Introduction to **Stochastic Thermodynamics:** from **Fluctuation Theorems** to **Thermodynamic Trade-off Relations**

Lecture 2

2022 ICTP-KIAS School on Statistical Physics for Life Sciences

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Jae Sung Lee

Korea Institute for Advanced Study

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Contents of Lecture 2

1. Entropy production (EP)

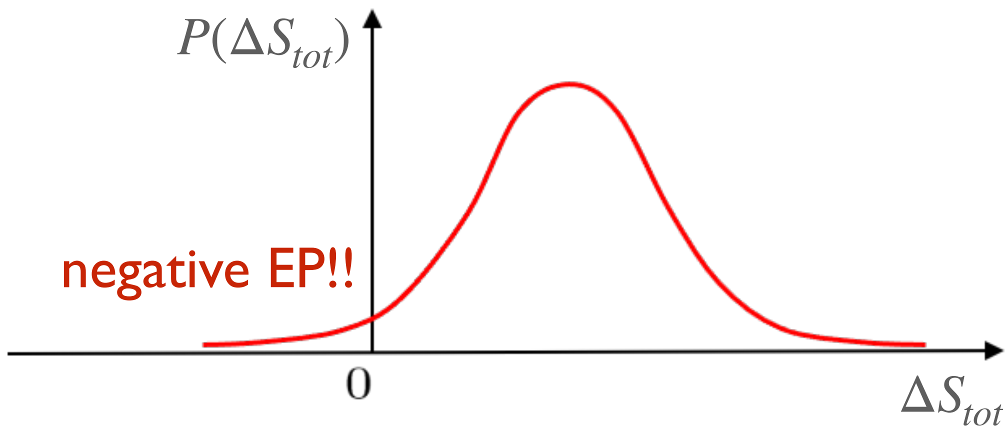
- Thermodynamic EP: Clausius EP = $\Delta S = \int \frac{\delta Q}{T}$ (defined in equilibrium)

- What is EP for general non-equilibrium stochastic processes?

2. Thermodynamic 2nd Law $\rightarrow$ Fluctuation Theorems

- negative EP region exists due to thermal fluctuation

- $\Delta S_{\text{tot}} \geq 0$?



Entropy Production

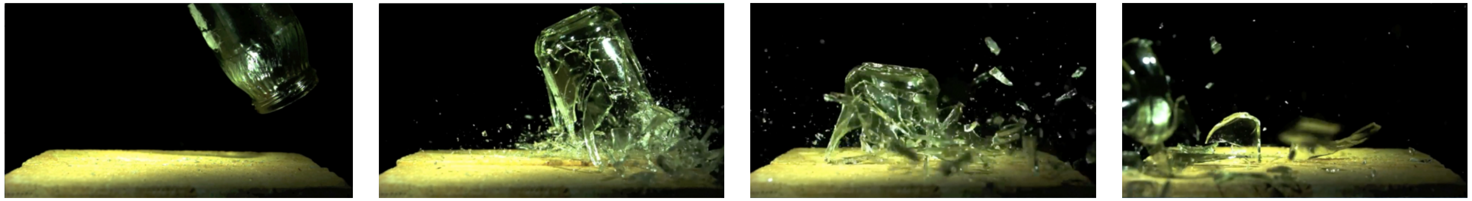
1. Irreversibility

Seifert, PRL 95, 040602 (2005)

irreversible process

forward: more probable

time-reversal: less probable



reversible process

forward, time-reversal

: equally probable

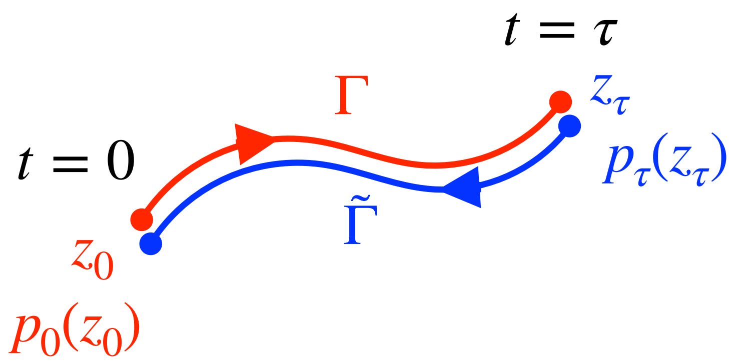
Entropy Production

1. Irreversibility

Seifert, PRL 95, 040602 (2005)

time-forward path probability: $\mathscr{P}(\Gamma) = p_0(z_0)\mathscr{P}(\Gamma \,|\, z_0)$

time-reverse path probability: $\tilde{\mathscr{P}}(\tilde{\Gamma}) = p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma} \,|\, \tilde{z}_\tau)$



$$R \equiv \ln \frac{p_0(z_0)\mathscr{P}(\Gamma \,|\, z_0)}{p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma} \,|\, \tilde{z}_\tau)}$$

= 0 (reversible)

≠ 0 (irreversible)

Entropy Production

2. Physical meaning of irreversibility (overdamped Langevin)

$$R \equiv \ln \frac{p_0(z_0)\mathscr{P}(\Gamma\,|\,z_0)}{p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma}\,|\,\tilde{z}_\tau)}$$

$x(t_0 = 0) \quad x(t_1) \quad \cdots \quad x(t_n) \quad \cdots \quad x(t_{N-1}) \quad x(t_N = \tau)$

$\tilde{x}(t_N = \tau) \quad \tilde{x}(t_{N-1}) \quad \cdots \quad \tilde{x}(\tau - t_n) \quad \cdots \quad \tilde{x}(t_1) \quad \tilde{x}(0)$

$\rightarrow \tilde{x}(t) = x(\tau - t)$

time-forward path probability

$$\mathscr{P}(\Gamma) = \prod_{n=0}^{N}\left(\frac{dx(t_n)}{\sqrt{4\pi k_B T/\gamma}}\right)\exp\left[\int_0^\tau dt\left(-\frac{1}{4k_B T/\gamma}\left\{\dot{x}(t) - f(x(t),t)/\gamma\right\}_\circ^2 - \frac{1}{2\gamma}\partial_x f(x)\right)\right]p_0(x(0))$$

time-reverse path probability

$$\tilde{\mathscr{P}}(\tilde{\Gamma}) = \prod_{n=0}^{N}\left(\frac{d\tilde{x}(t_n)}{\sqrt{4\pi k_B T/\gamma}}\right)\exp\left[\int_0^\tau dt\left(-\frac{1}{4k_B T/\gamma}\left\{\dot{\tilde{x}}(t) - f(\tilde{x}(t),\tau - t)/\gamma\right\}_\circ^2 - \frac{1}{2\gamma}\partial_{\tilde{x}} f(\tilde{x})\right)\right]p_\tau(x(\tau))$$

$t' \equiv \tau - t$

$$\rightarrow \tilde{x}(t) = x(t'), \quad \dot{\tilde{x}}(t) = \frac{d}{dt}\tilde{x}(t) = \frac{d}{dt}x(\tau - t) = -\frac{d}{dt'}x(t') = -\dot{x}(t')$$

$$= \prod_{n=0}^{N}\left(\frac{dx(t_n')}{\sqrt{4\pi k_B T/\gamma}}\right)\exp\left[\int_\tau^0 -dt'\left(-\frac{1}{4k_B T/\gamma}\left\{-\dot{x}(t') - f(x(t'),t')/\gamma\right\}_\circ^2 - \frac{1}{2\gamma}\partial_x f(x)\right)\right]p_\tau(x(\tau))$$

$t' \rightarrow t$

$$= \prod_{n=0}^{N}\left(\frac{dx(t_n)}{\sqrt{4\pi k_B T/\gamma}}\right)\exp\left[\int_0^\tau dt\left(-\frac{1}{4k_B T/\gamma}\left\{-\dot{x}(t) - f(x(t),t)/\gamma\right\}_\circ^2 - \frac{1}{2\gamma}\partial_x f(x)\right)\right]p_\tau(x(\tau))$$

Entropy Production

2. Physical meaning of irreversibility (overdamped Langevin)

$$R \equiv \ln \frac{p_0(z_0)\mathscr{P}(\Gamma\,|\,z_0)}{p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma}\,|\,\tilde{z}_\tau)}$$

$x(t_0 = 0) \quad x(t_1) \quad \cdots \quad x(t_n) \quad \cdots \quad x(t_{N-1}) \quad x(t_N = \tau)$

$\tilde{x}(t_N = \tau) \quad \tilde{x}(t_{N-1}) \quad \cdots \quad \tilde{x}(\tau - t_n) \quad \cdots \quad \tilde{x}(t_1) \quad \tilde{x}(0)$

$\rightarrow \tilde{x}(t) = x(\tau - t)$

time-forward path probability

$$\mathscr{P}(\Gamma) = \prod_{n=0}^{N} \left(\frac{dx(t_n)}{\sqrt{4\pi k_B T/\gamma}} \right) \exp\left[\int_0^\tau dt \left(-\frac{1}{4k_B T/\gamma} \left\{ \dot{x}(t) - f(x(t),t)/\gamma \right\}_\circ^2 - \frac{1}{2\gamma}\partial_x f(x) \right) \right] p_0(x(0))$$

time-reverse path probability

$$\tilde{\mathscr{P}}(\tilde{\Gamma}) = \prod_{n=0}^{N} \left(\frac{dx(t_n)}{\sqrt{4\pi k_B T/\gamma}} \right) \exp\left[\int_0^\tau dt \left(-\frac{1}{4k_B T/\gamma} \left\{ -\dot{x}(t) - f(x(t),t)/\gamma \right\}_\circ^2 - \frac{1}{2\gamma}\partial_x f(x) \right) \right] p_\tau(x(\tau))$$

$$R = \ln \frac{\mathscr{P}(\Gamma)}{\tilde{\mathscr{P}}(\tilde{\Gamma})}$$

$$= \ln \frac{p_0(x(0))}{p_\tau(x(\tau))} + \ln \frac{\mathscr{P}(\Gamma\,|\,x_0)}{\tilde{\mathscr{P}}(\tilde{\Gamma}\,|\,\tilde{x}_\tau)}$$

$$= \int_0^\tau dt \frac{-1}{4k_B T/\gamma} \left(\left\{ \dot{x}(t) - f(x(t),t)/\gamma \right\}_\circ^2 - \left\{ \dot{x}(t) + f(x(t),t)/\gamma \right\}_\circ^2 \right)$$

$$= \int_0^\tau dt \frac{\dot{x}(t) \circ f(x(t),t)}{k_B T} = -\frac{Q}{k_B T} = \Delta S_r / k_B$$

$\gamma \dot{x}(t) = f(x(t),t) + \xi \qquad = \dot{x}(t) \circ \big(\gamma \dot{x}(t) - \xi(t)\big)\, dt = -\,dQ$

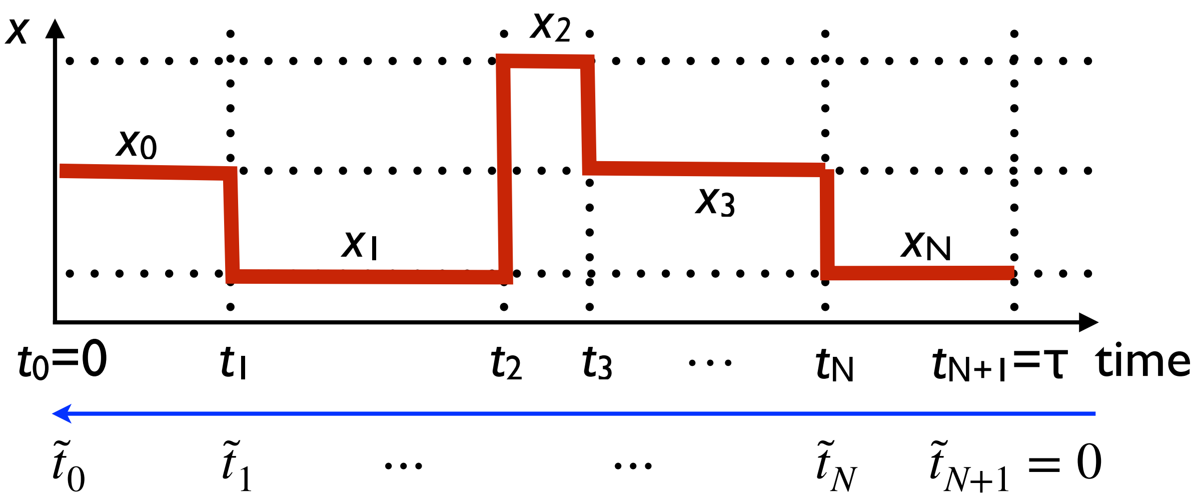
$$= \Delta S_{sys}/k_B + \Delta S_r/k_B = \Delta S_{tot}/k_B$$

$\Delta S_{sys} = S_{sys}(\tau) - S_{sys}(0) \quad$ where $S_{sys}(t) = -\,k_B \ln p_t(x(t))$

Entropy Production

3. Physical meaning of irreversibility (Markov jump process)

$$R \equiv \ln \frac{p_0(z_0)\mathscr{P}(\Gamma\,|\,z_0)}{p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde\Gamma\,|\,\tilde z_\tau)}$$



time-forward path probability:

$$\mathscr{P}(\Gamma) = p_{x_0}(0)\prod_{n=1}^{N}\left[e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1},x_{n-1}}(t)dt} R_{x_n,x_{n-1}}(t_n)dt\right] e^{\int_{t_N}^{\tau} R_{x_N,x_N}(t)dt}$$

$\rightarrow \tilde t_n = \tau - t_n$

time-reverse path probability

$$\tilde{\mathscr{P}}(\tilde\Gamma) = p_{x_\tau}(\tau) e^{\int_0^{\tilde t_N} R_{x_N,x_N}(\tau-\tilde t)d\tilde t} R_{x_{N-1},x_N}(\tau-\tilde t_N)$$

$$\times \prod_{n=2}^{N}\left[e^{\int_{\tilde t_n}^{\tilde t_{n-1}} R_{x_{n-1},x_{n-1}}(\tau-\tilde t)d\tilde t} R_{x_{n-2},x_{n-1}}(\tau-\tilde t_n)dt\right] e^{\int_{\tilde t_1}^{\tilde t_0} R_{x_0,x_0}(\tau-\tilde t)d\tilde t}$$

$$= p_{x_\tau}(\tau)\prod_{n=1}^{N}\left[e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1},x_{n-1}}(t)dt} R_{x_{n-1},x_n}(t_n)dt\right] e^{\int_{t_N}^{\tau} R_{x_N,x_N}(t)dt}$$

Entropy Production

3. Physical meaning of irreversibility (Markov jump process)

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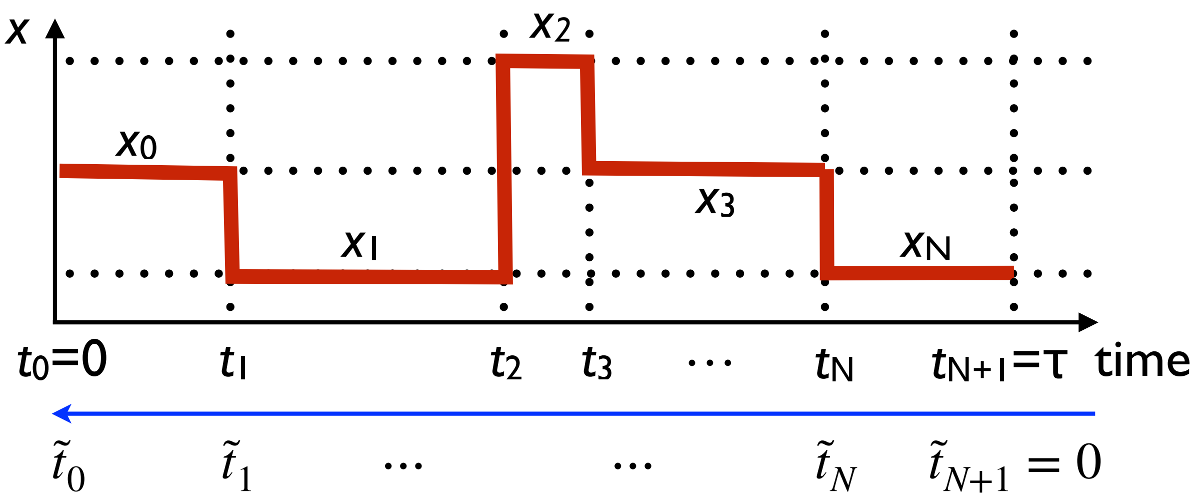


time-forward path probability:

$$\mathscr{P}(\Gamma) = p_{x_0}(0)\prod_{n=1}^{N}\left[e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1},x_{n-1}}(t)dt} R_{x_n,x_{n-1}}(t_n)dt\right]\ e^{\int_{t_N}^{\tau} R_{x_N,x_N}(t)dt}$$

$\rightarrow \tilde{t}_n = \tau - t_n$

time-reverse path probability

$$\tilde{\mathscr{P}}(\tilde{\Gamma}) = p_{x_\tau}(\tau)\prod_{n=1}^{N}\left[e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1},x_{n-1}}(t)dt} R_{x_{n-1},x_n}(t_n)dt\right]\ e^{\int_{t_N}^{\tau} R_{x_N,x_N}(t)dt}$$

$$R = \ln\frac{p_{x_0}(0)}{p_{x_\tau}(\tau)} + \sum_{n=1}^{N}\ln\frac{R_{x_n,x_{n-1}}(t_n)}{R_{x_{n-1},x_n}(t_n)} = -\frac{E_{x_n} - E_{x_{n-1}}}{k_B T} = -\frac{Q(t_n)}{k_B T}$$

(local detailed balance)

$$R_{ij}p_j^{\text{eq}} = R_{ji}p_i^{\text{eq}}$$

$$\rightarrow R_{ij}/R_{ji} = e^{-\beta(E_i - E_j)}$$

$$= \Delta S_{\text{sys}}/k_B + \Delta S_r/k_B = \Delta S_{\text{tot}}/k_B$$

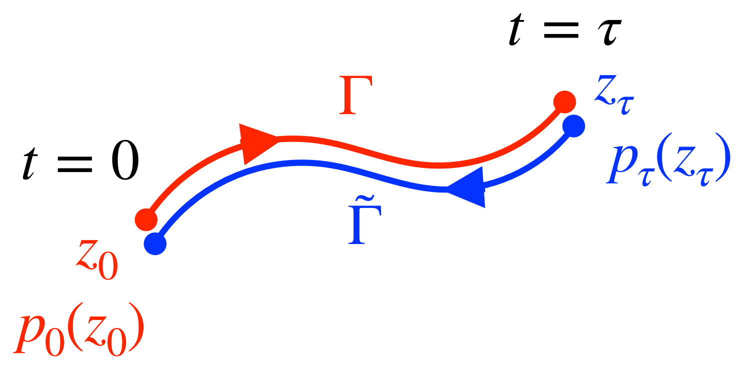
$\Delta S_{\text{sys}} = S_{\text{sys}}(\tau) - S_{\text{sys}}(0)$ where $S_{\text{sys}}(t) = -k_B \ln p_{x_t}(t)$

Fluctuation Theorems

1. Irreversibility and Fluctuation Theorems

time-forward path probability: $\mathscr{P}(\Gamma) = p_0(z_0)\mathscr{P}(\Gamma \mid z_0)$

time-reverse path probability: $\tilde{\mathscr{P}}(\tilde{\Gamma}) = p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma} \mid \tilde{z}_\tau)$



$$R \equiv \ln \frac{\mathscr{P}(\Gamma)}{\tilde{\mathscr{P}}(\tilde{\Gamma})} \quad \begin{array}{l} = 0 \text{ (reversible)} \\ \neq 0 \text{ (irreversible)} \end{array}$$

$$= \Delta S_{\text{sys}}/k_B - \frac{Q}{k_B T} \quad \rightarrow R = \Delta S_{\text{tot}}/k_B$$: (stochastic) total entropy production!

Property of R

$$\langle e^{-R} \rangle = \sum_{\text{all paths}} \mathscr{P}(\Gamma) e^{-R} = \sum_{\text{all paths}} \tilde{\mathscr{P}}(\tilde{\Gamma}) = 1$$

➡ $\langle e^{-\Delta S_{\text{tot}}/k_B} \rangle = 1$: Fluctuation Theorem

Jensen's inequality: $\langle f(x) \rangle \geq f(\langle x \rangle)$ for convex function $f(x)$

➡ $1 = \langle e^{-R} \rangle \geq e^{-\langle R \rangle} \rightarrow \langle R \rangle \geq 0 \rightarrow \langle \Delta S_{\text{tot}} \rangle \geq 0$

$\rightarrow \Delta S_{\text{tot}}$ can be negative, but its average is nonnegative. (2nd law in stochastic system)

Fluctuation Theorems

1. Irreversibility and Fluctuation Theorems

time-forward path probability: $\mathscr{P}(\Gamma) = p_0(z_0)\mathscr{P}(\Gamma \,|\, z_0)$

time-reverse path probability: $\tilde{\mathscr{P}}(\tilde{\Gamma}) = p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma} \,|\, \tilde{z}_\tau)$

$$R \equiv \ln \frac{\mathscr{P}(\Gamma)}{\tilde{\mathscr{P}}(\tilde{\Gamma})} \quad \rightarrow R = \Delta S_{\rm tot} / k_{\rm B}$$: (stochastic) total entropy production!

$$\langle e^{-\Delta S_{\rm tot}/k_{\rm B}} \rangle = 1$$: Fluctuation Theorem

different choice of denominator

$$R^* \equiv \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^*(\Gamma)} \qquad \sum_{\text{all paths}} \mathscr{P}^*(\Gamma) = 1$$

$$\langle e^{-R^*} \rangle = \sum_{\text{all paths}} \mathscr{P}(\Gamma) e^{-R} = \sum_{\text{all paths}} \mathscr{P}^*(\Gamma) = 1$$

Fluctuation Theorems

2. Various Fluctuation Theorems

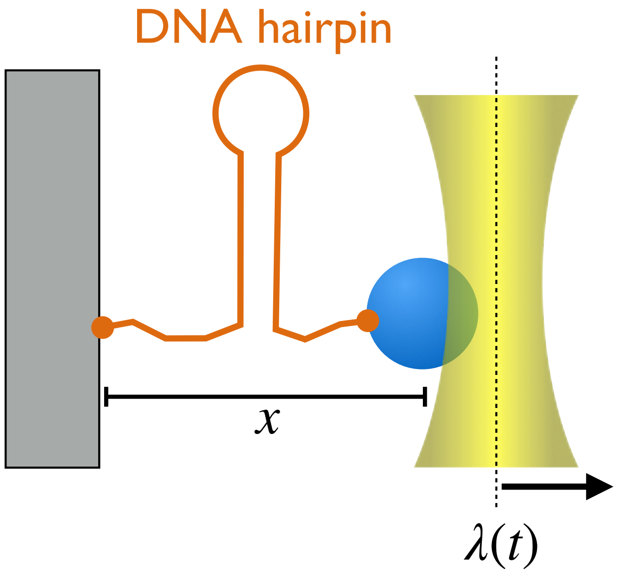
$$R^* \equiv \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^*(\Gamma)} \qquad \sum_{\text{all paths}} \mathscr{P}^*(\Gamma) = 1 \qquad \langle e^{-R^*} \rangle = 1$$

→ Jarzynski equality: $\langle e^{-\beta W} \rangle = e^{\beta \Delta F}$

1) Equilibrium initial distributions

Jarzynski, PRL 78, 2690 (1997)

ex) DNA-pulling experiment



$$\gamma \dot{x} = -k(x - \lambda(t)) + \xi, \qquad U\left(\lambda(t), x(t)\right) = \frac{k}{2}\left(x(t) - \lambda(t)\right)^2$$

Protocol:

$\lambda(t) = \lambda_0 \quad (t < 0)$ → initial state: equilibrium $\beta = \dfrac{1}{k_B T}$

$\quad\;\; = at + \lambda_0 \quad (t \geq 0)$

initial distribution: $p_0^{eq}(x) = \dfrac{e^{-\beta U(\lambda_0, x)}}{Z_0} = e^{\beta(-U(\lambda_0, x) + F_0)}$

$$Z_t = \int dx\; e^{-\beta U(\lambda(t), x)}$$

final distribution: $p_\tau(x)$ (arbitrary state)

$$F_t = -\beta^{-1} \ln Z_t$$

$\mathscr{P}(\Gamma) = p_0^{eq}(x_0)\mathscr{P}(\Gamma \mid x_0)$

$\mathscr{P}^*(\Gamma) = p_\tau^{eq}(x_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma} \mid \tilde{x}_\tau)$

$$p_\tau^{eq}(x) = e^{\beta(-U(\lambda(\tau), x) + F_\tau)}$$

$$\to R^* \equiv \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^*(\Gamma)} = \beta\left[U(\tau) - U(0) - (F_\tau - F_0) - Q\right]$$

$U(\tau) - U(0) = \Delta E$, $\quad F_\tau - F_0 = \Delta F$

$$= \beta(\Delta E - Q - \Delta F) = \beta(W - \Delta F)$$

Fluctuation Theorems

2. Various Fluctuation Theorems

$$R^* \equiv \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^*(\Gamma)} \qquad \sum_{\text{all paths}} \mathscr{P}^*(\Gamma) = 1 \qquad \langle e^{-R^*} \rangle = 1$$

1) Equilibrium initial distributions (Jarzynski equality) Jarzynski, PRL 78, 2690 (1997)

$$\mathscr{P}(\Gamma) = p_0^{\text{eq}}(x_0)\mathscr{P}(\Gamma \,|\, x_0)$$
$$\mathscr{P}^*(\Gamma) = p_\tau^{\text{eq}}(x_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma} \,|\, \tilde{x}_\tau)$$
$$\rightarrow \quad R^* \equiv \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^*(\Gamma)} = \beta(W - \Delta F)$$

→ Jarzynski equality: $\langle e^{-\beta W} \rangle = e^{\beta \Delta F}$

Equilibrium free energy can be evaluated by measuring nonequilibrium work.

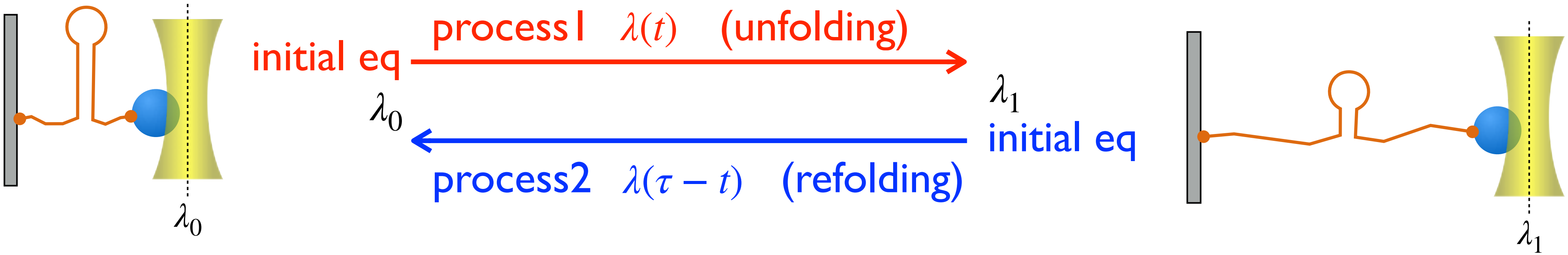
Fluctuation Theorems

2. Various Fluctuation Theorems

$$R^* \equiv \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^*(\Gamma)} \qquad \sum_{\text{all paths}} \mathscr{P}^*(\Gamma) = 1 \qquad \langle e^{-R^*} \rangle = 1$$

2) Crooks relation

Crooks, PRE 60, 2721 (1999)



[process1] $$R_1^*(\Gamma) = \ln \frac{\mathscr{P}_1(\Gamma)}{\mathscr{P}_1^*(\Gamma)}$$

$$\mathscr{P}_1(\Gamma) = p_{\lambda_0}^{\text{eq}}(x_0)\mathscr{P}_{\lambda_0 \to \lambda_1}(\Gamma \,|\, x_0)$$

$$\mathscr{P}_1^*(\Gamma) = p_{\lambda_1}^{\text{eq}}(x_\tau)\mathscr{P}_{\lambda_1 \to \lambda_0}(\tilde{\Gamma} \,|\, x_\tau)$$

probability for observing $R_1^*(\Gamma) = r$: $P_1(r) = \sum_{\Gamma} \mathscr{P}_1(\Gamma)\delta\left(r - R_1^*(\Gamma)\right)$

[process2] $$R_2^*(\Gamma') = \ln \frac{\mathscr{P}_2(\Gamma')}{\mathscr{P}_2^*(\Gamma')}$$

$$\mathscr{P}_2(\Gamma') = p_{\lambda_1}^{\text{eq}}(x_0')\mathscr{P}_{\lambda_1 \to \lambda_0}(\Gamma' \,|\, x_0')$$

$$\mathscr{P}_2^*(\Gamma') = p_{\lambda_0}^{\text{eq}}(x_\tau')\mathscr{P}_{\lambda_0 \to \lambda_1}(\tilde{\Gamma}' \,|\, x_\tau')$$

probability for observing $R_2^*(\Gamma) = -r$: $P_2(-r) = \sum_{\Gamma} \mathscr{P}_2(\Gamma)\delta\left(-r - R_2^*(\Gamma)\right)$

Fluctuation Theorems

2. Various Fluctuation Theorems

2) Crooks relation

Crooks, PRE 60, 2721 (1999)

[process1] $R_1^*(\Gamma) = \ln \dfrac{\mathscr{P}_1(\Gamma)}{\mathscr{P}_1^*(\Gamma)}$

$$\mathscr{P}_1(\Gamma) = p_{\lambda_0}^{\text{eq}}(x_0)\mathscr{P}_{\lambda_0\to\lambda_1}(\Gamma\,|\,x_0)$$
$$\mathscr{P}_1^*(\Gamma) = p_{\lambda_1}^{\text{eq}}(x_\tau)\mathscr{P}_{\lambda_1\to\lambda_0}(\tilde{\Gamma}\,|\,x_\tau)$$

probability for observing $R_1^*(\Gamma) = r$: $P_1(r) = \sum_\Gamma \mathscr{P}_1(\Gamma)\delta\left(r - R_1^*(\Gamma)\right)$

[process2] $R_2^*(\Gamma') = \ln \dfrac{\mathscr{P}_2(\Gamma')}{\mathscr{P}_2^*(\Gamma')}$

$$\mathscr{P}_2(\Gamma') = p_{\lambda_1}^{\text{eq}}(x_0')\mathscr{P}_{\lambda_1\to\lambda_0}(\Gamma'\,|\,x_0')$$
$$\mathscr{P}_2^*(\Gamma') = p_{\lambda_0}^{\text{eq}}(x_\tau')\mathscr{P}_{\lambda_0\to\lambda_1}(\tilde{\Gamma}'\,|\,x_\tau')$$

probability for observing $R_2^*(\Gamma) = -r$: $P_2(-r) = \sum_\Gamma \mathscr{P}_2(\Gamma)\delta\left(-r - R_2^*(\Gamma)\right)$

$$= \sum_\Gamma \mathscr{P}_1^*(\tilde{\Gamma})\delta\left(-r + R_1^*(\tilde{\Gamma})\right)$$
$$= \sum_{\tilde{\Gamma}} e^{-R_1^*(\tilde{\Gamma})}\mathscr{P}_1(\tilde{\Gamma})\delta\left(-r + R_1^*(\tilde{\Gamma})\right)$$
$$= e^{-r}\sum_\Gamma \mathscr{P}_1(\Gamma)\delta\left(-r + R_1^*(\Gamma)\right) = e^{-r}P_1(r)$$

➡ $\mathscr{P}_1(\Gamma) = \mathscr{P}_2^*(\tilde{\Gamma})$

$\mathscr{P}_1^*(\Gamma) = \mathscr{P}_2(\tilde{\Gamma})$

➡ $R_1^*(\Gamma) = \ln \dfrac{\mathscr{P}_1(\Gamma)}{\mathscr{P}_1^*(\Gamma)} = \ln \dfrac{\mathscr{P}_2^*(\tilde{\Gamma})}{\mathscr{P}_2(\tilde{\Gamma})}$

$= -R_2^*(\tilde{\Gamma})$

➡ $P_1(r)/P_2(-r) = e^r$ Crooks relation

Fluctuation Theorems

2. Various Fluctuation Theorems

2) Crooks relation

Crooks, PRE 60, 2721 (1999)

[process1] $R_1^*(\Gamma) = \ln \frac{\mathscr{P}_1(\Gamma)}{\mathscr{P}_1^*(\Gamma)}$

[process2] $R_2^*(\Gamma') = \ln \frac{\mathscr{P}_2(\Gamma')}{\mathscr{P}_2^*(\Gamma')}$

➡ $\mathscr{P}_1(\Gamma) = \mathscr{P}_2^*(\tilde{\Gamma})$ ➡ $P_1(r)/P_2(-r) = e^r$ Crooks relation

$\mathscr{P}_1^*(\Gamma) = \mathscr{P}_2(\tilde{\Gamma})$

e.g. total EP satisfies Crooks relation for a steady-state process

➡ $R_1^*(\Gamma) = \ln \frac{\mathscr{P}_1(\Gamma)}{\mathscr{P}_1^*(\Gamma)} = \ln \frac{\mathscr{P}_2^*(\tilde{\Gamma})}{\mathscr{P}_2(\tilde{\Gamma})}$

$= -R_2^*(\tilde{\Gamma})$

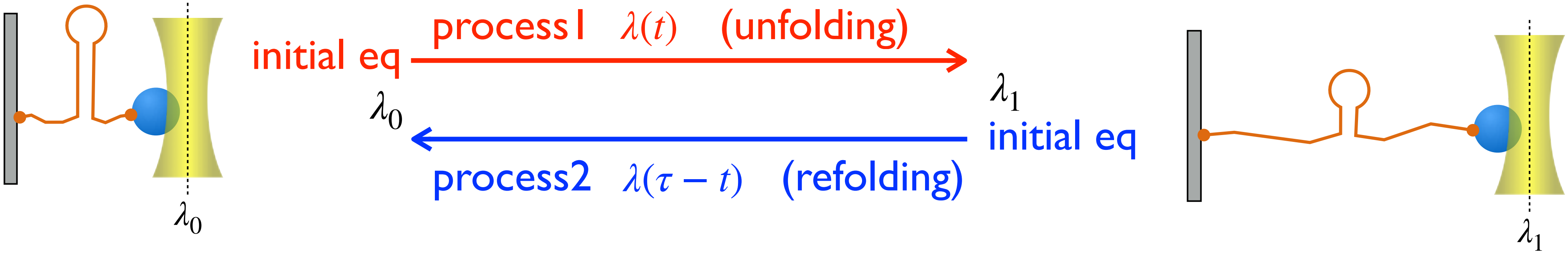
involution

Fluctuation Theorems

2. Various Fluctuation Theorems

2) Crooks relation   Crooks, PRE 60, 2721 (1999)

$P_1(r)/P_2(-r) = e^r$



[process1] $R_1^*(\Gamma) = \ln \dfrac{\mathscr{P}_1(\Gamma)}{\mathscr{P}_1^*(\Gamma)}$

$$\mathscr{P}_1(\Gamma) = p_{\lambda_0}^{\mathrm{eq}}(x_0)\mathscr{P}_{\lambda_0 \to \lambda_1}(\Gamma \mid x_0)$$

$$\mathscr{P}_1^*(\Gamma) = p_{\lambda_1}^{\mathrm{eq}}(x_\tau)\mathscr{P}_{\lambda_1 \to \lambda_0}(\tilde{\Gamma} \mid x_\tau)$$

$$= \beta(W - \Delta F)$$

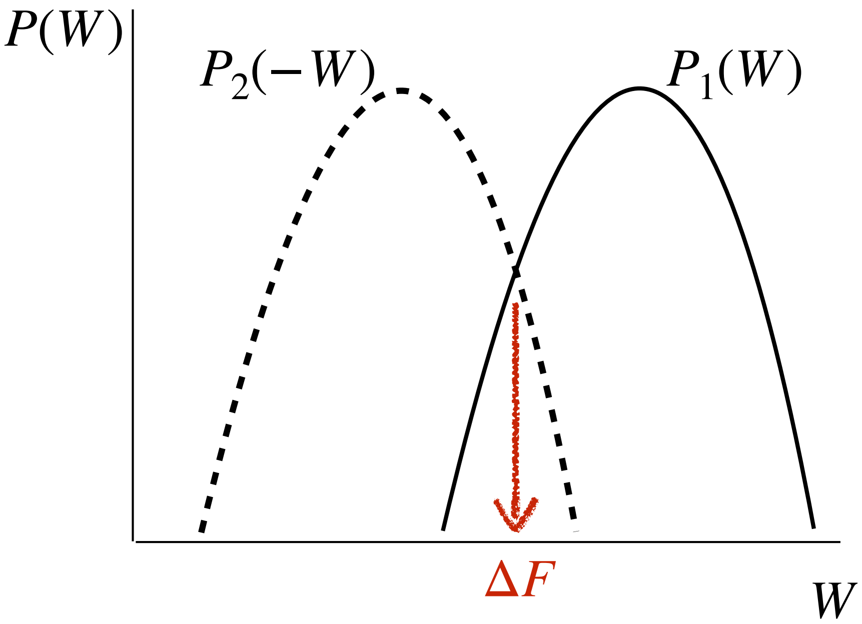
$$\Rightarrow \quad \frac{P_1(\beta(W - \Delta F))}{P_2(-(\beta(W - \Delta F)))} = e^{\beta(W - \Delta F)} \quad \Rightarrow \quad \frac{P_1(W)}{P_2(-W)} = e^{\beta(W - \Delta F)}$$

Fluctuation Theorems

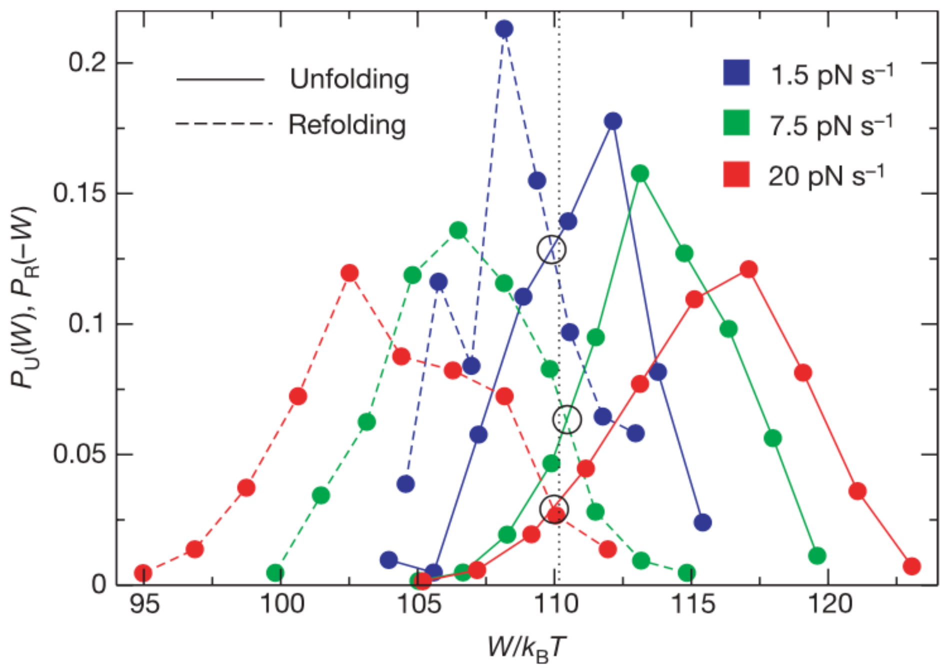
2. Various Fluctuation Theorems

2) Crooks relation Crooks, PRE 60, 2721 (1999)

$$\frac{P_1(W)}{P_2(-W)} = e^{\beta(W-\Delta F)} = 1 \text{ when } W = \Delta F$$



ΔF



Collin et al., Nature 437, 231 (2005)

Fluctuation Theorems

2. Various Fluctuation Theorems

3) Hatano-Sasa Fluctuation Theorem: separation of EP into two parts

Hatano and Sasa, PRL 86, 3463 (2001)

$$\Delta S_{\text{tot}}/k_B = \Delta S_{\text{sys}}/k_B - \beta Q = \ln \frac{p_{x_0}(0)\mathscr{P}(\Gamma | x_0)}{p_{x_\tau}(\tau)\tilde{\mathscr{P}}(\tilde{\Gamma} | \tilde{x}_\tau)}$$

$$\Delta S_{\text{sys}}/k_B = \ln \frac{p_{x_0}(0)}{p_{x_\tau}(\tau)} \qquad -\beta Q = \ln \frac{\mathscr{P}(\Gamma | x_0)}{\tilde{\mathscr{P}}(\tilde{\Gamma} | \tilde{x}_\tau)}$$

$$\langle e^{-\Delta S_{\text{sys}}/k_B} \rangle \stackrel{?}{=} 1$$

$$= \sum_\Gamma p_{x_0}(0)\mathscr{P}(\Gamma | x_0) e^{-\Delta S_{\text{sys}}/k_B} = \sum_\Gamma \mathscr{P}(\Gamma | x_0) p_{x_\tau}(\tau) \neq 1$$

$$\langle e^{\beta Q} \rangle \stackrel{?}{=} 1$$

$$= \sum_\Gamma p_{x_0}(0)\mathscr{P}(\Gamma | x_0) e^{\beta Q} = \sum_\Gamma p_{x_0}(0)\tilde{\mathscr{P}}(\tilde{\Gamma} | \tilde{x}_\tau) \neq 1$$

Is there any way such that two separated EPs satisfy FT simultaneously?

Fluctuation Theorems

2. Various Fluctuation Theorems

3) Hatano-Sasa Fluctuation Theorem: separation of EP into two parts

Hatano and Sasa, PRL 86, 3463 (2001)

$$\Delta S_{\text{tot}}/k_B = \ln \frac{p_{x_0}(0)}{p_{x_\tau}(\tau)} + \sum_{n=1}^{N} \ln \frac{R_{x_n,x_{n-1}}(t_n)}{R_{x_{n-1},x_n}(t_n)}$$

$$= \ln \frac{p_{x_0}(0)}{p_{x_\tau}(\tau)} + \sum_{n=1}^{N} \ln \frac{p^{\text{ss}}_{x_n}(t_n)}{p^{\text{ss}}_{x_{n-1}}(t_n)} + \sum_{n=1}^{N} \ln \frac{p^{\text{ss}}_{x_{n-1}}(t_n)}{p^{\text{ss}}_{x_n}(t_n)} + \sum_{n=1}^{N} \ln \frac{R_{x_n,x_{n-1}}(t_n)}{R_{x_{n-1},x_n}(t_n)}$$

$\equiv \Delta S_{\text{na}} = \Delta S_{\text{sys}} - Q_{\text{ex}}/T$

non-adiabatic EP (Hatano-Sasa EP)

$\equiv \Delta S_{\text{a}} = -Q_{\text{hk}}/T$

adiabatic EP

$$\Delta S_{\text{na}}/k_B = \ln \frac{p_{x_0}(0)}{p_{x_\tau}(\tau)} + \sum_{n=1}^{N} \ln \frac{R_{x_n,x_{n-1}}(t_n)}{R^{\dagger}_{x_{n-1},x_n}(t_n)} \qquad R^{\dagger}_{x,x'}(t_n) = \frac{R_{x',x}(t_n)\,p^{\text{ss}}_{x}(t_n)}{p^{\text{ss}}_{x'}(t_n)}$$

$$= \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^{\dagger}(\Gamma)} \quad \left(\sum_{\Gamma} \mathscr{P}^{\dagger}(\Gamma) = 1 \right) \qquad \sum_{x(\neq x')} R^{\dagger}_{x,x'}(t_n) = \sum_{x(\neq x')} R_{x,x'}(t_n) \quad \text{(same escape rate)}$$

$\rightarrow$ same staying probability

$$\rightarrow \quad \langle e^{-\Delta S_{\text{na}}} \rangle = 1$$

Fluctuation Theorems

2. Various Fluctuation Theorems

3) Hatano-Sasa Fluctuation Theorem: separation of EP into two parts

Hatano and Sasa, PRL 86, 3463 (2001)

$$\Delta S_{\rm tot} = \ln \frac{p_{x_0}(0)}{p_{x_\tau}(\tau)} + \sum_{n=1}^{N} \ln \frac{R_{x_n,x_{n-1}}(t_n)}{R_{x_{n-1},x_n}(t_n)}$$

$$= \ln \frac{p_{x_0}(0)}{p_{x_\tau}(\tau)} + \sum_{n=1}^{N} \ln \frac{p^{\rm ss}_{x_n}(t_n)}{p^{\rm ss}_{x_{n-1}}(t_n)} + \sum_{n=1}^{N} \ln \frac{p^{\rm ss}_{x_{n-1}}(t_n)}{p^{\rm ss}_{x_n}(t_n)} + \sum_{n=1}^{N} \ln \frac{R_{x_n,x_{n-1}}(t_n)}{R_{x_{n-1},x_n}(t_n)}$$

$\equiv \Delta S_{\rm na} = \Delta S_{\rm sys} - Q_{\rm ex}/T$

non-adiabatic EP (Hatano-Sasa EP)

$\equiv \Delta S_{\rm a} = -Q_{\rm hk}/T$

adiabatic EP

$$\Delta S_{\rm a} = \ln \frac{p_{x_0}(0)}{p_{x_0}(0)} + \sum_{n=1}^{N} \ln \frac{R_{x_n,x_{n-1}}(t_n)}{R^{\dagger}_{x_n,x_{n-1}}(t_n)}$$

$$= \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^{\dagger\dagger}(\Gamma)} \qquad \left(\sum_{\Gamma} \mathscr{P}^{\dagger\dagger}(\Gamma) = 1 \right)$$

$$\rightarrow \quad \langle e^{-\Delta S_{\rm a}} \rangle = 1$$

$$R^{\dagger}_{x,x'}(t_n) = \frac{R_{x',x}(t_n) p^{\rm ss}_{x}(t_n)}{p^{\rm ss}_{x'}(t_n)}$$

$$\sum_{x(\neq x')} R^{\dagger}_{x,x'}(t_n) = \sum_{x(\neq x')} R_{x,x'}(t_n) \quad \text{(same escape rate)}$$

Expression of Entropy Production Rate

1. Overdamped Langevin system

$$\dot{x} = \frac{1}{\gamma} f(x(t), t) + \frac{1}{\gamma}\xi(t) \Rightarrow \partial_t P(x,t) = -\partial_x J(x,t) \qquad J(x,t) = \frac{1}{\gamma}\left(f(x,t) - k_B T \partial_x\right) P(x,t)$$

Risken (The Fokker-Planck Equation)

$$\dot{S}_{sys} = -\frac{d}{dt} k_B \ln P(x,t) = -\frac{k_B}{P}\frac{dP}{dt} = -\frac{k_B}{P}\left(\partial_x P \circ \dot{x} + \partial_t P\right)$$

$$\partial_x P = \frac{f}{k_B T} P - \frac{\gamma}{k_B T} J$$

$$= -\frac{f}{T} \circ \dot{x} + \frac{\gamma}{T}\frac{J}{P} \circ \dot{x} - \frac{k_B}{P}\partial_t P$$

$$= \frac{1}{T}(-\gamma \dot{x} + \xi) \circ \dot{x} + \frac{\gamma}{T}\frac{J}{P} \circ \dot{x} - \frac{k_B}{P}\partial_t P$$

$$(-\gamma \dot{x} + \xi) \circ \dot{x} = \dot{Q}$$

$$\rightarrow \dot{S}_{tot} = \dot{S}_{sys} - \frac{\dot{Q}}{T} = \frac{\gamma}{T}\frac{J}{P} \circ \dot{x} - \frac{k_B}{P}\partial_t P$$

$$\rightarrow \langle \dot{S}_{tot} \rangle = \frac{\gamma}{T}\left\langle \frac{J}{P} \circ \dot{x} \right\rangle - \left\langle \frac{k_B}{P}\partial_t P \right\rangle$$

$$= \int dx \frac{\gamma}{T}\frac{J(x,t)^2}{P(x,t)}$$

$$\langle \cdots \rangle = \int dx \ \cdots \ P(x,t)$$

$$\left\langle \frac{k_B}{P}\partial_t P \right\rangle = k_B \partial_t \int dx P(x,t) = 0$$

$$\int dx P(x,t) = 1$$

$$\langle g(x(t),t) \circ \dot{x} \rangle = \int dx g(x,t) J(x,t)$$

Expression of Entropy Production Rate

1. Overdamped Langevin system

$$\dot{x} = \frac{1}{\gamma} f(x(t), t) + \frac{1}{\gamma} \xi(t) \quad \Rightarrow \quad \partial_t P(x,t) = -\partial_x J(x,t) \qquad J(x,t) = \frac{1}{\gamma}\left(f(x,t) - k_B T \partial_x\right) P(x,t)$$

Risken (The Fokker-Planck Equation)

Derivation of $\langle g(x(t)) \circ \dot{x} \rangle = \int dx g(x,t) J(x,t)$

$$\langle g(x(t)) \circ \dot{x} \rangle = \left\langle \frac{1}{2}\left(g(x(t) + dx(t)) + g(x(t))\right) \frac{dx(t)}{dt} \right\rangle = \left\langle \left(g(x(t)) + \frac{1}{2} g'(x(t)) dx(t)\right) \frac{dx(t)}{dt} \right\rangle$$

$$= \langle g(x(t)) \dot{x}(t) \rangle + \frac{1}{2} \langle g'(x(t)) dx dx / dt \rangle$$

$$= \frac{1}{\gamma} \langle g(x(t)) f(x(t)) \rangle + \frac{1}{\gamma} \underline{\langle g(x(t)) \xi(t) \rangle} + \frac{1}{2} \langle g'(x(t)) \rangle \underline{\langle dx dx \rangle} / dt$$

$= \langle g(x(t)) \rangle \langle \xi(t) \rangle = 0$ $\qquad = 2 k_B T / \gamma$

$$= \frac{1}{\gamma} \int dx g(x) f(x) P(x,t) + \frac{k_B T}{\gamma} \underline{\int dx g'(x) P(x,t)}$$

$= -\int dx g(x) \partial_x P(x,t)$ (integration by part)

$$= \int dx g(x) J(x,t)$$

Expression of Entropy Production Rate

2. Markov jump process

Entropy is produced only when jump occurs

$$\text{jump } y \to x : \text{EP during } \Delta t = \ln \frac{R_{xy}(t)p_y(t)\Delta t}{R_{yx}(t)p_x(t)\Delta t} = \ln \frac{R_{xy}(t)p_y(t)}{R_{yx}(t)p_x(t)}$$

$$\text{number of jump } y \to x \text{ during } \Delta t : R_{xy}(t)p_y(t)\Delta t$$

$$\Rightarrow \quad \langle \Delta S_{\text{tot}}(t) \rangle = \sum_{x \neq y}^{N} R_{x,y}(t)p_y(t)\Delta t \ln \frac{R_{x,y}(t)p_y(t)}{R_{y,x}(t)p_x(t)}$$

$$\langle \dot{S}_{\text{tot}}(t) \rangle = \sum_{x \neq y}^{N} R_{x,y}(t)p_y(t) \ln \frac{R_{x,y}(t)p_y(t)}{R_{y,x}(t)p_x(t)}$$

Summary

1. Entropy production (irreversibility)

$$R \equiv \ln \frac{p_0(z_0)\mathscr{P}(\Gamma\,|\,z_0)}{p_\tau(z_\tau)\tilde{\mathscr{P}}(\tilde{\Gamma}\,|\,\tilde{z}_\tau)} = \frac{\Delta S_{\mathrm{tot}}}{k_{\mathrm{B}}} = \frac{1}{k_{\mathrm{B}}}\left(\Delta S_{\mathrm{sys}} - \frac{Q}{T}\right)$$

2. Fluctuation Theorems (normalization of dual-path probability)

$$R^* \equiv \ln \frac{\mathscr{P}(\Gamma)}{\mathscr{P}^*(\Gamma)} \qquad \langle e^{-R^*}\rangle = \sum_{\text{all paths}} \mathscr{P}(\Gamma)e^{-R} = \sum_{\text{all paths}} \mathscr{P}^*(\Gamma) = 1$$

3. Various FTs

1) Jarzynski equality $\langle e^{-\beta W}\rangle = e^{\beta \Delta F}$

2) Crooks relation $P_1(r)/P_2(-r) = e^{r}$

3) Hatano-Sasa FT $\Delta S_{\mathrm{tot}} = \Delta S_{\mathrm{na}} + \Delta S_{\mathrm{a}} \rightarrow \langle e^{-\Delta S_{\mathrm{na}}/k_{\mathrm{B}}}\rangle = 1 \qquad \langle e^{-\Delta S_{\mathrm{a}}/k_{\mathrm{B}}}\rangle = 1$

4. Expression of EP rate

$$\langle \dot{S}_{\mathrm{tot}}\rangle = \int dx \frac{\gamma}{T}\frac{J(x,t)^2}{P(x,t)}$$

overdamped Langevin equation

$$\langle \dot{S}_{\mathrm{tot}}(t)\rangle = \sum_{x\neq y}^{N} R_{x,y}(t)p_y(t)\ln\frac{R_{x,y}(t)p_y(t)}{R_{y,x}(t)p_x(t)}$$

Markov jump process