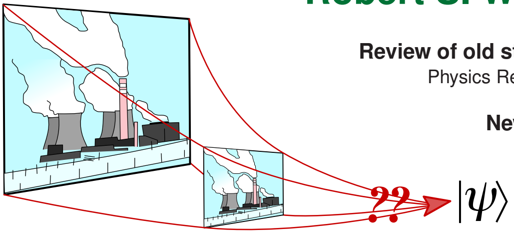
Laboratoire de Physique et Modélisation des Milieux Condensés
Univ. Grenoble Alpes & CNRS, Grenoble, France

Non-Markovian Quantum Thermodynamics

1st law, 2nd law & fluctuation theorems

Robert S. Whitney



Review of old stuff – Benenti, Casati, Saito, R.W.
Physics Reports **694**, 1 (2017) [section 8.10]

New stuff – R.W. arXiv:1611.00670

OVERVIEW

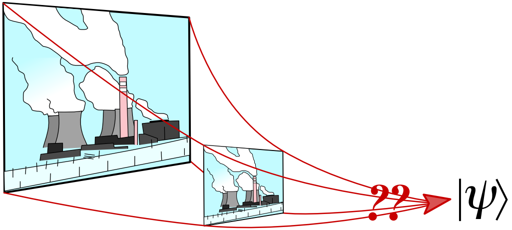
arXiv:1611.00670

QUESTION: Laws of thermodynamics same in quantum?

– Strong coupling : non-Markovian system dynamics?

– Initial state with system and reservoir entangled?

OBJECTIVE: laws of thermodynamics + fluctuation theorems



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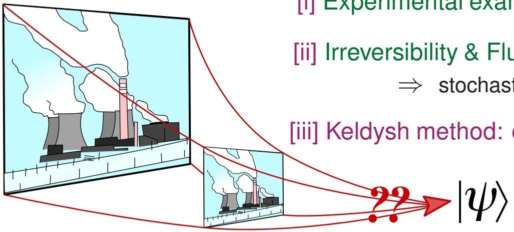
OBJECTIVE: laws of thermodynamics + fluctuation theorems

[i] Experimental examples

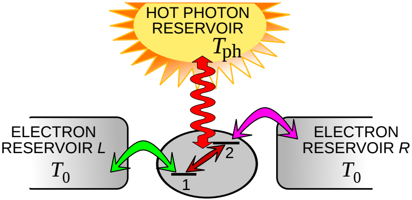
[ii] Irreversibility & Fluctuation theorems

$\Rightarrow$ stochastic thermodynamics (classical)

[iii] Keldysh method: quantum & strong coupling

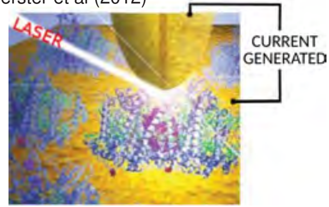


HAMILTONIAN



Experiment: photosynthetic molecule

Gerster et al (2012)



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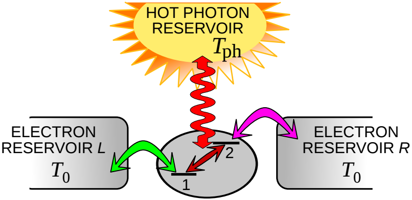

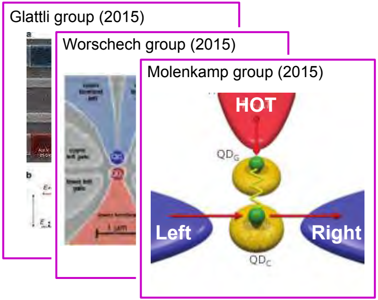

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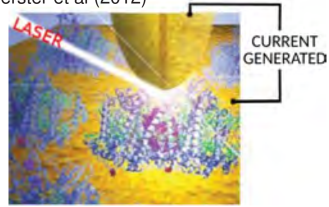
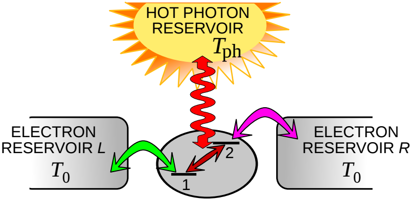
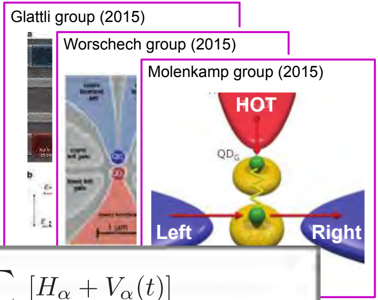


Theory (weak-coupling or linear-response)

- Sánchez & Büttiker(2011)
- Entin-Wohlmann et al (2011-2015)
- Strasberg-Schaller-Brandes-Esposito (2013)

HAMILTONIAN





Experime

Gerster et a

$$H_{\rm tot}(t) = H_{\rm sys}(t) + \sum_{\alpha\in {\rm res}} [H_\alpha + V_\alpha(t)]$$

Reservoir α: $H_\alpha = \sum_k E_{\alpha k}\hat{c}^\dagger_{\alpha k}\hat{c}_{\alpha k}$ ⇐ non-interacting

Coupling e reservoir α: $V_\alpha(t) = V_{nk}\hat{d}^\dagger_n\hat{c}_{\alpha k} + {\rm c.c.}$

Coupling ph reservoir α: $V_\alpha(t) = \sum_k V_{nmk}\hat{d}^\dagger_n\hat{d}_m\hat{c}_{\alpha k} + {\rm c.c.}$

HAMILTONIAN NOT ENOUGH!!

nse)

13)

NEED TO DEFINE IRREVERSIBILITY

CLASSICAL: Boltzmann postulated

loss of ALL microscopic info $\Longrightarrow$ THERMODYNAMICS

♣ Example: Fast relaxation to local thermal state

$\Rightarrow$ Boltzmann's PROOF of 2nd law

♣ Counter-example: *Maxwell's demon*

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QUANTUM: Assume *no Maxwell demons* in reservoirs

- Quantum system: all info available
- Reservoirs: microscopic info = LOST

$\Longrightarrow$ system-reservoir correlations/entanglement = LOST

$\Longrightarrow$ Entropy change $\Delta S = \Delta S_{\rm sys} + \Delta S_{\rm res}$ (drop correlations)

GOOD STATES, BAD STATES and FLUCTUATION THEOREMS

$$P_{\text{good}} = \frac{\text{N}^\circ \text{ of "good" states}}{\text{Total N}^\circ \text{ states}}$$

Entropy:

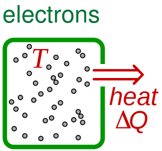
$$S_{\text{good}} = \ln\left[\,\text{N}^\circ \text{ of "good" states}\,\right]$$

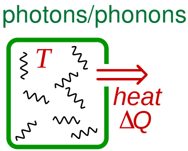
$$S_{\text{bad}} = \ln\left[\,\text{N}^\circ \text{ of "bad" states}\,\right]$$

A fluctuation theorem:

$$P_{\text{bad}\to\text{good}} \; = \; P_{\text{good}\to\text{bad}} \;\times\; \exp\left[-\,\Delta S_{\text{good}\to\text{bad}}\right]$$

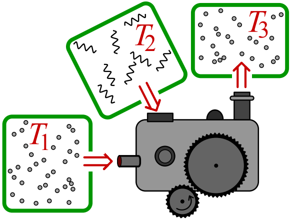
FLUCTUATION THEOREMS & 2nd LAW





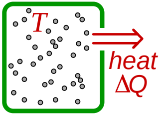
Any large reservoir
at thermal equilibrium

$$\Delta S = \frac{\Delta Q}{k_{\mathrm{B}} T}$$

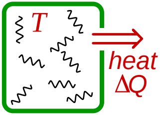


FLUCTUATION THEOREMS & 2nd LAW

electrons



photons/phonons



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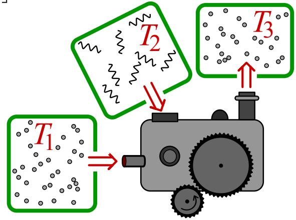
Fluctuation theorems:

- Under right conditions Evans-Searles (1994), Crooks (1998)

$$\overline{P}(-\Delta S) = P(\Delta S) \exp\left[-\Delta S \right]$$



$\Rightarrow$ 2nd law *on average* $\langle \Delta S \rangle \geq 0$

FLUCTUATION THEOREMS & 2nd LAW

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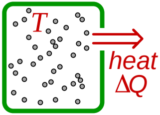

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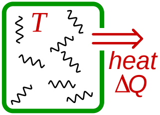

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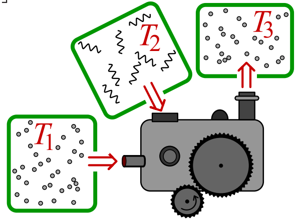
- Universal : Kawasaki (1967), Seifert (2005)

$$\left\langle \exp\left[\,-\Delta S\,\right]\right\rangle = 1$$

- Other relations: Jarzynski (1997), etc



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STOCHASTIC THERMODYNAMICS

for classical markovian systems

Seifert (2005), Schmiedl-Seifert (2007)

⇓

QUANTUM superpositions/entanglement

& **STRONG COUPLING** non-Markovian

Previous works: quantum thermodynamics

1) EXACT for system+reservoirs   review: Campisi, Hänggi, Talkner (2011)

Problem: cannot calculate power outputs ...

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2) WEAK-COUPLING $=$ Markovian $\simeq$ classical rate equations

+ coherent superposition review: Kosloff (2013) & see Elouard et al (2017)

Problem: weak-coupling = small power output

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3) KELDYSH for strong coupling

Non-interacting (quadratic) Hamiltonian — Ludovico et al (2014), Esposito Ochoa Galperin (2015), Bruch et al (2016)

+ interacting system with adiabatic driving — Ludovico et al (2016)

$Problem:$ not general $+$ no fluctuation theorems — also ambiguity $\langle E_{\rm coupling} \rangle$

REAL-TIME TRANSPORT THEORY

quantum + non-markov + interactions + far from equilibrium

Schoeller-Schön (1994)

Keldysh in system's many-body basis

exactly diagonalize $H_{\rm sys}$ including interactions

with NON-INTERACTING reservoirs in free-particle basis

PRICE TO PAY: system-reservoir interactions $\Longrightarrow$ NON-TRIVIAL

♣ Assumption: initial state is product state

Example Hamiltonian =

$$\underbrace{\left[E_n(t)\hat{d}_n^\dagger\hat{d}_n + U\hat{d}_n^\dagger\hat{d}_n\hat{d}_m^\dagger\hat{d}_m\right]}_{\text{interacting system}} + \sum_k \left[\underbrace{V_{nk}\hat{d}_n^\dagger\hat{c}_k + \text{c.c.}}_{\text{coupling}} + \underbrace{E_k\hat{c}_k^\dagger\hat{c}_k}_{\text{electron reservoirs}}\right] + \text{photon terms}$$

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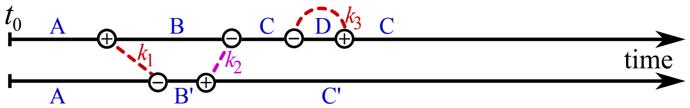

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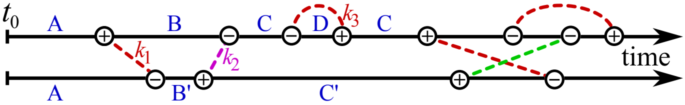

ENERGY CONSERVATION

1st law $0 = \langle \Delta W_{\rm drive} \rangle + \langle \Delta W_{\rm res} \rangle + \langle \Delta Q_{\rm res} \rangle + \langle \Delta E_{\rm sys+coupling} \rangle$

Having defined:

- Reservoir α energy: $\Delta E_\alpha =$ WORK $+$ HEAT
  $= \Delta W_\alpha + \Delta Q_\alpha$ with $\Delta Q_\alpha = T_\alpha \Delta S_\alpha$
- System non-equilib $\Leftrightarrow$ *CAN'T* separate $\langle \Delta E_{\rm sys+coupling} \rangle$ into work & heat

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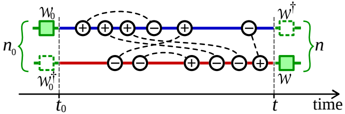
TECHNICAL DETAILS:

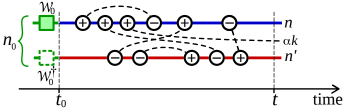
Energy change in reservoir, ΔE_{res}

Energy change in system, ΔE_{sys}



Energy change in coupling $\Delta E_{\text{coupling}}$

(diagrams same as for currents)



ENTROPY $\Longrightarrow$ FLUCTUATION THEOREMS

Assume no Maxwell demon

(no microscopic knowledge of reservoirs)

Entropy change $= \Delta S_{\mathrm{sys}} + \sum_\alpha \Delta S_\alpha$ (drop correlations)

♢ Reservoir α; $\Delta S_\alpha = \Delta Q_\alpha / T_\alpha$ (Claussius)

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$\diamondsuit$ System = non-equilib $\Rightarrow$ von Neumann

Initial system state $\Rightarrow$ its diagonal basis

$$\hat\rho_{\rm sys}(t_0) = \hat{\mathcal{W}}_0\, \hat{\mathbf{p}}^{\rm (initial)}\, \hat{\mathcal{W}}_0^\dagger \quad \Leftarrow \text{diagonal } \hat{\mathbf{p}}^{\rm (initiial)}$$

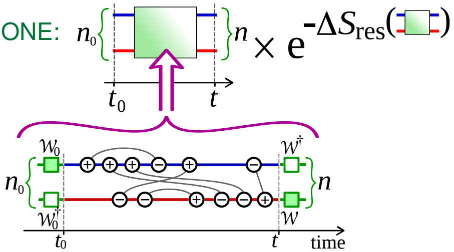
& *final* (reduced) system state $\Rightarrow$ its diagonal basis $\Leftarrow$ diagonal $\hat{\mathbf{p}}^{\rm (final)}$

HENCE $\Delta S_{\rm sys}^{n_0 \to n} = -\ln p_n^{\rm (final)} + \ln p_{n_0}^{\rm (initial)}$

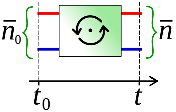
TIME REVERSING TRAJECTORIES

Diagonalize system state at beginning at end; with *rotations* $\mathcal{W}_0$ & $\mathcal{W}$

Ingredient ONE:



$=$



$\overline{n}$ is time-reverse of n

[Messiah textbook]

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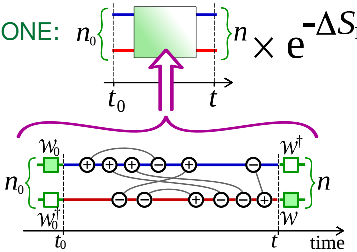
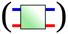


$\times\ e^{-\Delta S_{\mathrm{res}}(\;)}$



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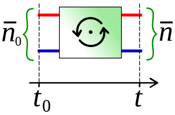

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Ingredient TWO: $\Delta S_{\mathrm{sys}}^{n_0 \to n} = -\ln p_n^{(\mathrm{final})} + \ln p_{n_0}^{(\mathrm{initial})}$

algebra
similar
stochastic
thermodyn

$\Longrightarrow$

FLUCTUATION THEOREMS

$\left\langle \exp[-\Delta S] \right\rangle = 1 \quad \Rightarrow$ 2nd LAW

also Crooks & Jarzynski under certain conditions

Fluctuation theorems in APPROXIMATE theories

Any approximation which:

(1) contains a time-reverse for every trajectory

(2) conserves probability

$\Longrightarrow$ Fluctuation theorems $\Longrightarrow$ no violation of 2nd LAW

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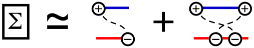
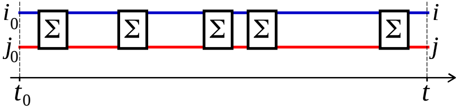
WORKS FOR STANDARD APPROXIMATION:

Irreducible blocks {

Seq. tunnelling approx 

Co-tunnelling approx 

& sum to all orders 

Non-factorizable initial state

Factorized state in the distant past (time $t_0 \to -\infty$)

Define $Q(\Delta S_{1\to 2})$ as entropy distribution† from t_1 to t_2

$$P(\Delta S_2) \equiv \int \mathrm{d}(\Delta S_1)\; Q(\Delta S_2 - \Delta S_1)\; P(\Delta S_1)$$

$$\Big\langle \exp\big[-\Delta S_{1\to 2})\big]\Big\rangle = 1$$

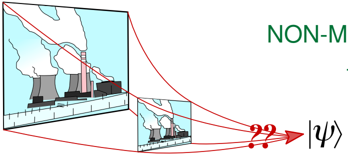
with average being over $Q(\Delta S_{1\to 2})$

$\Rightarrow$ 2nd LAW $\Big\langle \Delta S_{1\to 2} \Big\rangle \geq 0$

† should not measure state at time t_1, otherwise collapse to product state

$\Longrightarrow$ protocol with multiple identical set-ups

CONCLUSIONS



NON-MARKOVIAN TRAJECTORIES

from all-orders PERTURBATION THEORY

perturbation = sys-reservoir coupling

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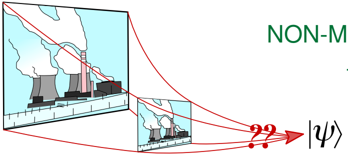

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♣ get FLUCTUATION THEOREMS for *arbitrary* quantum machine

$\Uparrow$ $\Uparrow$ $\Uparrow$ $\Uparrow$

stochastic thermodyn, 2ND LAW, etc   strong-coupling, interacting, t-dependent, etc

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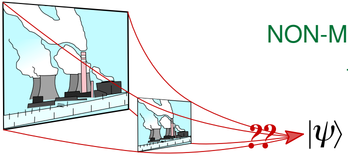

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♣ *for FAMILIES OF APPROXIMATIONS*

- sequential tunnelling = Born-Markov
- co-tunnelling = 1st non-Markov correction
- your favourite truncation ???
- EXACT TREATMENT

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— EXTRAS —

PERTURBATION THEORY as TRAJECTORIES

PERTURBATION
sys-reservoir coupling

$$U(t;t_0) = \hat{\mathcal{T}} \exp\left[-\mathrm{i}\int_{t_0}^{t} \mathrm{d}\tau \big(\hat{H}_{\mathrm{sys}}(\tau) + \hat{H}_{\mathrm{res}} + \hat{V}(\tau)\big)\right]$$

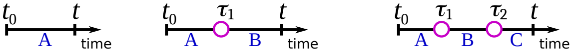
$$= \hat{\mathcal{T}} \exp\left[-\mathrm{i}\int_{t_0}^{t} \mathrm{d}\tau\ \hat{\mathcal{V}}(\tau)\right]$$

for interaction picture

$$\hat{\mathcal{V}}(\tau) = \hat{U}(\tau;t_0)\,\hat{V}(\tau)\,\hat{U}^\dagger(\tau;t_0)$$

with $\hat{U}(\tau;t_0) = \hat{\mathcal{T}} \exp\left[-\mathrm{i}\int_{t_0}^{t}\mathrm{d}\tau(\hat{H}_{\mathrm{sys}} + \hat{H}_{\mathrm{res}})\right]$

$$= \quad 1 \quad - \mathrm{i}\int_{t_0}^{t}\mathrm{d}\tau_1\ \hat{\mathcal{V}}(\tau_1) \ - \int_{t_0}^{t}\mathrm{d}\tau_2 \int_{t_0}^{\tau_2}\mathrm{d}\tau_1\ \hat{\mathcal{V}}(\tau_2)\,\hat{\mathcal{V}}(\tau_1) \ + \cdots$$



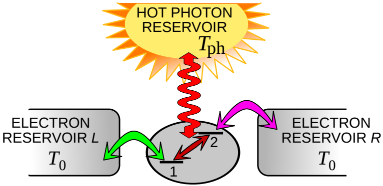
STOCHASTIC THERMODYNAMICS

Seifert (2005), Schmiedl-Seifert (2007)

derived fluctuation theorems

& laws of thermodynamics

from classical RATE EQUATION



ASSUMPTIONS (i) probabilities but no superpositions

(ii) weak-coupling – Markovian

(iii) No Maxwell demons in reservoirs

$\Longrightarrow$ Entropy change $\Delta S = \Delta S_{\rm sys} + \Delta S_{\rm res}$

[drop correlations]

WANT same thing with QUANTUM (superpositions/entanglement)

and STRONG COUPLING (non-Markovian)

Change of system entropy

Standard thermodynamics :

$$\Delta S_{\rm sys} \;=\; S_{\rm sys}(t) \,-\, S_{\rm sys}(t_0)$$

with Shannon entropy

$$S_{\rm sys} = -\sum_i p_i \ln p_i$$

Classical "Stochastic thermodynamics":

assign entropy to initial and final state for *each trajectory*

Seifert (2005)

$$\Delta S_{\rm sys}^{i_0 \to i} \;=\; -\big[\, \ln p_i(t) \,-\, \ln p_{i_0}(t_0)\,\big]$$

which means $\exp[-\Delta S_{\rm sys}^{i_0 \to i}] \;=\; \dfrac{p_i(t)}{p_{i_0}(t_0)}$ $\Longleftarrow$ 2nd ingredient for fluct. theorem

ENTROPY CHANGE IN QUANTUM SYSTEM

$$\Delta S_{\rm sys} \;=\; S_{\rm sys}(t) \;-\; S_{\rm sys}(t_0)$$

with von Neumann

$$S_{\rm sys}(\tau) = -{\rm Tr}\Big[\hat{\rho}_{\rm sys}(\tau)\ln\Big(\hat{\rho}_{\rm sys}(\tau)\Big)\Big]$$

$\Delta S_{\rm sys}$ for initial/final $QUANTUM$ state

Assign entropy to *each* state in initial and final diagonal bases

- *Initial* system density-matrix

$$\hat{\rho}_{\rm sys}(t_0) = \hat{\mathcal{W}}_0\,\hat{\mathbf{p}}^{(\rm initial)}\,\hat{\mathcal{W}}_0^\dagger \qquad \Leftarrow \text{diagonal } \hat{\mathbf{p}}^{(\rm initial)}$$

- *Final* (reduced) system density-matrix

$$\hat{\rho}_{\rm sys}(t) = \hat{\mathcal{W}}\,\hat{\mathbf{p}}^{(\rm final)}\,\hat{\mathcal{W}}^\dagger \qquad \Leftarrow \text{diagonal } \hat{\mathbf{p}}^{(\rm final)}$$

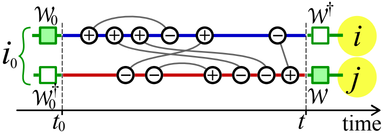
Take double trajectories as going from one diag. basis to the other

$$\Delta S_{\rm sys}^{i_0\to i} \;=\; \ln p_{i_0}^{(\rm initial)} \;-\; \ln p_i^{(\rm final)}$$

WHY assume we can NEGLECT:

- ♣ Entropy of entanglement between system & reservoirs

- ♣ Non-zero *off-diagonal* trajectories for entropy fluctuations



has *no* time-reverse for $j \neq i$

...they sum to *zero*

Assume we cannot use knowledge
of a reservoir's *microscopic* state to get *EXTRA work*