mathrm{eq}}(x)\, \exp\left[\frac{1}{2} \left(\langle \delta_{x(t),x} \mathcal{S}^{\mathrm{ex}} \rangle^{\mathrm{es}} - \langle \delta_{x(0),\widehat{x}} \mathcal{S}^{\mathrm{ex}} \rangle^{\mathrm{es}} + \mathrm{O}(\mu^3) \right) \right] \\
&= p^{\mathrm{eq}}(x)\, \exp\left[\frac{1}{2} \left(\langle \delta_{x(t),x} \mathcal{S}^{\mathrm{ex}} \rangle^{\mathrm{ss}} - \langle \delta_{x(0),\widehat{x}} \mathcal{S}^{\mathrm{ex}} \rangle^{\mathrm{ss}} + \mathrm{O}(\mu^3) \right) \right]
\end{aligned}$$

[a] By cumulant expansion: $\ln \langle \mathrm{e}^{X} \rangle \simeq \langle X \rangle + \frac{1}{2} \left(\langle X^2 \rangle - \langle X \rangle^2 \right) + \cdots$

A system with several reservoirs

Reservoir i with inverse temperature β_i

$$\begin{aligned}
\mathcal{Q}_i^{\mathrm{ex}}[\boldsymbol{x}] &= \mathcal{Q}_i[\boldsymbol{x}] - \mathcal{T} J_i^{\mathrm{ss}} \\
J_i^{\mathrm{ss}} &= \lim_{\mathcal{T}\to\infty} \frac{\mathcal{Q}_i[\boldsymbol{x}]}{\mathcal{T}} \\
E_i(x) &= \lim_{\mathcal{T}\to\infty} \frac{1}{2} \left[\langle \delta(x(\mathcal{T}) - x)\, \mathcal{Q}_i^{\mathrm{ex}}[\boldsymbol{x}] \rangle^{\mathrm{ss}} \right. \\
&\qquad \left. - \langle \delta(x(0) - \widehat{x})\, \mathcal{Q}_i^{\mathrm{ex}}[\boldsymbol{x}] \rangle^{\mathrm{ss}} \right] \\
\Phi(x) &= -\sum_i \beta_i E_i(x)
\end{aligned}$$

Special case: $\beta_i = \beta$, $\forall i$:

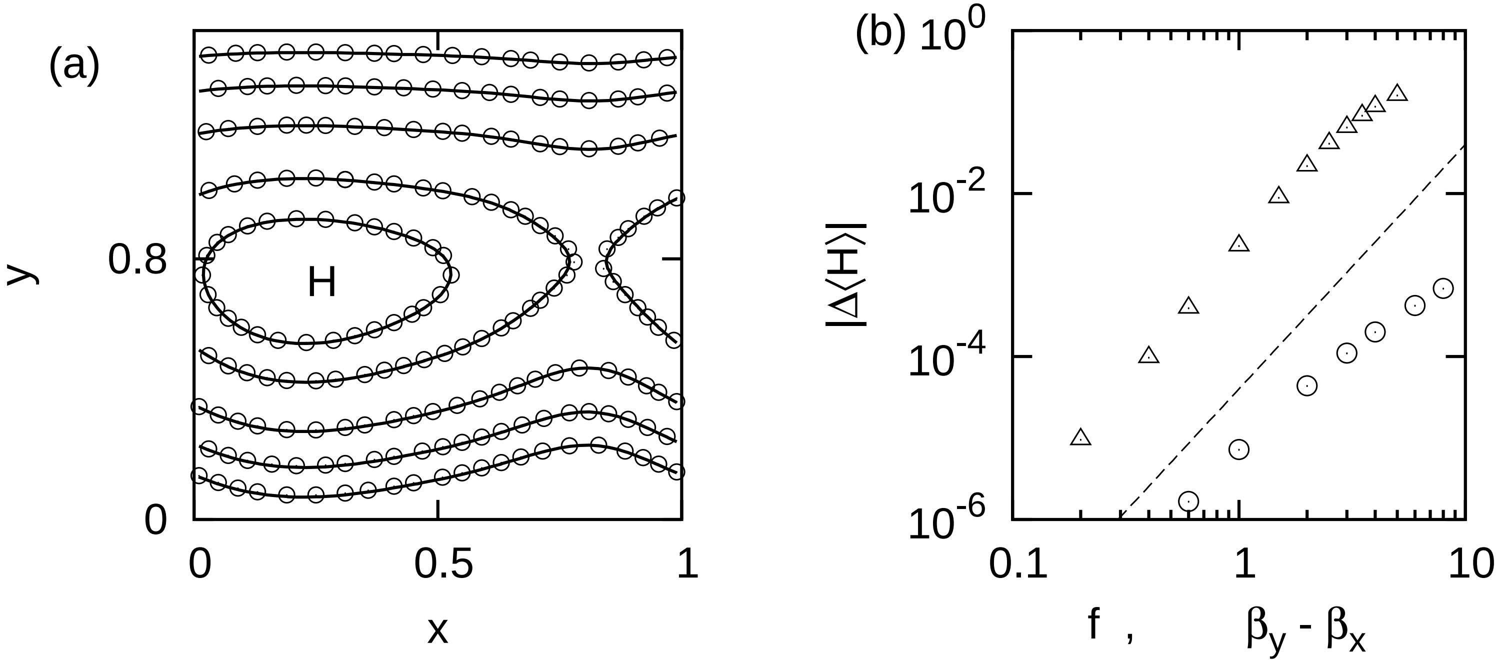
$$\Phi(x) = -\beta \sum_i E_i = -\beta \left[H(x) - \langle H \rangle^{\mathrm{eq}} \right]$$

Numerical check

A Langevin system:

$$
\begin{aligned}
\dot{x} &= -\frac{\partial U}{\partial x} + f + \sqrt{\frac{2}{\beta_x}}\eta_x(t) \\
\dot{y} &= -\frac{\partial U}{\partial y} + \sqrt{\frac{2}{\beta_y}}\eta_y(t) \\
U(x,y) &= \exp\left(-y + \phi(x)\right) + \frac{y^2}{2} \\
\phi(x) &= -\frac{1}{2}\sin(2\pi x) - \frac{1}{12}\sin 4\pi x + \frac{1}{2}
\end{aligned}
$$

Results



(a) $\Phi(x)$ (circles) vs. $\ln p^{\rm ss}(x)$ (lines) for $(\beta_x, \beta_y, f) = (1, 0, 0.8)$

(b) Error $|\Delta H|$ vs. f for $(\beta_x, \beta_y) = 2$ (triangles) and vs. β_y for $(\beta_x, f) = 2, 0$
The dotted line corresponds to μ^3

Comments

- This appears as a first step to identify the "Hamiltonian" of nonequilibrium steady-states
- Application is difficult, because it requires evaluation of $\mathcal{S}^{\mathrm{ex}}$, which in turns requires solving the time-dependent problem
- So far, no application, e.g., to exclusion processes has been made
- Experimental checks? Require reliable measures of heat transfer. Colloidal particles in a potential? Mesoscopic systems?

Quasi-static nonequilibrium transformations

Komatsu et al., 2007

Komatsu-Nakagawa:

$$\langle \dots \rangle_{x,x'} = \left\langle \delta_{x(\mathcal{T}),x} \delta_{x(0),x'} \cdots \right\rangle$$

$$\ln p^{\mathrm{ss}}(x,\mu) = -\Sigma(\mu) + \frac{1}{2}\left[\langle \mathcal{S}^{\mathrm{ex}}[\boldsymbol{x}] \rangle^{\mathrm{ss}}_{x,\mathrm{ss}} - \langle \mathcal{S}^{\mathrm{ex}}[\boldsymbol{x}] \rangle^{\mathrm{ss}}_{\mathrm{ss},\widehat{x}} \right] + \mathrm{O}(\mu^3)$$

Quasi-static protocol: $\boldsymbol{\mu} = \mu(t)$

$$p^{\mathrm{ss}}(x_{\mathrm{f}},\mu_{\mathrm{f}}) \left\langle \mathrm{e}^{-\mathcal{S}_{\boldsymbol{\mu}}/2} \right\rangle^{\boldsymbol{\mu}}_{x_{\mathrm{f}},x_{\mathrm{i}}} = p^{\mathrm{ss}}(x_i,\mu_{\mathrm{i}}) \left\langle \mathrm{e}^{-\mathcal{S}_{\widehat{\boldsymbol{\mu}}}/2} \right\rangle^{\widehat{\boldsymbol{\mu}}}_{\widehat{x}_{\mathrm{i}},\widehat{x}_{\mathrm{f}}}$$

$$\left\langle \mathcal{S}^{\mathrm{ex}} \right\rangle^{\boldsymbol{\mu}}_{x_{\mathrm{f}},x_{\mathrm{i}}} = \left\langle \mathcal{S}^{\mathrm{ex}} \right\rangle^{\mathrm{ss},\mu_{\mathrm{f}}}_{\mathrm{ss},x_{\mathrm{i}}} + \left\langle \mathcal{S}^{\mathrm{ex}} \right\rangle^{\mathrm{ss},\mu_{\mathrm{i}}}_{x_{\mathrm{f}},\mathrm{ss}} + \left\langle \mathcal{S}^{\mathrm{ex}} \right\rangle^{\boldsymbol{\mu}}_{\mathrm{ss},\mathrm{ss}}$$

Nonequilibrium Clausius relation

For infinitesimal protocols ($|\Delta\mu|$ small), one has

$$\ln\left[\left\langle \mathrm{e}^{-\mathcal{S}_{\boldsymbol{\mu}}/2}\right\rangle_{x_\mathrm{f},x_\mathrm{i}}^{\boldsymbol{\mu}} \Big/ \left\langle \mathrm{e}^{-\mathcal{S}_{\widehat{\boldsymbol{\mu}}}/2}\right\rangle_{\widehat{x}_\mathrm{i},\widehat{x}_\mathrm{f}}^{\widehat{\boldsymbol{\mu}}}\right] = -\frac{1}{2}\left[\langle \mathcal{S}^{\mathrm{ex}}\rangle_{x_\mathrm{f},x_\mathrm{i}}^{\boldsymbol{\mu}} - \langle \mathcal{S}^{\mathrm{ex}}\rangle_{\widehat{x}_\mathrm{i},\widehat{x}_\mathrm{f}}^{\widehat{\boldsymbol{\mu}}}\right] + \mathrm{O}(\mu^3, \mu^2\,\Delta\mu)$$

Then

$$\begin{aligned}\Sigma(\mu_\mathrm{f}) - \Sigma(\mu_\mathrm{i}) &= \frac{1}{2}\left[\langle \mathcal{S}^{\mathrm{ex}}\rangle^{\widehat{\boldsymbol{\mu}}} - \langle \mathcal{S}^{\mathrm{ex}}\rangle^{\boldsymbol{\mu}}\right] + \mathrm{O}(\mu^3, \mu^2\,\Delta\mu) \\ &= -\langle \mathcal{S}^{\mathrm{ex}}\rangle^{\boldsymbol{\mu}} + \mathrm{O}(\mu^3, \mu^2\,\Delta\mu)\end{aligned}$$

Thus $\mathrm{d}\,\langle \mathcal{S}^{\mathrm{ex}}\rangle$ is an “exact” differential!

Gibbs-like expression for $\Sigma(\mu)$

Komatsu *et al.* show that

$$\Sigma(\mu) = -\frac{1}{2}\int \mathrm{d}x\, p^{\mathrm{ss}}(x,\mu)\ln\left(p^{\mathrm{ss}}(x,\mu)p^{\mathrm{ss}}(\widehat{x},\mu)\right) + \mathrm{O}(\mu^3) \quad (1)$$

Thus, in particular, the Gibbs expression of the entropy should hold if $\widehat{x} = x$!

Denoting by β a “reference” inverse temperature, and by ν_i some controllable parameters, one has, *in some cases*,

$$\mathrm{d}\Sigma = \beta\,\mathrm{d}E + \beta\sum_i f_i\,\mathrm{d}\nu_i + \mathrm{O}(\mu^2\,\Delta\mu)$$

identical in form to equilibrium thermodynamics

Comments

- These results are derived in a Hamiltonian setting (with coupling to thermostats) but should be more general
- The “exactness” of $\mathrm{d}\left\langle \mathcal{S}^{\mathrm{ex}} \right\rangle$ should be checked experimentally, e.g., on colloidal particles
- The difficulty is having a reliable evaluation of $\mathcal{S}^{\mathrm{ex}}$, which is defined by the subtraction of two large terms
- The realizability of the conditions for the equilibrium-like expression of $\mathrm{d}\Sigma$ are not clear

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