Non-equilibrium Work Relations

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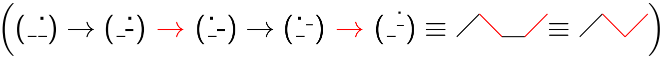
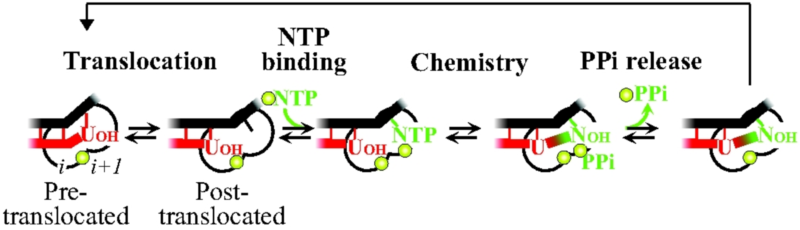


Motivation

RNA Polymerase reads your genes



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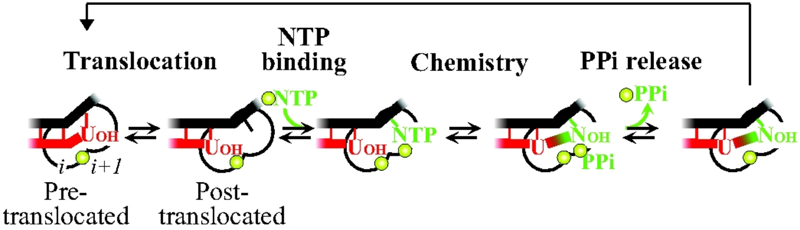

- Copies black→red: Fwd Rxn builds red piece-by-piece.
- Reverse Rxn breaks red apart.

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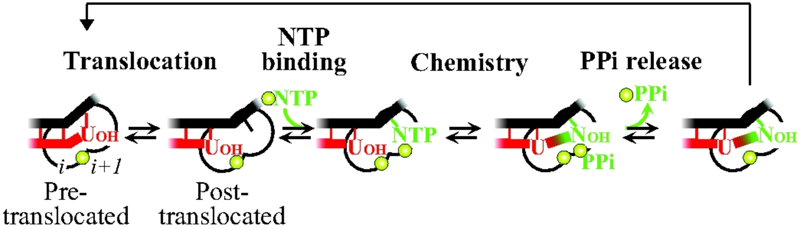

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- Ratchet and Pawl w/ $\frac{1}{2}kx^2 \sim \Delta G_{\mathrm{NTP/NOH}}$

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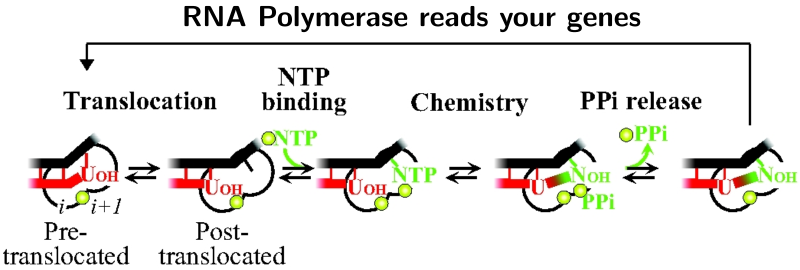

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- $W_{irr} \geq W_{rev} = \Delta G$ ... But by how much?

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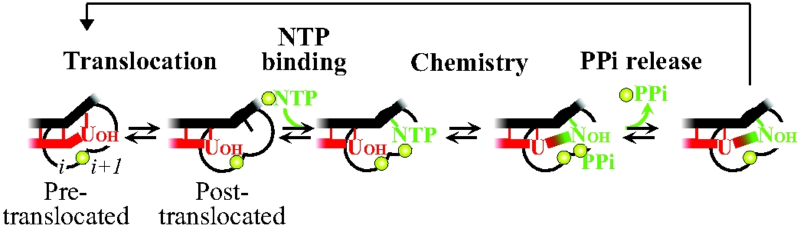

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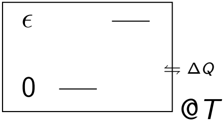
- Ratchet and Pawl w/ $\frac{1}{2}kx^2 \sim \Delta G_{\mathrm{NTP/NOH}}$
- $W_{irr} \geq W_{rev} = \Delta G$ … But by how much?
- Micro. Reversibility & AoT meet $\Rightarrow \langle W \rangle$ and ΔS_{path} Needed!

Overview

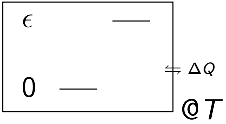
- Two-State System
- Thermodynamic Perturbation Theory
- Jarzynski Equality
- Crooks Fluctuation Theorem

Two-State System



$\equiv ({}_{-}{}^{-}) \equiv (0, \epsilon)$

Two-State System

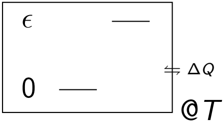


$$\equiv (\_\,^{-}) \equiv (0, \epsilon)$$

$$p_\epsilon^{eq} = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \qquad (1)$$

$$\rho \equiv \binom{p_\epsilon}{1 - p_\epsilon}$$

Two-State System



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$$\rho \equiv \binom{p_\epsilon}{1 - p_\epsilon}$$

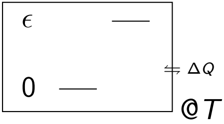
Markovian Transitions:

$$\begin{tikzcd} \epsilon \arrow[d, bend left, "\pi^-"] \\ 0 \arrow[u, bend left, "\pi^+"] \end{tikzcd} \qquad \rho' = \Pi \rho$$

Π "Balanced": Preserves ρ^{eq}

$$\rho^{eq} = \Pi \rho^{eq} \tag{2}$$

Two-State System



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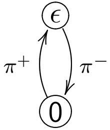

$$\rho' = \Pi\rho$$

$$p_\epsilon^{eq} = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \qquad (1)$$

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Π "Balanced": Preserves ρ^{eq}

$$\rho^{eq} = \Pi\rho^{eq} \qquad (2)$$

Canonical PDF (1) **&** Balanced Π (2) $\Longrightarrow \boxed{\dfrac{\pi^+}{\pi^-} = \dfrac{p^{eq}}{1 - p^{eq}} = e^{-\beta\epsilon}}$

Thermodynamic Perturbation Theory

State Sampling

$$Z' \geq Z_0 e^{-\beta\langle\delta\mathcal{H}\rangle}$$

1. Known system **@ eq**: $Z_0 = Tr\ e^{-\beta\mathcal{H}_0}$
2. Perturb it ∞-**fast**: $\mathcal{H}' = \mathcal{H}_0 + \delta\mathcal{H}$

$$e^{-\beta\delta F} = \frac{Z'}{Z_0} = \frac{Tr\ e^{-\beta(\mathcal{H}_0+\delta\mathcal{H})}}{Tr\ e^{-\beta\mathcal{H}_0}} = \left\langle e^{-\beta\delta\mathcal{H}} \right\rangle_0$$

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- β is inverse temperature **of Reservoir**!
- e.g. $(\_\,\_) \rightarrow (\_\,^{-}) \Rightarrow \ e^{-\beta\Delta F} = \frac{1}{2}(1 + e^{-\beta\epsilon})$

3. Observing/Computing $\Rightarrow$ learn about Z'.

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Path Sampling

$$(0,0) \to (0,\epsilon) \quad : \quad e^{-\beta\Delta F} = \tfrac{1}{2}(1 + e^{-\beta\epsilon})$$

TRANSITIONS	PATH	PROB	ΔE	$e^{-\beta\Delta E}$
$\left(\_\,\overset{\cdot}{\_}\right) \to \left(\_\,\overset{\cdot}{-}\right)$	/			
$\left(\overset{\cdot}{\_}\,\_\right) \to \left(\overset{\cdot}{\_}\,-\right)$	—			

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$(\underline{\cdot}\,\underline{\ }) \to (\underline{\ }\,\dot{-})$	/	1/2	ϵ	$e^{-\beta\epsilon}$
$(\underline{\cdot}\,\underline{\ }) \to (\underline{\cdot}\,-)$	_	1/2	0	1

$$\langle e^{-\beta\delta E}\rangle_{paths} = \tfrac{1}{2}(1+e^{-\beta\epsilon}) \Rightarrow \textbf{O.K.!}$$

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TRANSITIONS	PATH	PROB	ΔE	$e^{-\beta\Delta E}$
$(\_\,\dot{-}) \to (\_\,\dot{\overline{}})$	$\diagup$	p	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\dot{\_}\,-) \to (\dot{\_}\,\overline{})$	$\_$	q	0	1

$$\langle e^{-\beta\delta E}\rangle_{paths} = q + pe^{-\beta(\epsilon'-\epsilon)}$$

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$(\dot{\_}\,-) \to (\dot{\_}\,\overline{\ \ })$	_	q	0	1

$$\langle e^{-\beta\delta E}\rangle_{paths} = q + pe^{-\beta(\epsilon'-\epsilon)} = \frac{1+e^{-\beta\epsilon}e^{-\beta(\epsilon'-\epsilon)}}{1+e^{-\beta\epsilon}} \Rightarrow \textbf{O.K.!}$$

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TRANSITIONS	PATH	PROB	ΔE	$e^{-\beta\Delta E}$
$({}_{-}\dot{-}) \to ({}_{-}\dot{\overline{\ }})$	/	p	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\dot{{}_{-}}-) \to (\dot{{}_{-}}\overline{\ })$	_	q	0	1

... but what about equilibration?

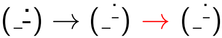
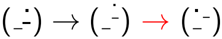
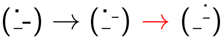
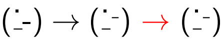
$$\langle e^{-\beta\delta E}\rangle_{paths} = q + pe^{-\beta(\epsilon'-\epsilon)} = \frac{1 + e^{-\beta\epsilon}e^{-\beta(\epsilon'-\epsilon)}}{1 + e^{-\beta\epsilon}} \Rightarrow \textbf{O.K.!}$$

Extending TPT?

We cannot *measure* ∞-fast... **Let's add a heat step**:

$$(0,\epsilon)^{eq} \to (0,\epsilon') \quad \pm\Delta q$$

$$Z'/Z_0 = q + pe^{-\beta(\epsilon'-\epsilon)}$$

TRANSITIONS	PATH	PROB	ΔE	$e^{-\beta\Delta E}$
		$p(1-\pi^-)$	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
		$p\pi^-$	$0 - \epsilon$	$e^{+\beta\epsilon}$
		$q\pi^+$	$\epsilon' - 0$	$e^{-\beta\epsilon'}$
		$q(1-\pi^+)$	$0 - 0$	1

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$(\_\,\dot{-}) \to (\_\,\dot{-}) \to (\_\,\dot{-})$		$p(1-\pi^-)$	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\_\,\dot{-}) \to (\_\,\dot{-}) \to (\dot{\_}\,-)$		$p\pi^-$	$0-\epsilon$	$e^{+\beta\epsilon}$
$(\dot{\_}\,-) \to (\dot{\_}\,-) \to (\_\,\dot{-})$		$q\pi^+$	$\epsilon' - 0$	$e^{-\beta\epsilon'}$
$(\dot{\_}\,-) \to (\dot{\_}\,-) \to (\dot{\_}\,-)$		$q(1-\pi^+)$	$0-0$	1

$$\langle e^{-\beta\Delta E}\rangle_{paths} = \frac{\pi^- e^{-2\beta\epsilon'} + (1-2\pi^-)e^{-\beta\epsilon'} + 1 + \pi^-}{1+e^{-\beta\epsilon}}$$

$$\text{If } \left\{\frac{Z'}{Z} \equiv \langle e^{-\beta\Delta E}\rangle_{paths}\right\} \Rightarrow \left\{0 = \left(e^{-\beta\epsilon'}\right)^2 - 2\left(e^{-\beta\epsilon'}\right) + 1\right\}$$

$$\therefore \; \boxed{\epsilon' \equiv 0}$$

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We cannot *measure* ∞-fast… **Let's add a heat step**:

$$(0,\epsilon)^{eq} \to (0,\epsilon') \quad \pm \Delta q$$

$$Z'/Z_0 = q + pe^{-\beta(\epsilon'-\epsilon)}$$

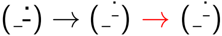
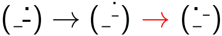
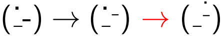
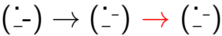
TRANSITIONS	PATH	PROB	ΔE	$e^{-\beta \Delta E}$
$(\ ) \to (\ ) \to (\ )$		$p(1-\pi^-)$	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\ ) \to (\ ) \to (\ )$		$p\pi^-$	$0 - \epsilon$	$e^{+\beta\epsilon}$
$(\ ) \to (\ ) \to (\ )$		$q\pi^+$	$\epsilon' - 0$	$e^{-\beta\epsilon'}$
$(\ ) \to (\ ) \to (\ )$		$q(1-\pi^+)$	$0 - 0$	1

WRONG!!!

If we performed the perturbation ∞-slowly, then by Gibbs' def. of ΔF: $\langle W \rangle_{paths} = W_{rev} = \Delta F$… **Let's try $e^{-\beta W}$ instead!**

Extending TPT?

$$(0,\epsilon) \to (0,\epsilon') \ \color{red}{\pm \Delta q}$$
$$Z'/Z_0 = q + pe^{-\beta(\epsilon'-\epsilon)}$$

Transitions	Path	Prob	ΔE	ΔQ_{IN}	W_{ON}	$e^{-\beta W_{ON}}$
		$p(1-\pi^-)$	$\epsilon' - \epsilon$			
		$p\pi^-$	$-\epsilon$			
		$q\pi^+$	ϵ'			
		$q(1-\pi^+)$	0			

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Transitions	path	prob	ΔE	ΔQ_{IN}	W_{ON}	$e^{-\beta W_{ON}}$
$(\ ) \to (\ ) \to (\ )$		$p(1-\pi^-)$	$\epsilon' - \epsilon$	0		
$(\ ) \to (\ ) \to (\ )$		$p\pi^-$	$-\epsilon$	$-\epsilon'$		
$(\ ) \to (\ ) \to (\ )$		$q\pi^+$	ϵ'	$+\epsilon'$		
$(\ ) \to (\ ) \to (\ )$		$q(1-\pi^+)$	0	0		

Extending TPT?

$$(0,\epsilon) \to (0,\epsilon') \ \ {\color{red}\pm \Delta q}$$

$$Z'/Z_0 = q + pe^{-\beta(\epsilon'-\epsilon)}$$

$$W_{ON} \equiv \Delta E - \Delta Q_{IN}$$

Transitions	Path	Prob	ΔE	ΔQ_{IN}	W_{ON}	$e^{-\beta W_{ON}}$
		$p(1-\pi^-)$	$\epsilon' - \epsilon$	0	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
		$p\pi^-$	$-\epsilon$	$-\epsilon'$	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
		$q\pi^+$	ϵ'	$+\epsilon'$	0	1
		$q(1-\pi^+)$	0	0	0	1

Extending TPT?

$$(0,\epsilon) \rightarrow (0,\epsilon') \quad \pm \Delta q$$
$$Z'/Z_0 = q + pe^{-\beta(\epsilon'-\epsilon)}$$
$$W_{ON} \equiv \Delta E - \Delta Q_{IN}$$

TRANSITIONS	PATH	PROB	ΔE	ΔQ_{IN}	W_{ON}	$e^{-\beta W_{ON}}$
$(\_\dot{-}) \rightarrow (\_^{\dot{-}}) \rightarrow (\_^{\dot{-}})$		$p(1-\pi^-)$	$\epsilon' - \epsilon$	0	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\_\dot{-}) \rightarrow (\_^{\dot{-}}) \rightarrow (\dot{\_}^{-})$		$p\pi^-$	$-\epsilon$	$-\epsilon'$	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\dot{\_}-) \rightarrow (\dot{\_}^{-}) \rightarrow (\_^{\dot{-}})$		$q\pi^+$	ϵ'	$+\epsilon'$	0	1
$(\dot{\_}-) \rightarrow (\dot{\_}^{-}) \rightarrow (\dot{\_}^{-})$		$q(1-\pi^+)$	0	0	0	1

- Confirmation of $\langle e^{-\beta W} \rangle_{paths} = \frac{Z'}{Z}$ follows trivially.
- TPT still works with relaxation, **if we use W**!
- Z' final state **only after** equilibration.

Extending TPT?

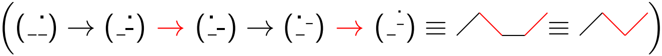
$$(0,\epsilon) \to (0,\epsilon') \quad \color{red}{\pm \Delta q}$$
$$Z'/Z_0 = q + pe^{-\beta(\epsilon'-\epsilon)}$$
$$W_{ON} \equiv \Delta E - \Delta Q_{IN}$$

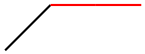
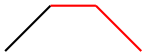
TRANSITIONS	PATH	PROB	ΔE	ΔQ_{IN}	W_{ON}	$e^{-\beta W_{ON}}$
$(\,) \to (\,) \to (\,)$		$p(1-\pi^-)$	$\epsilon' - \epsilon$	0	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\,) \to (\,) \to (\,)$		$p\pi^-$	$-\epsilon$	$-\epsilon'$	$\epsilon' - \epsilon$	$e^{-\beta(\epsilon'-\epsilon)}$
$(\,) \to (\,) \to (\,)$		$q\pi^+$	ϵ'	$+\epsilon'$	0	1
$(\,) \to (\,) \to (\,)$		$q(1-\pi^+)$	0	0	0	1

- Confirmation of $\langle e^{-\beta W} \rangle_{paths} = \frac{Z'}{Z}$ follows trivially.
- TPT still works with relaxation, **if we use W**!
- Z' final state **only after** equilibration.
- ... But the πs cancelled! Maybe I am tricking you?

How far can we push this?

$$Z_{final}/Z_0 = \frac{1+e^{-\beta\epsilon_2}}{1+e^{-\beta\epsilon_0}} = q + pe^{-\beta(\epsilon_2-\epsilon_0)}$$



PATH	PROB	$\Delta E - \Delta Q_{IN}$	$e^{-\beta W}$
	$p(1-\pi_1^-)(1-\pi_2^-)$	$(\epsilon_2-\epsilon_0)-0$	$e^{-\beta(\epsilon_2-\epsilon_0)}$
	$p(1-\pi_1^-)\pi_2^-$	$(-\epsilon_0)-(-\epsilon_2)$	$e^{-\beta(\epsilon_2-\epsilon_0)}$
	$p\pi_1^-\pi_2^+$	$(\epsilon_2-\epsilon_0)-(\epsilon_2-\epsilon_1)$	$e^{-\beta(\epsilon_1-\epsilon_0)}$
	$p\pi_1^-1(1-\pi_2^+)$	$(-\epsilon_0)-(-\epsilon_1)$	$e^{-\beta(\epsilon_1-\epsilon_0)}$
	$q\pi_1^+(1-\pi_2^-)$	$(\epsilon_2)-(+\epsilon_1)$	$e^{-\beta(\epsilon_2-\epsilon_1)}$
	$q\pi_1^+\pi_2^-$	$0-(\epsilon_1-\epsilon_2)$	$e^{-\beta(\epsilon_2-\epsilon_1)}$
	$q(1-\pi_1^+)\pi_2^+$	$(\epsilon_2)-(+\epsilon_2)$	1
	$q(1-\pi_1^+)(1-\pi_2^+)$	$0-0$	1

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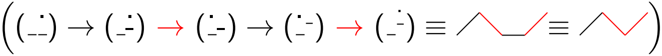
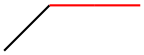
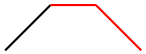


PATH	PROB	$\Delta E - \Delta Q_{IN}$	$e^{-\beta W}$
	$p(1-\pi_1^-)(1-\pi_2^-)$	$(\epsilon_2-\epsilon_0)-0$	$e^{-\beta(\epsilon_2-\epsilon_0)}$
	$p(1-\pi_1^-)\pi_2^-$	$(-\epsilon_0)-(-\epsilon_2)$	$e^{-\beta(\epsilon_2-\epsilon_0)}$
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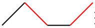
$$\Big((\dot{\_\,\_}) \rightarrow (\_\dot{\_}) \textcolor{red}{\rightarrow} (\dot{\_}\,\text{-}) \rightarrow (\dot{\_}\,\text{-}) \textcolor{red}{\rightarrow} (\_\,\dot{\text{-}}) \equiv$$  $$\equiv$$  $$\Big)$$

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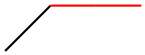
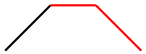
	$p(1-\pi_1^-)(1-\pi_2^-)$	$(\epsilon_2-\epsilon_0)-0$	$e^{-\beta(\epsilon_2-\epsilon_0)}$
	$p(1-\pi_1^-)\pi_2^-$	$(-\epsilon_0)-(-\epsilon_2)$	$e^{-\beta(\epsilon_2-\epsilon_0)}$
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★ That's eq. (2) from looong ago, before you fell asleep.

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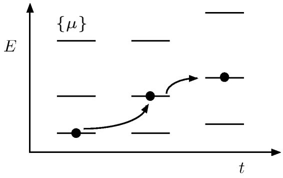
$\Rightarrow$ Time to actually prove something.

Next on CMT-TV

- Two-State System
- Thermodynamic Perturbation Theory
- Jarzynski Equality
- Crooks Fluctuation Theorem

Crooks Fluctuation Theorem 1/3



- Discrete time and unique microstates.
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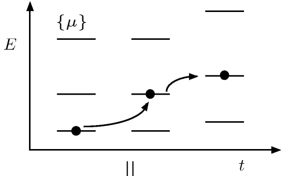
Crooks Fluctuation Theorem 1/3



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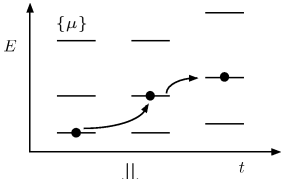

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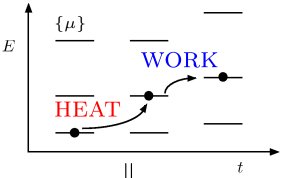

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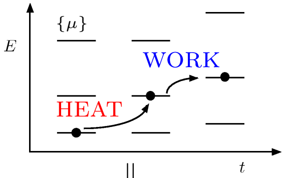

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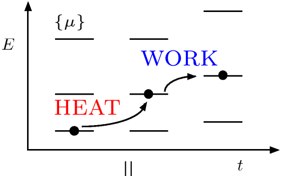

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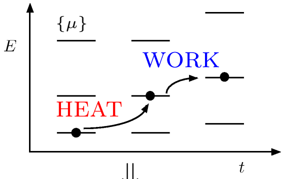

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- Consistent with First Law!

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$$\boxed{\Delta E=\Delta Q(\Upsilon)+W(\Upsilon)=E[\Upsilon,\mu(\Upsilon)]-E[0,\mu(0)]}$$

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Crooks Fluctuation Theorem 3/3

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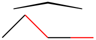
$$\widehat{\mu(t)} \equiv \hat{\mu}(t) = \mu(\Upsilon - t) :$$ () $\equiv$ ()

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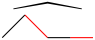
$$\widehat{\mu(t)} \equiv \hat{\mu}(t) = \mu(\Upsilon - t) : ($$  $$) \equiv ($$  $$)$$

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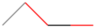
  e.g. $\mathcal{P}\Big[$  $\Big] = \pi^-(1 - \pi^+)$

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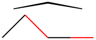

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$$\boxed{\Big\langle g[\mu]\Big\rangle_{FWD} = \Big\langle g[\mu]e^{-\beta W_d}\Big\rangle_{REV}}$$

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- "Heat": $\beta \Delta Q = -\ln \frac{\pi}{\hat{\pi}}$
- Relative entropy summarizes Second-Law for paths:

$$\beta W_d = \beta(\Delta E - \Delta Q - \Delta F) = \ln \frac{\mathcal{P}_{fwd}}{\mathcal{P}_{rev}}$$

$$\therefore \boxed{\langle \beta W_d \rangle_{fwd\ \ paths} = D_{KL}\left(\mathcal{P}_{fwd} || \mathcal{P}_{rev}\right)} > 0$$