Fluctuation theorem in systems in contact with different heath baths: theory and experiments.

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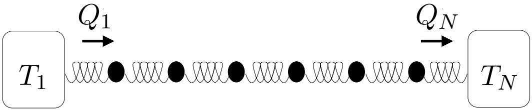
Motivations and Overview

- Fluctuation theorems set constraints on energy and matter fluctuations
- 1D system of particles in contact with heath (or particle) reservoirs as typical example of out-of-equilibrium systems see, e.g.,
  S. Lepri, R. Livi, and A. Politi, Phys. Rep. (2003);
  A. Dhar, Adv. in Phys 2008.
- Review the asymptotic FT in a system with a general potential
  - a few remarks on the harmonic chain
- Correction to the asymptotic limit: exact result
- Experimental verification
- Another exact result

A prototypical example: linear chain of harmonic oscillators



- Two stochastic heat baths
- harmonic springs
- Exact solution for the position and momentum PDF
  Z. Rieder, J.L. Lebowitz, F. Lieb (1967)
- $\langle Q_1 \rangle_t = - \langle Q_N \rangle_t$
- One expects $\langle Q_1 \rangle_t \propto t(T_1 - T_N)$
- $\langle Q_1 \rangle_t$ does not depend on the system size N
- while the Fourier's law predicts $\langle Q_1 \rangle_t \sim L^{-1}$

The equations

$$
\begin{aligned}
\frac{dq_n}{dt} &= p_n, \\
\frac{dp_n}{dt} &= -\partial_{q_n} U(q_1, \dots q_N), \quad n = 2, \cdots N-1, \\
\frac{dp_1}{dt} &= -\partial_{q_1} U(q_1, \dots q_N) - \Gamma p_1 + \xi_1, \\
\frac{dp_N}{dt} &= -\partial_{q_N} U(q_1, \dots q_N) - \Gamma p_N + \xi_N, \\
\langle \xi_l(t) \xi_m(t') \rangle &= 2\Gamma\, T_l\, \delta_{lm} \delta(t-t'), \qquad l, m = 1, N
\end{aligned}
$$

Definition of Q_1 (Q_N)

- Heat flow Q_1 because of the coupling to the reservoirs
- The heat Q_1 is the *work* done by the left reservoir on the first particle

$$\frac{dp_1}{dt} = -\partial_{q_1} U - \Gamma p_1 + \xi_1,$$

$$\boxed{\frac{dQ_1}{dt} = p_1(-\Gamma p_1 + \xi_1)}$$

$-\Gamma p_1$ is the friction force, and ξ_1 is the stochastic force

- Analogous definition for Q_N
- In the following $Q \equiv Q_1$

Heat probability distribution function

- We are interested in the steady state probability distribution function (PDF) $P_{\rm ss}(Q) = P(Q, t \to \infty)$
- We expect the fluctuation theorem (FT) to hold

$$\frac{P_{\rm ss}(Q)}{P_{\rm ss}(-Q)} = \exp\left[-Q\left(\frac{1}{T_1} - \frac{1}{T_N}\right)\right]$$

- see, e.g.,
  G. Gallavotti and E. G. D. Cohen (1995);
  J. L. Lebowitz and H. Spohn, (1999)

Generating function

- The math for $P(Q,t)$ is far too complicated, so one introduces the cumulant generating function $\mu(\lambda)$

$$\int_{-\infty}^{\infty} \mathrm{d}Q \, \mathrm{e}^{\lambda Q} P(Q, t \to \infty) \equiv \mathrm{e}^{t\mu(\lambda)}$$

  Example: $\langle Q_1 \rangle = t \, \partial_\lambda \, \mu(\lambda)|_{\lambda=0}$

- Requiring the FT

$$P_{\mathrm{ss}}(Q)/P_{\mathrm{ss}}(-Q) = \mathrm{e}^{-Q/\tau}$$

  with $\tau = (1/T_1 - 1/T_N)^{-1}$
  is equivalent to require the symmetry

$$\mu(\lambda) = \mu(1/\tau - \lambda)$$

General Interaction potential U

- $H = \sum_{i=1}^{N} \frac{p_i^2}{2} + U(q_1, q_2, \ldots, q_N)$
-

$$
\begin{aligned}
\frac{\partial P}{\partial t} &= \mathcal{L}_0 P \\
&= \{P, H\} + \Gamma \left[\partial_{p_1}\left(p_1 + T_1 \partial_{p_1}\right) + \partial_{p_N}\left(p_N + T_N \partial_{p_N}\right)\right] P \\
\{P, H\} &= \sum_{n=1}^{N} \left[\frac{\partial P}{\partial p_n}\frac{\partial H}{\partial q_n} - \frac{\partial P}{\partial q_n}\frac{\partial H}{\partial p_n}\right]
\end{aligned}
$$

Joint probability distribution function

- $\phi(\mathbf{q}, \mathbf{p}, Q, t)$

$$\frac{\partial \phi}{\partial t} = \mathcal{L}_0 \phi + \Gamma \left[\partial_Q (p_1^2 + T_1) + T_1 p_1^2 \partial_Q^2 + 2 T_1 p_1 \partial_Q \partial_{p_1} \right] \phi$$

- $\psi(\mathbf{q}, \mathbf{p}, \lambda, t) \equiv \int \mathrm{d}\lambda \, \mathrm{e}^{\lambda Q} \, \phi(\mathbf{q}, \mathbf{p}, Q, t)$

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \mathcal{L}_0 \psi + \Gamma \left[-\lambda T_1 + \lambda(\lambda T_1 - 1) p_1^2 - 2\lambda T_1 p_1 \partial_{p_1} \right] \psi \\ &= \mathcal{L}_\lambda \psi \end{aligned}$$

- $\Psi(\lambda, t) = \int \mathrm{d}\mathbf{q} \, \mathrm{d}\mathbf{p} \, \psi(\mathbf{q}, \mathbf{p}, \lambda, t)$
- If $\mu_0(\lambda)$ is the largest eigenvalue of $\mathcal{L}_\lambda$: $\Psi(\lambda, t \to \infty) \sim \mathrm{e}^{t \mu_0(\lambda)}$

Proof of the asymptotic FT in the general case

- $\mu_0(\lambda)$ maximal eigenvalue of $\mathcal{L}_\lambda$
- $\mathcal{L}_\lambda^*$ adjoint of $\mathcal{L}_\lambda$
- $\mathcal{L}_\lambda$ and $\mathcal{L}_\lambda^*$ have the same max. eigenvalue
- One can prove that $\mathcal{L}_\lambda$ and $\mathcal{L}_{1/\tau-\lambda}^*$ have identical spectra
- $\boxed{\mu_n(\lambda) = \mu_n(1/\tau - \lambda)}$ holds for each eigenvalue
- in particular $\mu_0(\lambda) = \mu_0(1/\tau - \lambda)$ which proves the FT

$$\frac{P_{ss}(Q)}{P_{ss}(-Q)} = \exp\left[-Q\left(\frac{1}{T_1} - \frac{1}{T_N}\right)\right]$$

- A similar symmetry can be proved for the eigenfunctions $\psi_n(\mathbf{q},\mathbf{p},\lambda) = \exp\left[-H(\mathbf{q},\mathbf{p})/T_N\right]\psi_n^*(\mathbf{q},-\mathbf{p},1/\tau-\lambda)$

AI, H. Fogedby, J. Stat. Mec. 2012
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Properties of the operator $\mathcal{L}_\lambda$

- time-reversal operator $\mathcal{T}P(\mathbf{q},\mathbf{p}) = P(\mathbf{q},-\mathbf{p})$
- new operator

$$\boxed{\tilde{\mathcal{L}}_\lambda = \mathcal{T}^{-1}\mathrm{e}^{\beta H}\mathcal{L}_\lambda \mathrm{e}^{-\beta H}\mathcal{T},}$$

- if $\psi_n(\mathbf{q},\mathbf{p},\lambda)$ is an eigenfunction of $\mathcal{L}_\lambda$: $\mathcal{L}_\lambda\psi_n = \mu_n(\lambda)\psi_n$, then

$$\tilde{\psi}_n(\mathbf{q},\mathbf{p},\lambda) = \mathcal{T}^{-1}\mathrm{e}^{\beta H}\psi_n,$$

  is an eigenfunction for $\tilde{\mathcal{L}}_\lambda$ with the same eigenvalue $\mu_n(\lambda)$

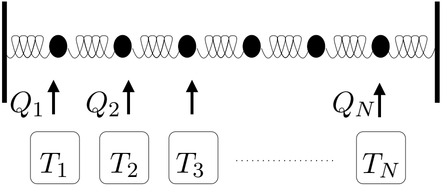
$$\tilde{\mathcal{L}}_\lambda\tilde{\psi}_n(\mathbf{q},\mathbf{p},\lambda) = \mu_n(\lambda)\tilde{\psi}_n,$$

- One can prove that, *if* $\beta = 1/T_N$

$$\boxed{\tilde{\mathcal{L}}_\lambda = \mathcal{L}^*_{1/\tau-\lambda}}$$

  where $\mathcal{L}^*_\lambda$ is the adjoint operator of $\mathcal{L}_\lambda$

Can be generalized



- define the vector $\mathbf{Q} = (Q_1, Q_2, \dots Q_N)$
- Define $\tau_{ij} = (1/T_i - 1/T_j)^{-1}$
- Fix any reservoir number k
- $$P(\mathbf{Q})/P(-\mathbf{Q}) = \exp\left(-\sum_{i(i\neq k)} Q_i/\tau_{ik}\right)$$ *AI, H. Fogedby, in prepar.*

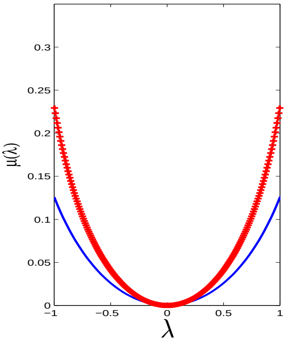
Generating function for the harmonic chain

The problem of finding $\mu_0(\lambda)$ for the harmonic chain can be solved exactly
K. Saito and A. Dhar, (2007), (2011).

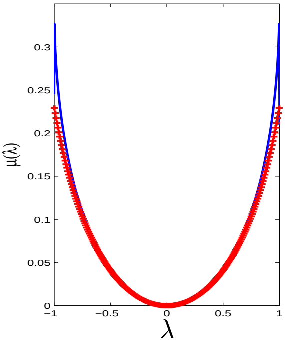
Generating function

In the limit $N \to \infty$

$$\mu(\lambda) = -\int_0^\pi \frac{dp}{2\pi}\sqrt{\kappa}\cos(p/2)\ln\left[1 + \frac{8\Gamma\kappa^{-1/2}\sin(p/2)\sin(p)f(\lambda)}{1+4(\Gamma^2/\kappa)\sin^2(p/2)}\right]$$



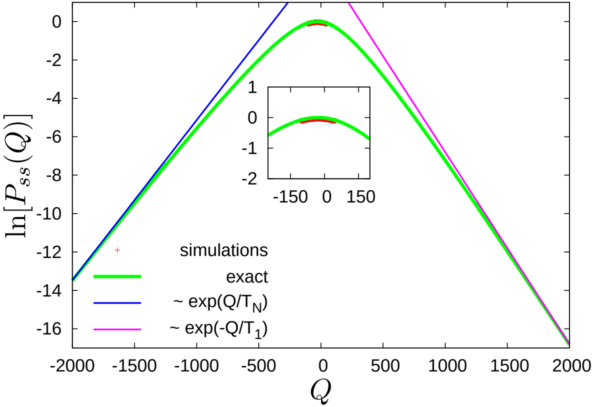
$N = 2$



$N = 10$

Exponential tails?

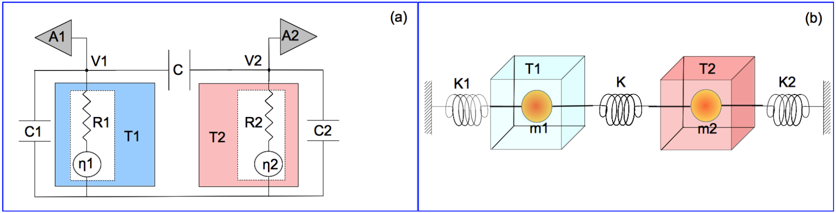
$\mu_0(\lambda)$ exhibits two branch points at $\lambda_- = -1/T_N$, $\lambda_+ = 1/T_1$, where $\mu_0'(\lambda)$ diverges
AI and H. Fogedby (2012).



$\Gamma = 10$, $\kappa = 60$, $T_1 = 100$, $T_N = 120$, $N = 10, t = 100$

An electric circuit with viscous coupling

S. Ciliberto, AI, A. Naert e M. Tanase, 2013



$$(C_1 + C)\dot{V}_1 = -\frac{V_1}{R_1} + C\dot{V}_2 + \eta_1$$
$$(C_1 + C)\dot{V}_2 = -\frac{V_2}{R_2} + C\dot{V}_1 + \eta_2$$

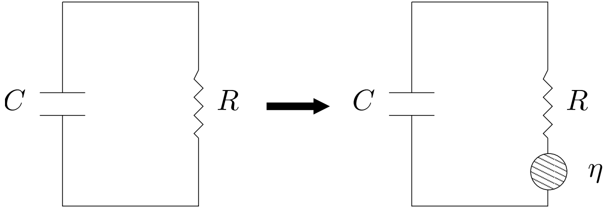
where η_i is the usual white noise: $\left\langle \eta_i \eta_j' \right\rangle = 2\delta_{ij} \frac{T_i}{R_i} \delta(t - t')$.

Nyquist effect

The potential difference across a dipole fluctuates because of the thermal noise

$$C\dot{V} = -\frac{V}{R} + \eta$$

$$\text{with } \langle \eta(t)\eta(t') \rangle = 2\frac{T}{R}\delta(t-t')$$



Thermodynamic quantities

- Work done by circuit 2 on circuit 1

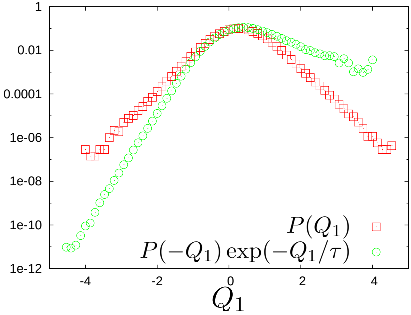
$$W_1(t,\Delta t) = \int_t^{t+\Delta t} \mathrm{d}t'\, C \frac{\mathrm{d}V_2}{\mathrm{d}t'} V_1(t') = \int_t^{t+\Delta t} \mathrm{d}t'\, V_1(f_2 + \xi_2(t'))$$

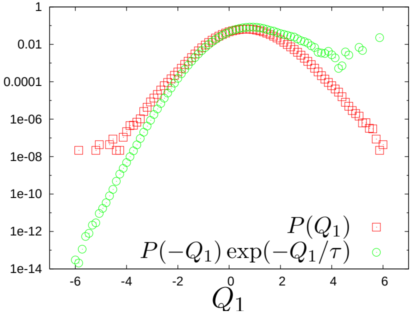
- Heat dissipated in resistor 1

$$\begin{aligned} Q_1(t,\Delta t) &= \int_t^{t+\Delta t} \mathrm{d}t'\, C V_1(t') \frac{\mathrm{d}V_2}{\mathrm{d}t'} - (C_1 + C) V_1(t') \frac{\mathrm{d}V_1}{\mathrm{d}t'} \\ &= \int_t^{t+\Delta t} \mathrm{d}t'\, V_1(t') \left(\frac{V_1(t')}{R_1} - \eta_1(t') \right) \end{aligned}$$

- Analogous definition for W_2 and Q_2

FT for Q_1: slow convergence





$\Delta t = 0.2$ s, $\Delta t = 0.5$ s

$$\log \frac{P_{\rm ss}(Q_1)}{P_{\rm ss}(-Q_1)} = \frac{Q_1}{\tau}$$

$T_1 = 88$ K, $T_2 = 296$ K, $C = 100pF$, $C_1 = 680pF$, $C_2 = 420pF$ and $R_1 = R_2 = 10M\Omega$

A FT that holds at any time?

- So far we considered the limit $t \to \infty$
- Is there a FT for any $t > 0$?
- Consider the total entropy variation for the system

A few definitions

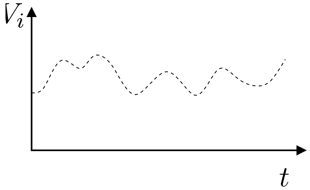
- $\Delta S_{r,\Delta t}$: the entropy due to the heat exchanged with the reservoirs up to the time Δt

$$\Delta S_{r,\Delta t} = Q_{1,\Delta t}/T_1 + Q_{2,\Delta t}/T_2$$

- the reservoir entropy $\Delta S_{r,\Delta t}$ is not the only component of the total entropy production: entropy variation of the system?

A trajectory entropy

- The system follows a stochastic trajectory through its phase space, the dynamical variables are the voltages $V_i(t)$.



- Following *Seifert, PRL 2005*, for such a system we can define a time dependent trajectory entropy

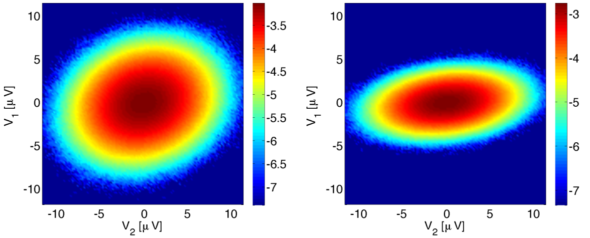
$$S_s(t) = -k_B \log P(V_1(t), V_2(t))$$

- Thus, the system entropy variation reads

$$\Delta S_{s,\Delta t} = -k_B \log \left[\frac{P(V_1(t+\Delta t), V_2(t+\Delta t))}{P(V_1(t), V_2(t))} \right].$$

These are measurable quantities

- Q_i can be measured as discussed earlier
- $P(V_1, V_2)$ can be easily sampled



Left: $T_1 = 296$ K (eq.) right: $T_1 = 88$ K

- The system is in a steady state: $P(V_1, V_2)$ does not change with t

Total entropy

- Measure the voltages V_i at time $t = 0$ and $t = \Delta t$, and thus obtain

$$\Delta S_{s,\Delta t} = -k_B \log \left[\frac{P(V_1(\Delta t), V_2(\Delta t))}{P(V_1(0), V_2(0))} \right].$$

- Measure the heats Q_1 and Q_2 flowing from/towards the reservoirs in the time interval $[0, \Delta t]$ and thus obtain

$$\Delta S_{r,\Delta t} = Q_{1,\Delta t}/T_1 + Q_{2,\Delta t}/T_2$$

- Define the total entropy as

$$\Delta S_{tot,\Delta t} = \Delta S_{r,\Delta t} + \Delta S_{s,\Delta t}$$

FT for the total entropy

- one can show that the following equality holds

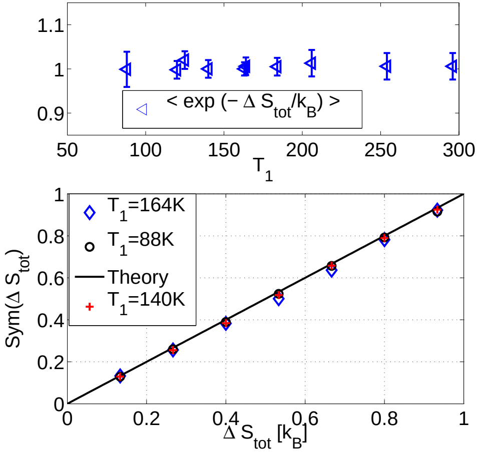
$$\langle \exp(-\Delta S_{tot}/k_B) \rangle = 1,$$

- which implies that $P(\Delta S_{tot})$ should satisfy a fluctuation theorem of the form

$$\log[P(\Delta S_{tot})/P(-\Delta S_{tot})] = \Delta S_{tot}/k_B, \;\; \forall \Delta t, \Delta T,$$

FT for the total entropy: experimental verification

$$\left\langle e^{-\Delta S_{tot}/k_B} \right\rangle = 1, \qquad Sym(\Delta S_{tot}) = \log\left[\frac{P(\Delta S_{tot})}{P(-\Delta S_{tot})}\right] = \frac{\Delta S_{tot}}{k_B}, \;\; \forall \Delta t, \Delta T,$$



Second law?

- Jensen's inequality: $\left\langle \mathrm{e}^{X} \right\rangle \geq \mathrm{e}^{\langle X \rangle}$
- $\langle \Delta S_{tot} \rangle \geq 0$

Recap and next question

- An asymptotic FT for the heat current alone
  $P_{\rm ss}(Q) = P(Q, t \to \infty)$
  The system is already in a steady state at $t < 0$, and at $t = 0$ one starts sampling the heat currents

$$\frac{P_{\rm ss}(Q)}{P_{\rm ss}(-Q)} = \exp\left[-Q\left(\frac{1}{T_1} - \frac{1}{T_N}\right)\right]$$

- An exact FT that holds $\forall t > 0$

$$\Delta S_{s,\Delta t} = -k_B \log\left[\frac{P(\mathbf{x}(\Delta t))}{P(\mathbf{x}(0))}\right]; \qquad \Delta S_{r,\Delta t} = \sum_i Q_{i,\Delta t}/T_i$$

$$\Delta S_{tot,\Delta t} = \Delta S_{r,\Delta t} + \Delta S_{s,\Delta t}; \qquad \left\langle \mathrm{e}^{-\Delta S_{r,\Delta t}/k_B} \right\rangle = 1$$

- Can we find a FT for the heat currents $Q_{i,\Delta t}$ alone and that *holds* $\forall t > 0$?

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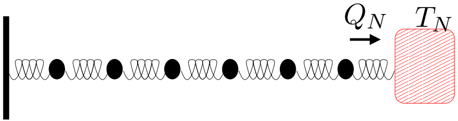
A different approach

- At $t < 0$ the system is at equilibrium with the bath at T_1



- At $t = 0$ connect the other bath at T_N and start sampling Q_1 (or Q_N)

- One finds

$$\frac{P(Q_1,t)}{P(-Q_1,t)} = \exp\left[-Q_1\left(\frac{1}{T_1} - \frac{1}{T_N}\right)\right] \qquad \forall t > 0$$

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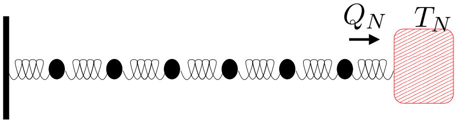

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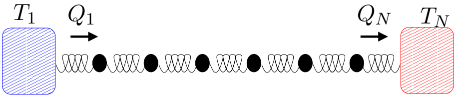

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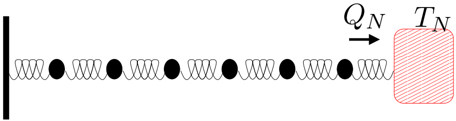

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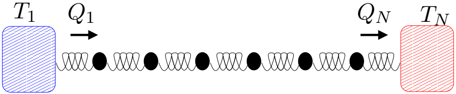

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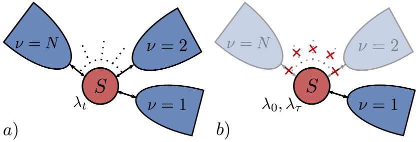
More in general



- A system S in contact with N energy and particle reservoirs with $\beta_\nu = T_\nu^{-1}$ and μ_ν
- at $t < 0$, S is at equilibrium with reservoir $\nu = 1$ and disconnected from reservoirs $\nu = 1, \dots, N$.
- At $t > 0$ connect all the reservoirs and start sampling the energy and particle currents
- Even more general, for $t > 0$ perform some work w_λ on the system by changing some parameter $\lambda(t)$ (e.g. pressure, magnetic field...)

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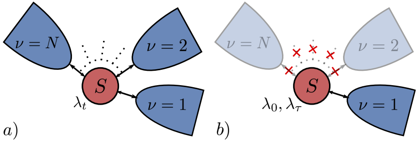

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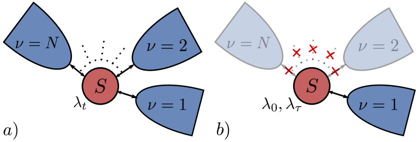
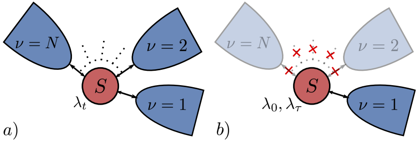
More in general



- A system S in contact with N energy and particle reservoirs with $\beta_\nu = T_\nu^{-1}$ and μ_ν
- at $t < 0$, S is at equilibrium with reservoir $\nu = 1$ and disconnected from reservoirs $\nu = 1, \ldots, N$.
- At $t > 0$ connect all the reservoirs and start sampling the energy and particle currents
- Even more general, for $t > 0$ perform some work w_λ on the system by changing some parameter $\lambda(t)$ (e.g. pressure, magnetic field...)

More in general



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More in general II

- The following FT holds $\forall t > 0$

$$\ln \frac{P(w_\lambda, \{j_\nu^\epsilon\}, \{j_\nu^n\})}{\tilde{P}(-w_\lambda, \{-j_\nu^\epsilon\}, \{-j_\nu^n\})} = \beta_1 \left(w_\lambda - \Delta\Phi_1 \right) + t \sum_{\nu=2}^{N} \left(A_\nu^\epsilon j_\nu^\epsilon + A_\nu^n j_\nu^n \right),$$

where the thermodynamic forces read

$$A_\nu^\epsilon = \beta_1 - \beta_\nu, \qquad A_\nu^n = \beta_\nu \mu_\nu - \beta_1 \mu_1,$$

and the energy and particle currents read

$$j_\nu^\epsilon = \Delta\epsilon_\nu / t \qquad j_\nu^n = \Delta n_\nu / t$$

- Involves only measurable currents
- The knowledge of the PDF $P(x(t), \lambda(t), t)$, for $t \geq 0$ is not required.

Prefactors matter!!

See, e.g. *van Zon, Cohen 2004*

$$
\begin{aligned}
\frac{\partial \psi}{\partial t} &= \mathcal{L}_\lambda \psi \\
\Psi(\lambda, t) &= \int \mathrm{d}\mathbf{q}\, \mathrm{d}\mathbf{p}\, \psi(\mathbf{q}, \mathbf{p}, \lambda, t) = \int \mathrm{d}\mathbf{q}\, \mathrm{d}\mathbf{p} \sum_n c_n(\lambda) \psi_n(\mathbf{q}, \mathbf{p}, \lambda) \mathrm{e}^{t\mu_n(\lambda)} \\
&= \sum_n b_n(\lambda) \mathrm{e}^{t\mu_n(\lambda)} \\
b_n(\lambda) &= c_n(\lambda) \int \mathrm{d}\mathbf{q}\, \mathrm{d}\mathbf{p}\, \psi_n(\mathbf{q}, \mathbf{p}, \lambda)
\end{aligned}
$$

- we know that $\mu_n(\lambda) = \mu_n(1/\tau - \lambda)$
- with our choice for the initial condition, also the prefactors satisfy

$$
\boxed{b_n(\lambda) = b_n(1/\tau - \lambda)}
$$

Summary and perspectives

- FT for Q in the limit $t \to \infty$ in 1D systems coupled with stochastic heat baths
- Not restricted in 1D: can be easily generalized to the 3D case and for any potential, based on the FP operator symmetries, see *AI, H. Fogedby 2012*
- FT for the total entropy that holds for any $t > 0$
- FT for the currents alone that holds for any $t > 0$
  Experimental check in single electron boxes ?
  See, e.g., *J. Koski et al, Nat. Phys. (2013)*

Acknowledgments

Hans Fogedby, AU

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