Stochastic Thermodynamics and Thermodynamics of Information

Lecture II: Fluctuation relations and their uses

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Summary

- Master equation:

$$\frac{\mathrm{d}p_x}{\mathrm{d}t} = \sum_{x'\,(\neq x)}{}' \left[R_{xx'}p_{x'} - R_{x'x}p_x\right]$$

- Detailed balance:

$$\frac{R_{xx'}}{R_{x'x}} = \mathrm{e}^{-\mathcal{Q}_{xx'}/k_\mathrm{B}T} = \mathrm{e}^{\Delta S^{(\mathrm{r})}_{xx'}/k_\mathrm{B}}$$

- Seifert's identity:

$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})} = \mathrm{e}^{(\Delta S^{(\mathrm{r})}(\boldsymbol{x})+\Delta s)/k_\mathrm{B}} = \mathrm{e}^{\Delta_\mathrm{i} S(\boldsymbol{x})/k_\mathrm{B}}$$

- Integral fluctuation theorem:

$$\left\langle \mathrm{e}^{-\Delta_\mathrm{i} S(\boldsymbol{x})/k_\mathrm{B}} \right\rangle = 1$$

Jarzynski's equality

- Start from equilibrium: $p_x(t_0) = p_x^{\mathrm{eq}}(\lambda_0)$, $p_{\hat{x}}(t_0) = p_{x_\mathrm{f}}^{\mathrm{eq}}(\lambda_\mathrm{f})$:

$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})} = \mathrm{e}^{-(\mathcal{Q}(\boldsymbol{x})+F_\mathrm{f}-E_{x_\mathrm{f}}-(F_0-E_{x_0}))/k_\mathrm{B}T}$$
$$= \mathrm{e}^{-(\mathcal{Q}(\boldsymbol{x})-\Delta E)/k_\mathrm{B}T}\,\mathrm{e}^{-\Delta F/k_\mathrm{B}T} = \mathrm{e}^{\mathcal{W}(\boldsymbol{x})/k_\mathrm{B}T}\,\mathrm{e}^{-\Delta F/k_\mathrm{B}T}$$

- *Jarzynski's equality*:

$$\underbrace{\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T}\right\rangle}_{\text{non-eq.}} = \underbrace{\mathrm{e}^{-\Delta F/k_\mathrm{B}T}}_{\text{eq}}$$

- Examples:
  - Quasi-static transformation: $p_x(t) = p_x^{\mathrm{eq}}(\lambda(t))$:

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T}\right\rangle \simeq \exp\left[-\frac{1}{k_\mathrm{B}T}\int \mathrm{d}t\;\dot{\lambda}(t)\;\langle\partial_\lambda E\rangle_{p^{\mathrm{eq}}(\lambda(t))}\right] = \mathrm{e}^{-\Delta F/k_\mathrm{B}T}$$

  - Sudden transformation $E_x(\lambda_\mathrm{i}) \longrightarrow E_x(\lambda_\mathrm{f})$:

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T}\right\rangle = \int \mathrm{d}x\;\mathrm{e}^{-(E_{\lambda_F}(x)-E_{\lambda_\mathrm{i}}(x))/k_\mathrm{B}T}\,\mathrm{e}^{(F_{\lambda_\mathrm{i}}-E_{\lambda_\mathrm{i}}(x))/k_\mathrm{B}T}$$
$$= \mathrm{e}^{-(F_{\lambda_\mathrm{f}}-F_{\lambda_\mathrm{i}})/k_\mathrm{B}T}$$

Jarzynski's equality

- Probability distribution of $\mathcal{W}$:

$$P_{\boldsymbol{\lambda}}(W) = \int \mathcal{D}\boldsymbol{x}\, \mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})\, \delta(\mathcal{W}(\boldsymbol{x}) - W)$$

- Relative entropy of $\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})$ and $\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})$:

$$\begin{aligned} D_{\mathrm{KL}}(\mathcal{P}_{\boldsymbol{\lambda}} \| \mathcal{P}_{\hat{\boldsymbol{\lambda}}}) &= \int \mathcal{D}\boldsymbol{x}\, \mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x}) \log \frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})} = \int \mathcal{D}\boldsymbol{x}\, \mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})\, \frac{\mathcal{W}(\boldsymbol{x}) - \Delta F}{k_{\mathrm{B}} T} \\ &= \int \mathrm{d}W\; P_{\boldsymbol{\lambda}}(W)\, \frac{W - \Delta F}{k_{\mathrm{B}} T} = \int \mathrm{d}W\; P_{\boldsymbol{\lambda}}(W) \log \frac{P_{\boldsymbol{\lambda}}(W)}{P_{\hat{\boldsymbol{\lambda}}}(-W)} \\ &= \frac{1}{k_{\mathrm{B}} T} \left\langle \mathcal{W}^{\mathrm{diss}} \right\rangle \end{aligned}$$

- Let $P_{\boldsymbol{\lambda}}(W)$ be close to a Gaussian:

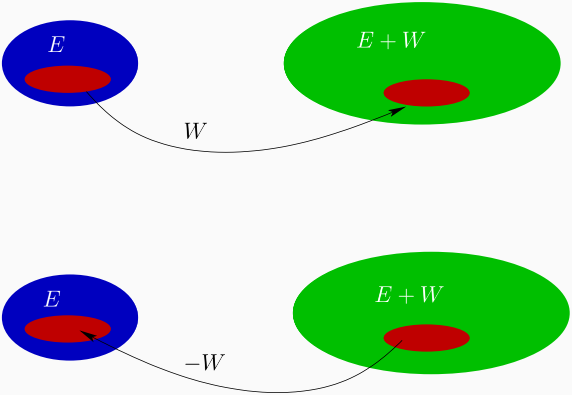
$$P_{\boldsymbol{\lambda}}(W) \propto \exp\left[-\frac{(W - \langle \mathcal{W} \rangle)^2}{2\sigma_W^2}\right]$$

then

$$\left\langle \mathcal{W}^{\mathrm{diss}} \right\rangle = \langle \mathcal{W} \rangle - \Delta F = \frac{\sigma_W^2}{2 k_{\mathrm{B}} T}$$

A Microcanonical Perspective

Cleuren et al., 2006



A Microcanonical Perspective

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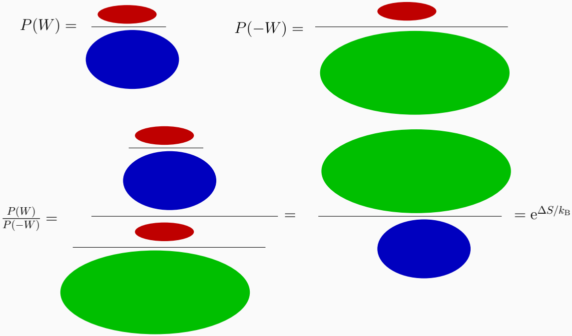
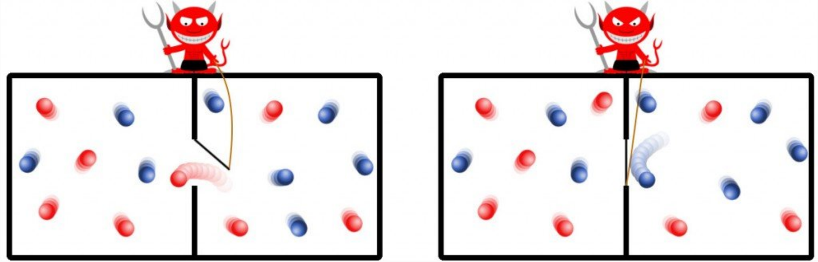


Information: Maxwell’s Demon



Information: Maxwell's Demon

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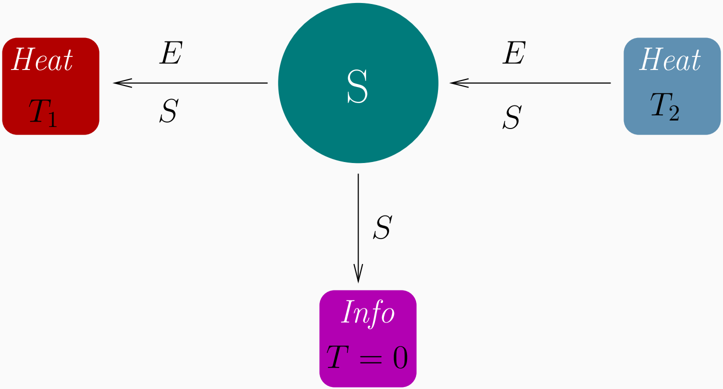
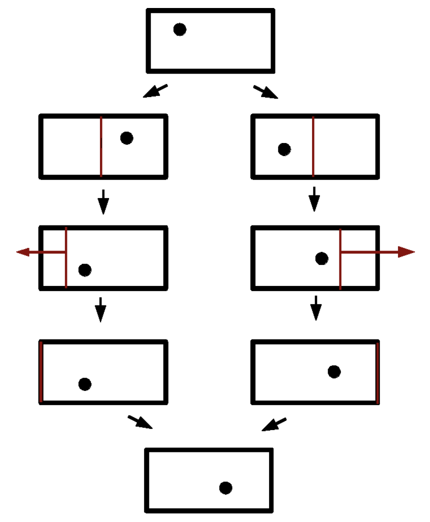
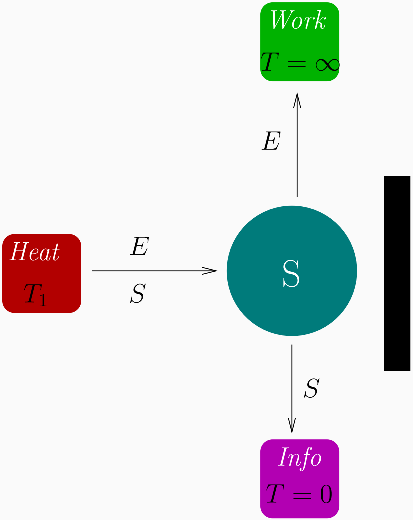


Information: Szilárd's Demon



Information: Szilárd’s Demon



Landauer bound

How can we reconcile Maxwell’s or Szilárd’s demons with the Second Principle?

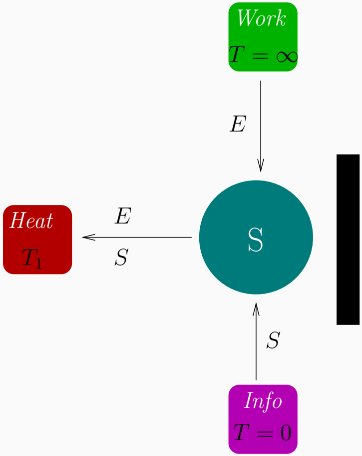
- The demon D is a physical system, initially isolated from S
- Measurement introduces correlations between D and S
- Correlations in D remain after the transformation
- Resetting the demon’s memory requires dissipation (Landauer, 1961)

Landauer bound

> *Any logically irreversible manipulation of information, such as the erasure of a bit or the merging of two computation paths, must be accompanied by a corresponding entropy increase in non-information bearing degrees of freedom of the information processing apparatus or its environment.*

Bennett, 2003

Information: Landauer's Eraser



2nd Law and Landauer's principle out of equilibrium

Esposito and van den Broeck, 2011

- A ST system described by probability distribution p, equilibrium distribution p^{eq}
- Define
$$I = D_{\mathrm{KL}}(p \| p^{\mathrm{eq}}) = \left(\mathcal{F}^{\mathrm{non-eq}} - F^{\mathrm{eq}}\right) / k_{\mathrm{B}} T$$
- Manipulate the system: $p(0) \longrightarrow p(1)$ $\left(p^{\mathrm{eq}}(0) \longrightarrow p^{\mathrm{eq}}(1)\right)$ then
$$\langle W \rangle - \Delta F \geq k_{\mathrm{B}} T \Delta I$$

2nd Law and Landauer's principle out of equilibrium

Esposito and van den Broeck, 2011

Proof:

- Master equation:

$$\frac{\mathrm{d}p_x}{\mathrm{d}t} = \sum_{x'\,(\neq x)}{}' \left[R_{xx'}(t)p_{x'}(t) - R_{xx'}(t)p_x(t)\right]$$

- Heat and work:

$$\dot{Q} = \sum_x E_x(t)\frac{\mathrm{d}p_x}{\mathrm{d}t}; \qquad \dot{W} = \sum_x \frac{\mathrm{d}E_x}{\mathrm{d}t}\,p_x(t)$$

- Change in I:

$$\frac{\mathrm{d}I}{\mathrm{d}t} = \underbrace{\sum_x \frac{\mathrm{d}p_x}{\mathrm{d}t}\log p_x}_{-\dot{S}/k_\mathrm{B}} \underbrace{- \sum_x \frac{\mathrm{d}p_x}{\mathrm{d}t}\log p_x^\mathrm{eq}}_{\dot{Q}/k_\mathrm{B}T} \underbrace{- \sum_x p_x \frac{\mathrm{d}}{\mathrm{d}t}\log p_x^\mathrm{eq}}_{-(\dot{F}^\mathrm{eq}-\dot{W})/k_\mathrm{B}T}$$

$$= \underbrace{-(\dot{S} + \dot{S}^{(\mathrm{r})})/k_\mathrm{B}}_{-\dot{S}_\mathrm{i}/k_\mathrm{B}\leq 0} + \left(\dot{W} - \dot{F}^\mathrm{eq}\right)/k_\mathrm{B}T$$

2nd Law and Landauer's principle out of equilibrium

Esposito and van den Broeck, 2011

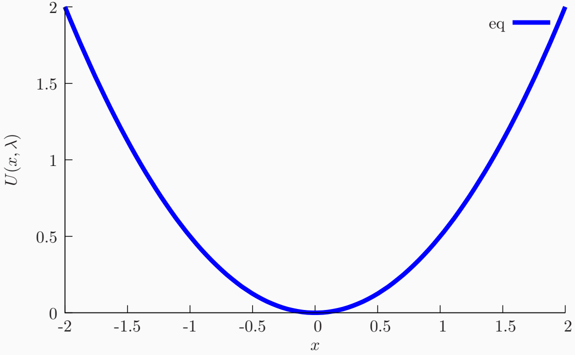
- Work extraction from non-equilibrium distribution:

$$p \neq p^{\mathrm{eq}} \quad \Rightarrow W - \Delta F^{\mathrm{eq}} \geq -k_{\mathrm{B}} T D_{\mathrm{KL}}(p \| p^{\mathrm{eq}})$$

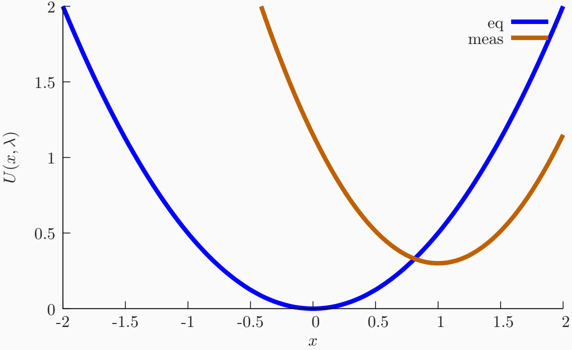
- Landauer's principle: If $\Delta I \geq 0$ there is a minimal dissipation

$$W^{\mathrm{diss}} = W - \Delta F \geq k_{\mathrm{B}} T \, \Delta I$$

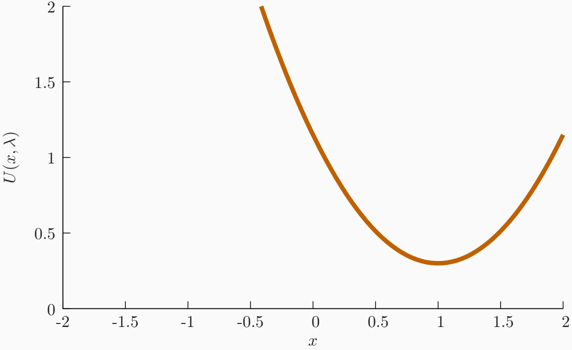
Work-extraction protocol



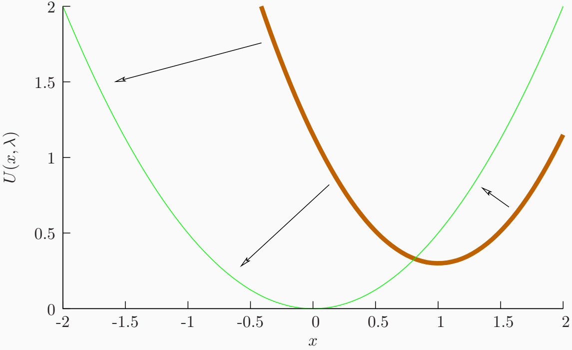
Work-extraction protocol



Work-extraction protocol



Work-extraction protocol

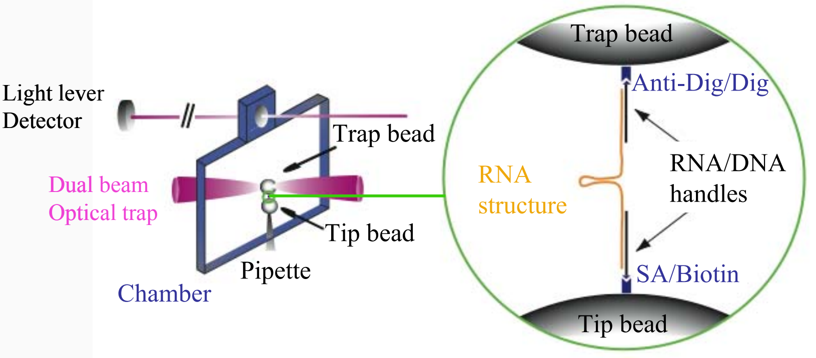


Probability distribution of W

- $P_{\hat{\boldsymbol{\lambda}}}(-W) = P_{\boldsymbol{\lambda}}(W)\, \mathrm{e}^{-(W-\Delta F)/k_\mathrm{B}T}$
- $P_{\hat{\boldsymbol{\lambda}}}(-W^*) = P_{\boldsymbol{\lambda}}(W^*) \Rightarrow W^* = \Delta F$
- Need to find an *overlap* between $P_{\boldsymbol{\lambda}}(W)$ and $P_{\hat{\boldsymbol{\lambda}}}(-W)$
- Properties of $P(W)$?

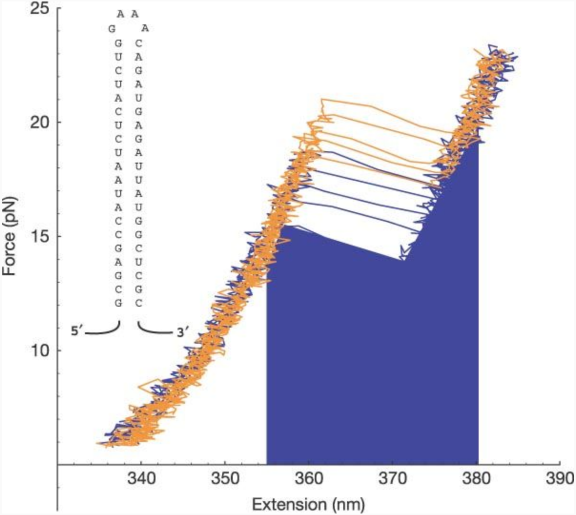
Unfolding and refolding a RNA hairpin

Collin et al. 2005



Unfolding and refolding a RNA hairpin

Collin et al. 2005



Unfolding and refolding a RNA hairpin

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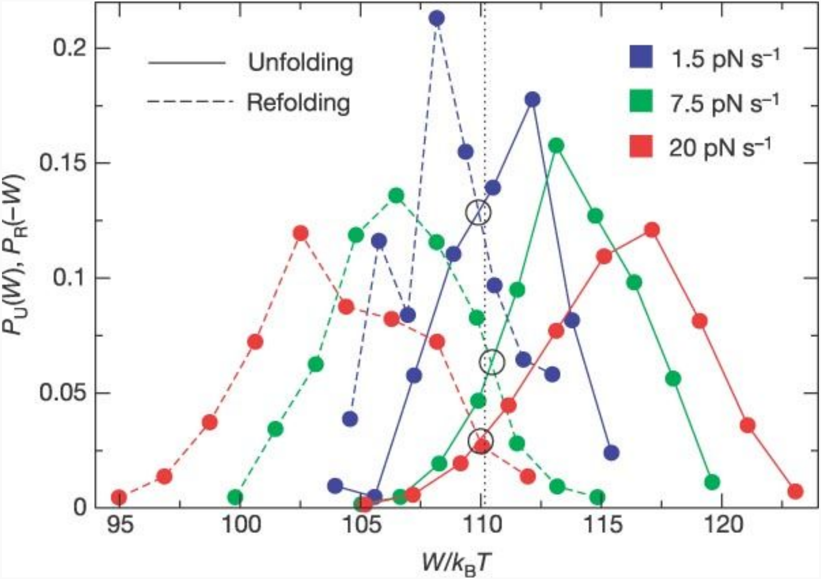
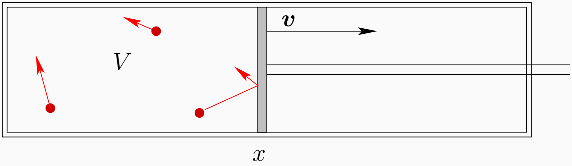


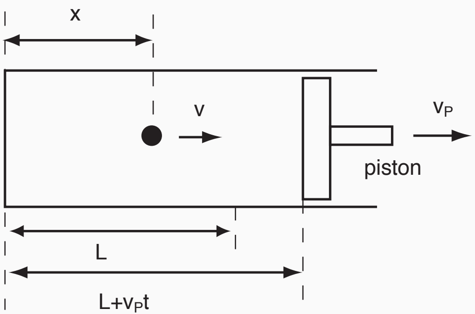
$P(W)$ for isothermal expansion



- Ideal gas N particles, temperature T
- $V \longrightarrow 2V \Rightarrow \Delta F = T\,\Delta S = N k_{\mathrm{B}} T \log 2$
- But: If $v \gg c$ (speed of sound) $\Rightarrow$ no collisions $\Rightarrow W \simeq 0$?

A $N = 1$ ideal gas

Lua and Grosberg, 2005

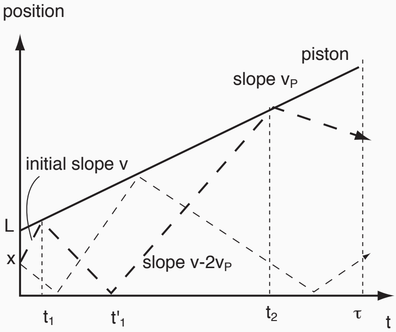


- Set $k_\mathrm{B}T, m = 1$ for simplicity

$$\langle \mathrm{e}^{-W} \rangle = \int_0^L \mathrm{d}x \int_{-\infty}^{+\infty} \mathrm{d}v \; \mathrm{e}^{-v^2/2} \, \mathrm{e}^{-w_\tau(x,v)} \Big/ \int_0^L \mathrm{d}x \int_{-\infty}^{+\infty} \mathrm{d}v \; \mathrm{e}^{-v^2/2}$$

A $N = 1$ ideal gas

Lua and Grosberg, 2005



$$m, \tau, k_{\mathrm{B}}T = 1$$

$$v' = 2v_{\mathrm{p}} - 1$$

$$w^{(n)} = \frac{1}{2}\left(v^{(n)^2} - v^{(n-1)^2}\right) = 2v_{\mathrm{p}}\left(v_{\mathrm{p}} - v^{(n-1)}\right)$$

$$W(v, n) = 2n^2v_{\mathrm{p}}^2 - 2nvv_{\mathrm{p}}$$

A $N = 1$ ideal gas

Lua and Grosberg, 2005

Fast moving piston:

$$v_\mathrm{p} \gg 1, \quad L \gg v_\mathrm{p} \quad \Rightarrow \quad n = 0, 1$$

$$v(W) = v_\mathrm{p} - \frac{W}{2v_\mathrm{p}}, \qquad x > L - (v - v_\mathrm{p}) = L + \frac{W}{2v_\mathrm{p}}$$

$$P(W) \simeq P_0\,\delta(W) - \underbrace{\frac{W}{4v_\mathrm{p}L}\,\frac{\mathrm{e}^{-(v_\mathrm{p}-W/2v_\mathrm{p})^2/2}}{\sqrt{2\pi}v_\mathrm{p}}}_{P(W|W<0,W>-4Lv_\mathrm{p})}$$

$$P(W<0) \simeq \frac{1}{\sqrt{2\pi}Lv_\mathrm{p}^2}\,\mathrm{e}^{-v_\mathrm{p}^2/2}$$

$$\left\langle \mathrm{e}^{-W} \right\rangle \simeq 1 + \frac{v_\mathrm{p}}{L} = \mathrm{e}^{\Delta S/k_\mathrm{B}} \qquad (\tau = 1)$$

$$\langle W \rangle \simeq -\frac{4}{\sqrt{2\pi}Lv_\mathrm{p}^2}\,\mathrm{e}^{-v_\mathrm{p}^2/2} = -4P(W<0)$$

Collective coordinates

- Exploring equilibrium free-energy landscapes: Collective coordinate M_x (e.g., RNA hairpin opening)
- We wish to evaluate the free-energy landscape of M:

$$F^{(0)}(M) = -k_\mathrm{B}T \log \sum_x \delta(M - M_x)\, \mathrm{e}^{-E_x^{(0)}/k_\mathrm{B}T}$$

- Equilibrium probability distribution for M:

$$P^\mathrm{eq}(M) = \mathrm{e}^{-\left(F^{(0)}(M) - F^{(0)}\right)/k_\mathrm{B}T}$$

- Manipulation via a potential which depends on M (e.g., harmonic potential):

$$U(M_x, \lambda) \longrightarrow E_x(\lambda) = E_x^{(0)} - U(M_x, \lambda)$$

Work probability distribution

Evolution operator $\mathcal{L}_\lambda$ (e.g., master equation):

$$\begin{aligned} \frac{\mathrm{d}p_x}{\mathrm{d}t} &= \left(\mathcal{L}_{\lambda(t)}\, p\right)_x \\ \mathcal{L}_\lambda\, p^{\mathrm{eq}}(\lambda) &= 0 \end{aligned}$$

Work:

$$\mathcal{W} = -\int_0^t \mathrm{d}t'\ \dot{\lambda}(t')\,\partial_\lambda U\left(M_{x(t')}, \lambda(t')\right)$$

$\Phi_x(W,t)$: Joint probability of x and of the accumulated work W:

$$\frac{\partial \Phi_x(W,t)}{\partial t} = \left(\mathcal{L}_{\lambda(t)}\Phi\right)_x + \dot{\lambda}(t)\partial_\lambda U(M_x, \lambda(t))\frac{\partial \Phi}{\partial W}$$

The generating function

Define

$$\Psi_x(\mu, t) = \int \mathrm{d}W \, \mathrm{e}^{-W/k_\mathrm{B}T} \, \Phi_x(W, t)$$

Then

$$\frac{\partial \Psi_x}{\partial t} = \left(\mathcal{L}_{\lambda(t)} \Psi\right)_x - \frac{\dot{\lambda}(t)}{k_\mathrm{B}T} \partial_\lambda U(M_x, \lambda(t)) \, \Psi_x$$

Thus one obtains

$$\begin{aligned} \Psi_x &= \mathrm{e}^{\left(F_{\lambda(0)} - E_x(\lambda(t))\right)/k_\mathrm{B}T} \\ &= p_x^{\mathrm{eq}}(\lambda(t)) \, \mathrm{e}^{-(F_{\lambda(t)} - F_{\lambda(0)})/k_\mathrm{B}T} \end{aligned} \tag{1}$$

$$\sum_x \Psi_x(t) = \left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle = \mathrm{e}^{-(F_{\lambda(t)} - F_{\lambda(0)})/k_\mathrm{B}T}$$

Proof of (1)

Define

$$\psi_x(t) = \mathrm{e}^{(F_{\lambda(0)} - E_x(\lambda(t)))/k_\mathrm{B}T}$$

Then $\psi(x,t)$ satisfies

$$\begin{aligned}
\psi_x(0) &= p_x^{\mathrm{eq}}(\lambda(0)) = \Psi_x(-1/k_\mathrm{B}T, 0) \\
\partial_t \psi_x &= -\frac{\dot\lambda}{k_\mathrm{B}T}\partial_\lambda E_x(\lambda(t))\,\psi_x(t) \\
&= \underbrace{\left(\mathcal{L}_{\lambda(t)}\,\psi_x(x,\lambda(t))\right)_x}_{=0} - \frac{\dot\lambda}{k_\mathrm{B}T}\partial_\lambda E_x(\lambda(t))\,\psi_x(t)
\end{aligned}$$

Thus

$$\psi_x(t) = \Psi_x(t)$$

The basic identity

Multiply (1) by $\delta(M - M_x)$ and sum over x:

$$\begin{aligned}\left\langle \delta(M - M_x)\,\mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle &= \sum_x \delta(M - M_x)\,\mathrm{e}^{(F_{\lambda_0} - E_x(\lambda(t)))/k_\mathrm{B}T} \\ &= \exp\left[-\left(F^{(0)}(M) - U(M,\lambda(t)) - F^{(0)}\right]\right]\end{aligned}$$

Multiply both sides by $\mathrm{e}^{U(M,\lambda(t))/k_\mathrm{B}T}$:

$$\mathrm{e}^{U(M,\lambda(t))/k_\mathrm{B}T} \left\langle \delta(M - M_x)\,\mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle = \mathrm{e}^{(F^{(0)}(M) - F^{(0)})/k_\mathrm{B}T}$$

Crooks 1999, Hummer and Szabo 2001

Summary

- We have discussed systems satisfying detailed balance (with time-dependent energy) at all times
- Fluctuation relations allow to obtain equilibrium properties from non-equilibrium measurements
- The fluctuation relations are dominated by tails of work or entropy-production distribution
- Reliably sampling the tails requires good control of the statistics

Thank you!

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