The entropy flow in out-of-equilibrium systems

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Summary

- Work and heat in Markov systems
- The distribution of entropy flow
- Applications: A two-state system and a precessing particle
- Work and heat for a Brownian system
- Work and heat distributions
- Experiments on a dragged Brownian particle
- Conclusions

A time-dependent Markovian system

Master equation:

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \sum_{j \neq i} \left[W_{ij}(t) p_j - W_{ji}(t) p_i \right], \qquad i = 1, \ldots, N$$

Path $\omega(t)$ and its reverse $\widetilde{\omega}(t)$ for $t_0 \leq t \leq t_\mathrm{f}$:

$$\begin{aligned} \omega(t) &= i_k, \qquad t_k \leq t < t_{k+1}, \quad k = 0, 1, \ldots, M, \quad t_{M+1} = t_\mathrm{f} \\ \widetilde{\omega}(t) &= i_k, \qquad \tilde{t}_{k+1} \leq t < \tilde{t}_k, \quad \tilde{t} = t_0 + t_\mathrm{f} - t \end{aligned}$$

Time-reversed protocol $\widetilde{W}_{ij}(t) = W_{ij}(\tilde{t})$

Path probabilities $\mathcal{P}(\omega)$, $\widetilde{\mathcal{P}}(\widetilde{\omega})$

Entropy flow in a Markovian system

Define

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

Shannon entropy:

$$\begin{aligned} S(t) &= -\sum_i p_i(t) \ln p_i(t) \\ \frac{\mathrm{d}S}{\mathrm{d}t} &= \underbrace{-\sum_{i\neq j} W_{ij} p_j \ln\left(\frac{W_{ji} p_i}{W_{ij} p_j}\right)}_{\text{entropy production}} \underbrace{-\sum_{i\neq j} W_{ij} p_j \ln\frac{W_{ij}}{W_{ji}}}_{\text{entropy flow}} \end{aligned}$$

Probability distribution

Thus

$$\frac{\mathrm{d}\left\langle Q\right\rangle_t}{\mathrm{d}t} = \sum_{i\neq j} W_{ij} p_j \ln\left[\frac{W_{ij}}{W_{ji}}\right] = \frac{\mathrm{d}S_{\mathrm{f}}}{\mathrm{d}t}$$

Entropy jump: $\Delta s_{ij} = \ln\left[W_{ji}(t)/W_{ij}(t)\right]$

Joint pdf of i and Q: $\phi_i(Q,t)$

Change in $\phi_i(Q,t)$ over a small time interval τ:

$$\begin{aligned}\Delta\phi_i(Q,t) &\simeq \tau \sum_{j\,(\neq i)} \left[W_{ij}\phi_j(Q-\Delta s_{ij},t) - W_{ji}\phi_i(Q,t)\right]\\ &= \tau \sum_{j\,(\neq i)} \left[W_{ij}\exp\left(-\Delta s_{ij}\frac{\partial}{\partial Q}\right)\phi_j - W_{ji}\phi_i\right]\end{aligned}$$

The generating function

Define

$$\psi_i(\lambda,t) = \int \mathrm{d}Q\; \mathrm{e}^{\lambda Q}\, \phi_i(Q,t)$$

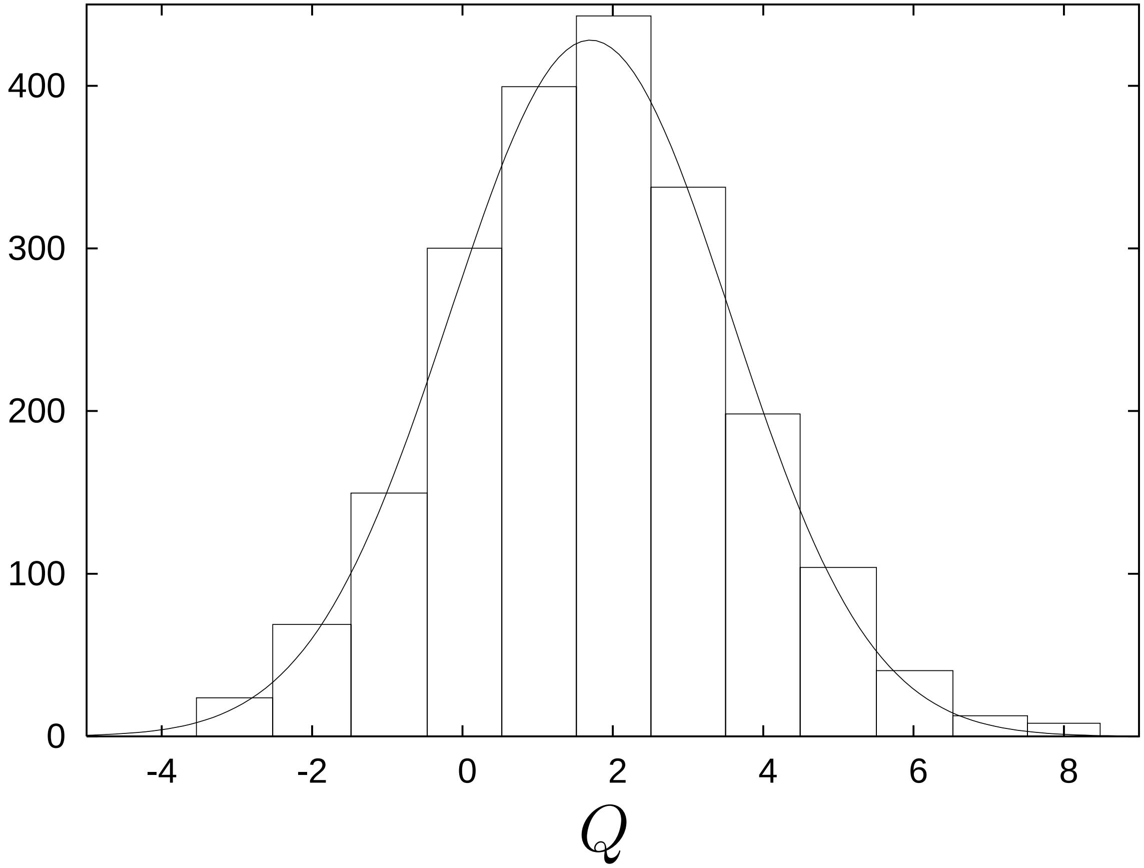
Then, since $\partial/\partial Q \leftrightarrow \lambda$,

$$\frac{\partial \psi_i}{\partial t} = \sum_{j\,(\neq i)} \left[W_{ij} \left(\frac{W_{ji}}{W_{ij}} \right)^{\lambda} \psi_j(\lambda,t) - W_{ji}\psi_i(\lambda,t) \right]$$

Lebowitz and Spohn, J Stat Phys ***95*** *333 (1999)*

Application: A two-state system

Data by Tietz *et al.*, *PRL* **97**, 050602 (2006)
Defect center in diamond, optically driven from fluorescent to non-fluorescent state



Application: A molecular motor

Model by Nishihari *et al.*, *PRL* **95**, 118101 (2005)
States:

1: Bound to ATP

2: Bound to ADP or empty

Moves:

Brownian motion: $(i,2) \xrightarrow{\omega_{\mathrm{B}}} (i\pm 1, 2)$

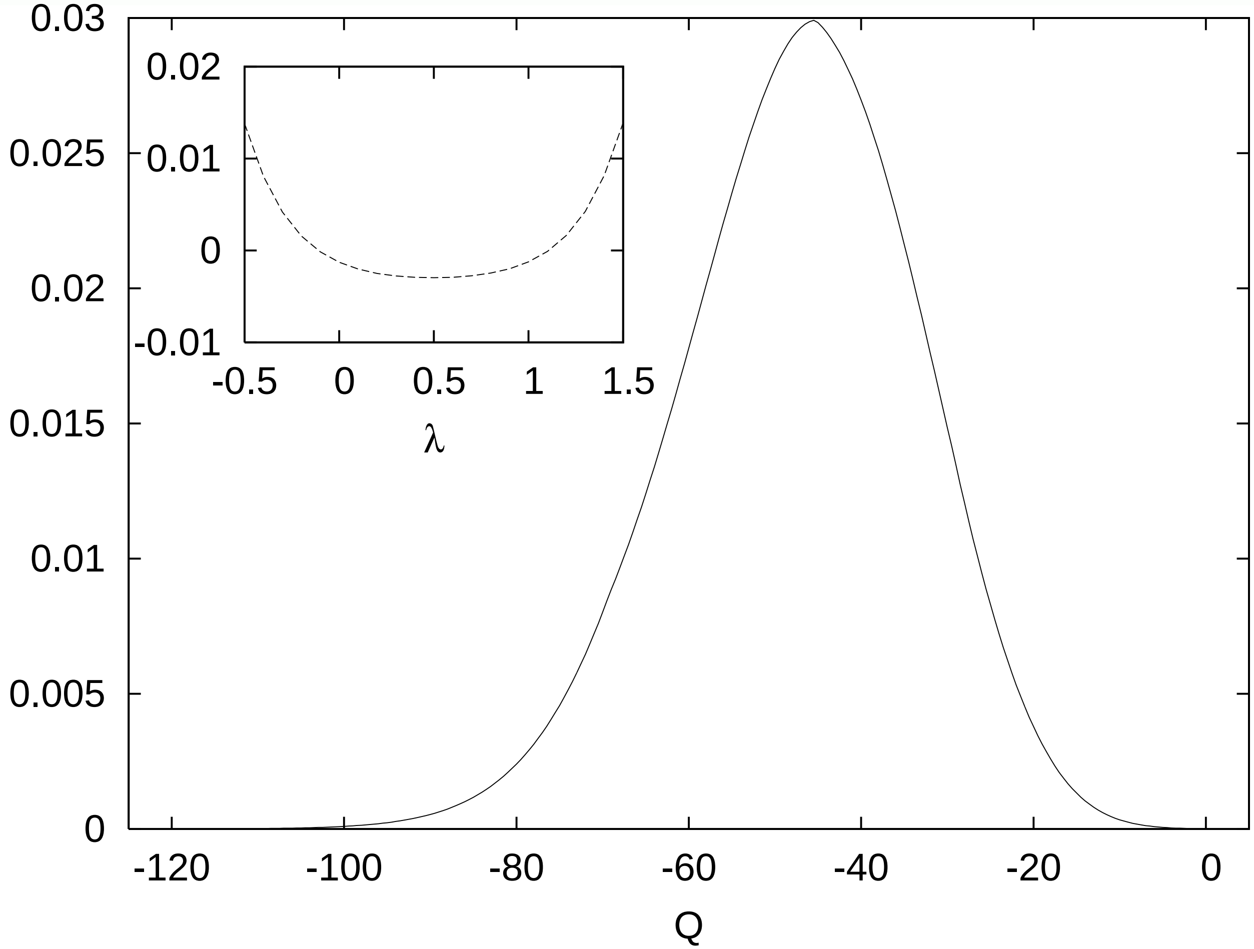
ATP binding: $(i,2) \xrightarrow{\omega_{\mathrm{s}}} (i,1)$

Ratchet: $(i,1) \xrightarrow{\omega_{+}} (i+1,2)$

Reverse ratchet: $(i,2) \xrightarrow{\omega_{-}} (i-1,1)$

Hydrolysis: $(i,1) \xrightarrow{\omega_{\mathrm{h}}} (i,2)$

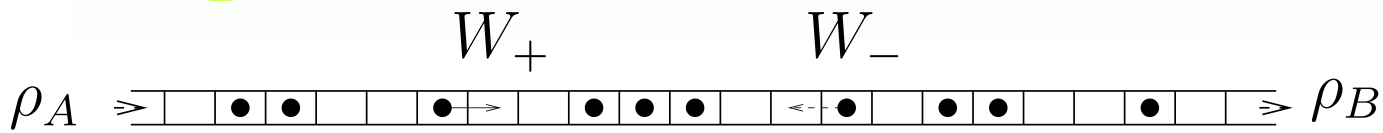
Molecular motor: The entropy flow



$\omega_{\rm B} = 0.6\ {\rm ms}^{-1};\qquad \omega_{\rm s} = 0.145\ {\rm ms}^{-1};\qquad \omega_{\rm h} = 0.1\ {\rm ms}^{-1};$

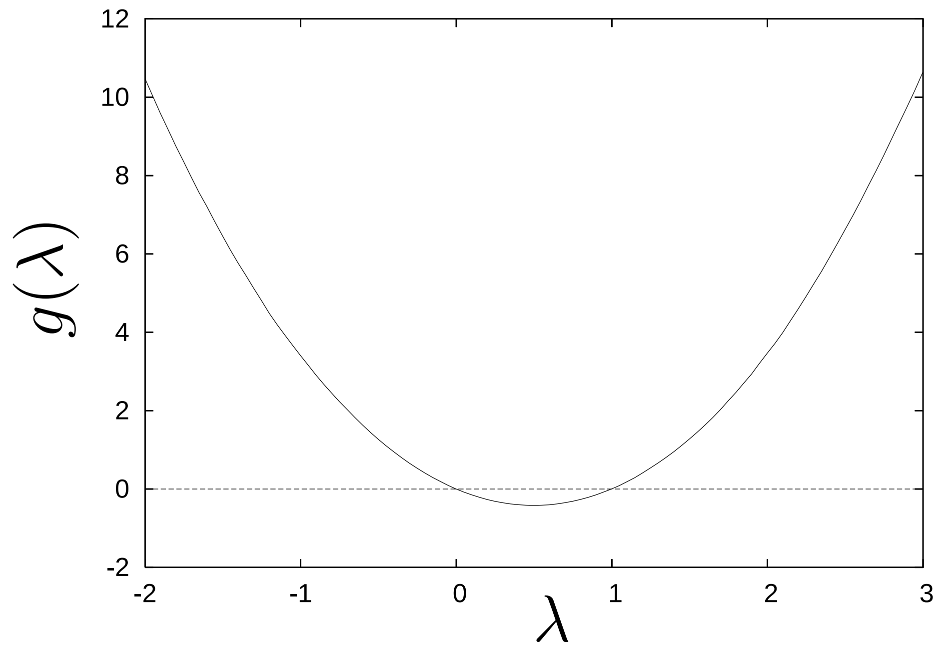
$\omega_+ = 0.0055\ {\rm ms}^{-1};\qquad \omega_- = \omega_+/100;\qquad t = 5\ {\rm s}$

The Asymmetric Exclusion Process (ASEP)

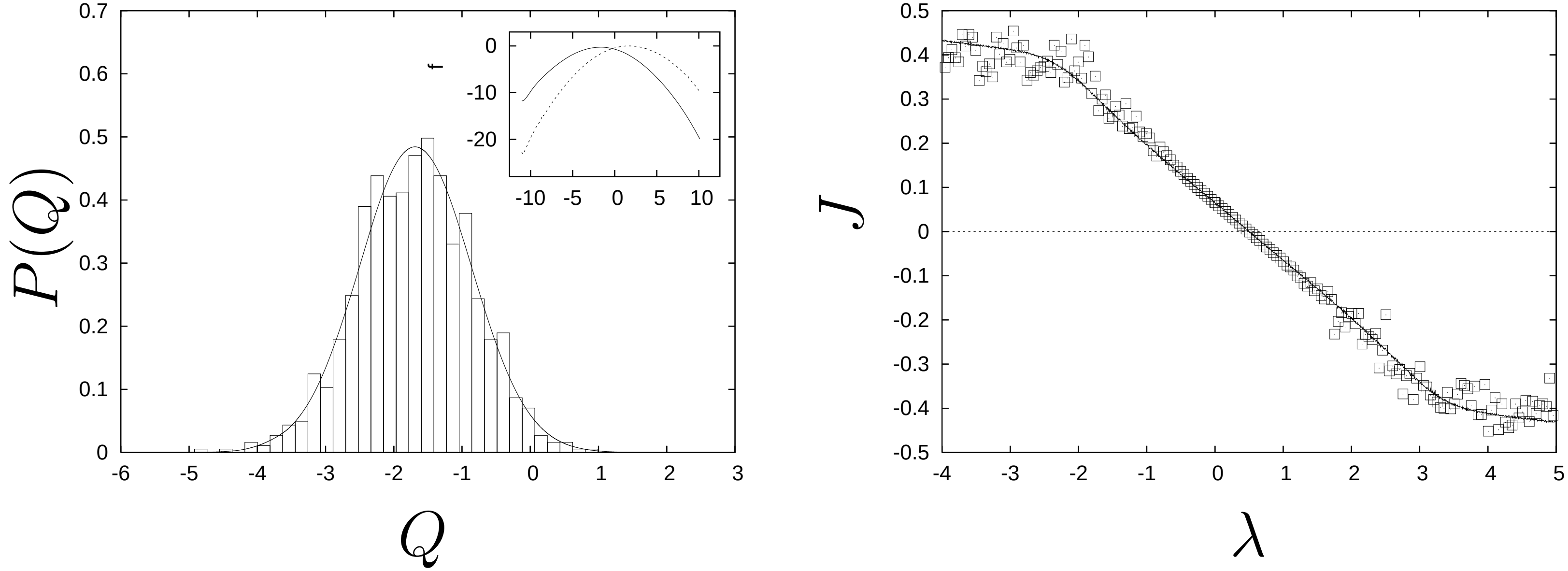


Large-deviation function:

$$g(\lambda) = \lim_{t\to\infty} -\frac{1}{t} \log \psi(\lambda, t)$$



Comparison with simulations



The evaluation is obtained via a *biased sampling*:

$$\langle Q \rangle_\lambda = \frac{\langle Q/\Pi \rangle_{\lambda,\Pi}}{\langle 1/\Pi \rangle_{\lambda,\Pi}}$$

A. I. and L. P., JSTAT L02001 (2007)

Brownian systems

Langevin equation ($\beta = 1/k_{\mathrm{B}}T$):

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}t} &= -\Gamma U'(x, X(t)) + \eta(t) \\ \langle \eta(t)\eta(t')\rangle &= \frac{2\Gamma}{\beta}\,\delta(t-t') \end{aligned}$$

Fokker-Planck equation:

$$\partial_t p(x,t) = \Gamma \frac{\partial}{\partial x}\left[U'(x, X(t))p\right] + \frac{\Gamma}{\beta}\frac{\partial^2 p}{\partial x^2}$$

Work and heat

$$W = \int \mathrm{d}X \, \frac{\partial U}{\partial X} = \int_0^{t_\mathrm{f}} \mathrm{d}t \, \dot{X}(t) \, \frac{\partial U(x(t), X(t))}{\partial X}$$

$$Q = \int \mathrm{d}x \, U'(x, X(t)) = \underbrace{\int_0^{t_\mathrm{f}} \mathrm{d}t \, \dot{x}(t) \, U'(x(t), X(t))}_{\text{Stratonovich integral}}$$

$$\Delta U = W + Q$$

Equation for the work pdf:

$$\partial_t \phi(x, W, t) = \Gamma \frac{\partial}{\partial x} \left(U' \, \phi \right) + \frac{\Gamma}{\beta} \frac{\partial^2 \phi}{\partial x^2} - \dot{X} \frac{\partial U}{\partial X} \frac{\partial \phi}{\partial W}$$

Differential equation for the flow distribution

Stochastic differential equation for (x, Q):

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = U' \frac{\mathrm{d}x}{\mathrm{d}t} = U' \left(-\Gamma U' + \eta(t) \right)$$

Joint stochastic differential equation for $\mathbf{y} = (x, Q)$

Equation for the distribution $\varphi(x, Q, t)$:

$$\mathbf{F} = \begin{pmatrix} -\Gamma U' \\ -\Gamma U'^2 \end{pmatrix}, \qquad \underline{\mathbf{B}} = \begin{pmatrix} \Gamma/\beta, & (\Gamma/\beta)U' \\ (\Gamma/\beta)U', & (\Gamma/\beta)U'^2 \end{pmatrix}$$

$$\partial_t \varphi(x, Q, t) = -\frac{\partial}{\partial \mathbf{y}} \left(\mathbf{F} \varphi \right) + \frac{\partial}{\partial \mathbf{y}} \left(\underline{\mathbf{B}} \cdot \frac{\partial}{\partial \mathbf{y}} \varphi \right)$$

The equation for the generating function

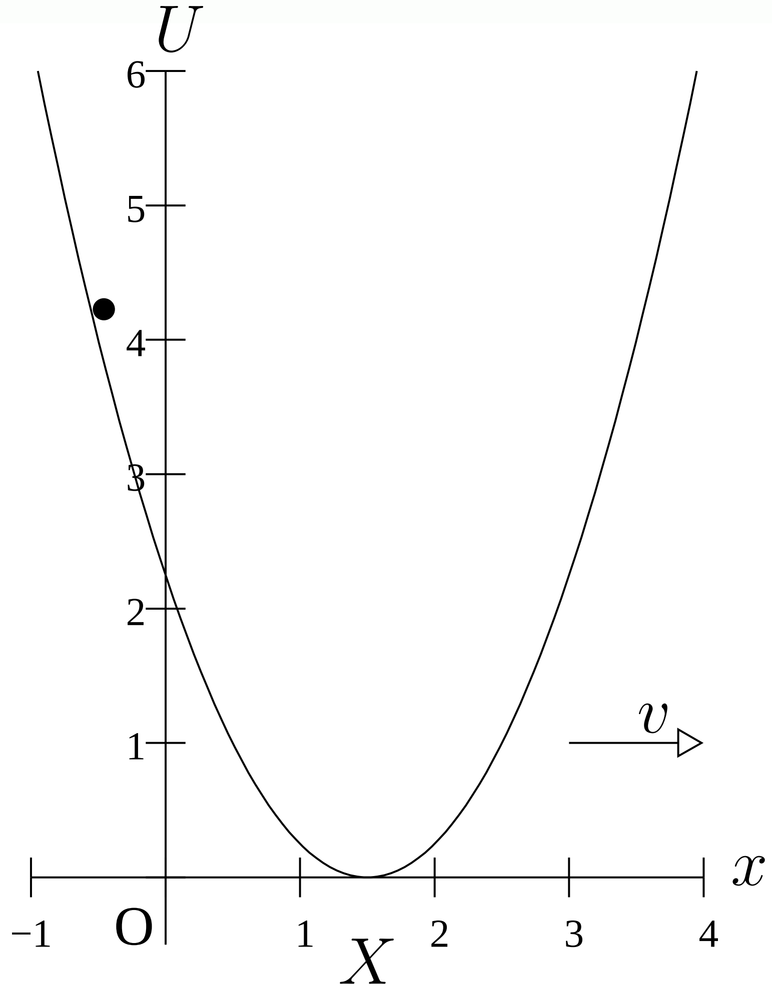
$$\chi(x,\lambda,t) = \int \mathrm{d}\lambda\, \exp(\lambda Q)\varphi(x,Q,t)$$

$$\begin{aligned}\partial_t \chi(x,\lambda,t) &= \mathcal{L}_\lambda \chi = \frac{\Gamma}{\beta}\frac{\partial^2 \chi}{\partial x^2} + \Gamma\left(1-\frac{\lambda}{\beta}\right)\partial_x\left(U'\chi\right) \\ &\quad - \Gamma\frac{\lambda}{\beta}U'\partial_x\chi + \lambda\left(\frac{\lambda}{\beta}-1\right)\Gamma U'^2\chi\end{aligned}$$

*Lebowitz and Spohn, J Stat Phys **95** 333 (1999)*

GC symmetry: $\mathcal{L}_{\beta-\lambda} = \mathcal{L}_\lambda^\dagger$

A Brownian particle in an optical trap



$k = 6.67 \times 10^{-7}$N/m; $v = 1\ \mu$m/s; Particle radius 2.00 μm; $T = 23.5\ ^\circ$C

Work and heat for a dragged Brownian particle

Trap potential:

$$U(x, X(t)) = \frac{k}{2}(x - X(t))^2, \qquad X(t) = vt$$

Work distribution:

$$\phi(x, W, t) = \mathcal{N}_t \exp\left[-\frac{(W - W(x,t))^2}{2\sigma^2(t)} - \frac{\beta k}{2}(x - \xi(t))^2\right]$$

With $\tau = 1/\Gamma k$, $\alpha(t) = \mathrm{e}^{-t/\tau}$, $\mathcal{N}_t^{-1} = \sqrt{4\pi^2\sigma^2(t)/(\beta k)}$:

$$\begin{aligned} W(x,t) &= tv^2\tau k(2 - \alpha(t)) - vx\tau k(1 - \alpha(t)) - v^2\tau^2 k\left(2 + \alpha^2(t) + 3\alpha(t)\right) \\ \xi(t) &= v\tau\left(\alpha(t) - 1 + t/\tau\right), \quad \sigma^2(t) = v^2\tau^2\frac{k}{\beta}\left(\frac{2t}{\tau} + 1 - (2 - \alpha(t))^2\right) \end{aligned}$$

Heat distribution

Analogy with the Schrödinger equation for a harmonic oscillator

$$
\begin{aligned}
\chi(x,\lambda,t) &= \exp\left[-\frac{\delta(\lambda)}{2}U(x,X(t)) - \frac{\beta v}{2\Gamma}z(x,t)\right] \\
&\quad \times \sum_{n=0}^{\infty} \mathrm{e}^{\gamma_n t} c_n(\lambda)\psi_n(z(x,t)) \\
\gamma_n &= \left(-\Gamma k n + \delta^2(\lambda)v^2/4\Gamma\beta - \beta v^2/4\Gamma\right) \\
\delta(\lambda) &= \beta - 2\lambda \\
z(x,t) &= x - vt + \delta(\lambda)v\tau/\beta
\end{aligned}
$$

Check: A fixed trap

For $v = 0$:

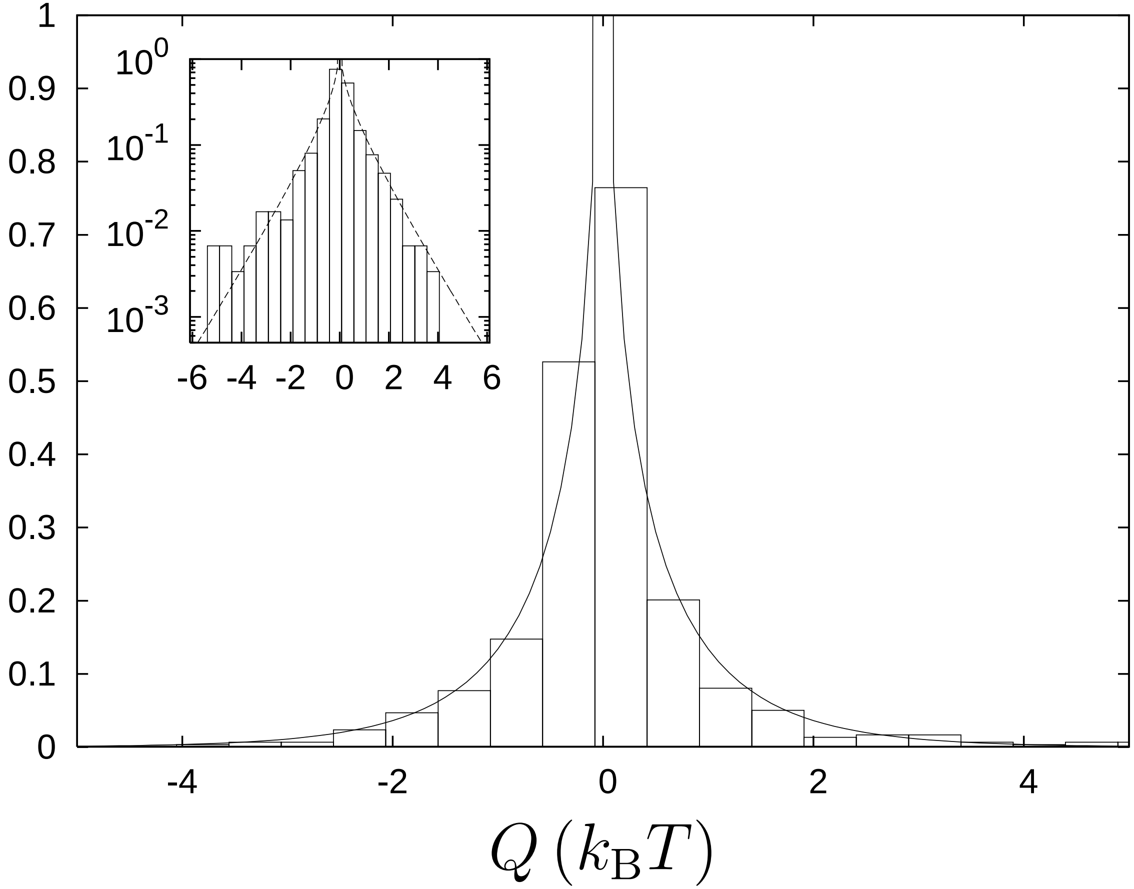
$$\chi(x,\lambda,t\to\infty) = \exp\left[-\frac{\delta(\lambda)}{2}U(x,0)\right] c_0(\lambda)\psi_0(x)$$

$$\Psi(\lambda,t\to\infty) = \int \mathrm{d}x\,\chi(x,\lambda,t\to\infty) = \left(1-(\lambda/\beta)^2\right)^{-1/2}$$

$$\varphi(Q,t\to\infty) = \frac{1}{2\pi i}\int \mathrm{d}\lambda\,\Psi(\lambda,t\to\infty)\,\mathrm{e}^{-\lambda Q} = \beta\frac{K_0(\beta|Q|)}{\pi}$$

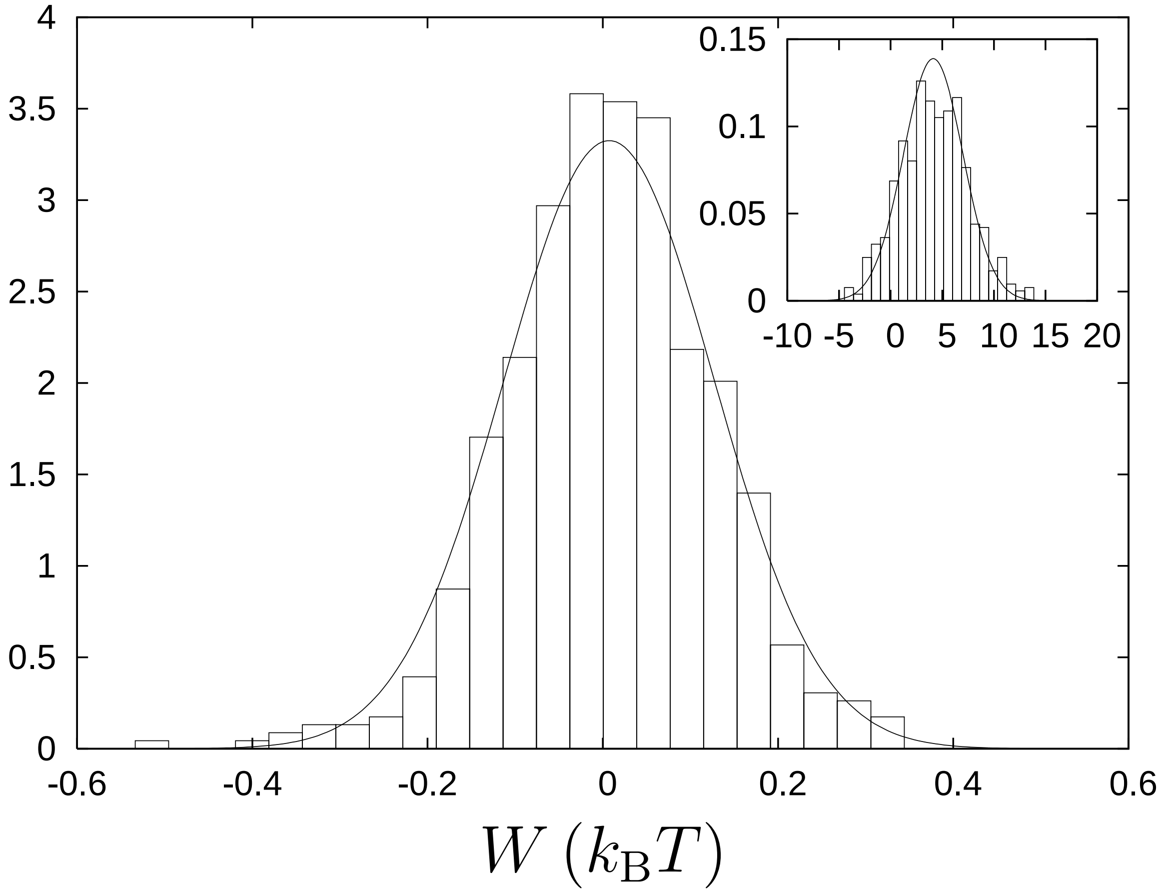
$K_0(x)$: modified Bessel function of the 2nd kind

Heat exchange for a fixed trap



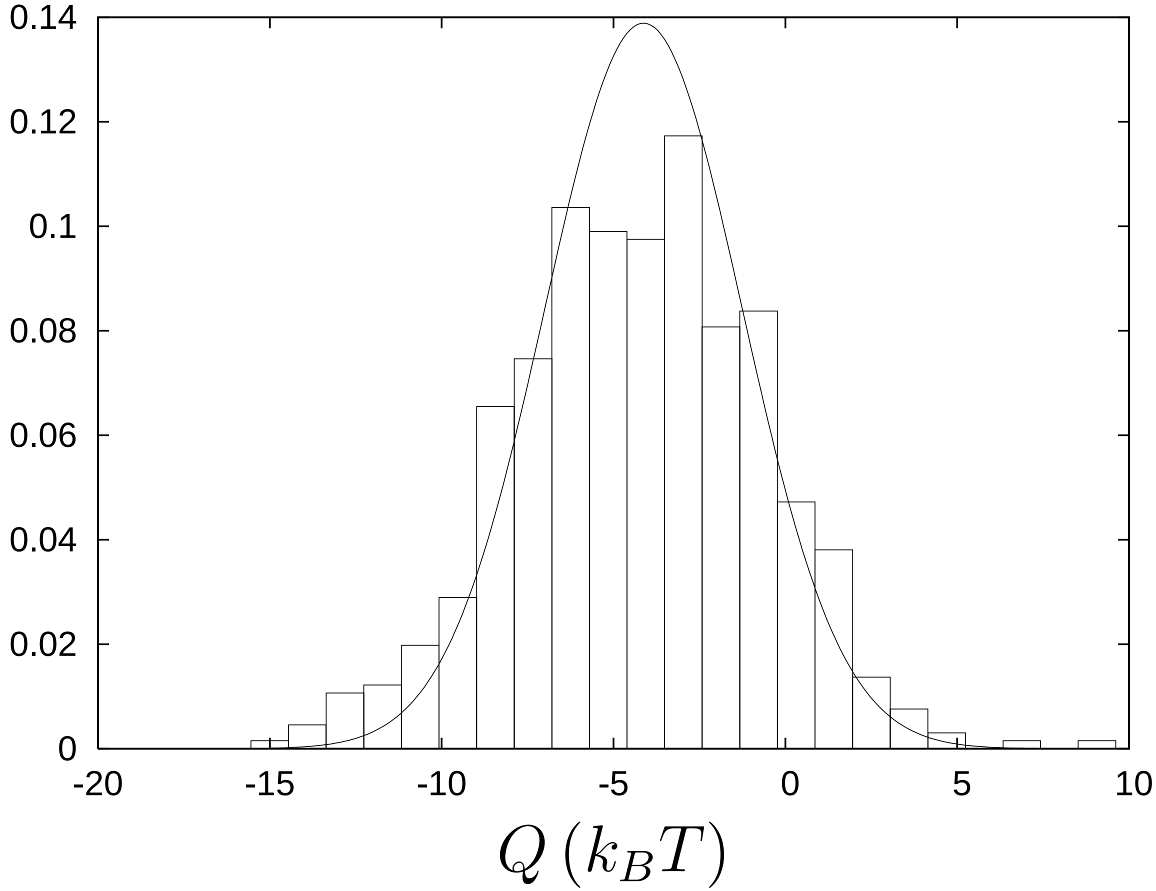
Data by A. I., G. Pesce, G. Rusciano, A. Sasso

Moving trap: Work distribution



Main figure: $t = 0.01$ s; Inset: $t = 1$ s

Moving trap: Heat distribution



Conclusions

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- These predictions are in agreement with Jarzynski-like and Gallavotti-Cohen-like fluctuation theorems
- These predictions can be verified in experimentally accessible systems
- This provides a new tool for accessing the microscopic dynamics of micro- and nanosystems