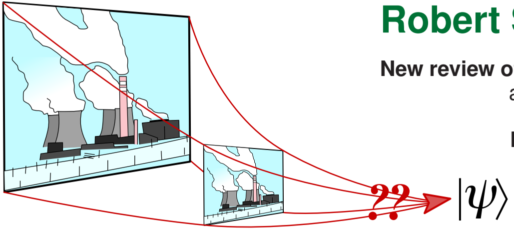
Laboratoire de Physique et Modélisation des Milieux Condensés
Univ. Grenoble Alpes & CNRS, Grenoble, France

Trajectories for non-Markovian quantum thermodynamics



Robert S. Whitney

New review of old stuff – Benenti et al
arXiv:1608.05595 (section 8.10)

New stuff – arXiv:1611.00670

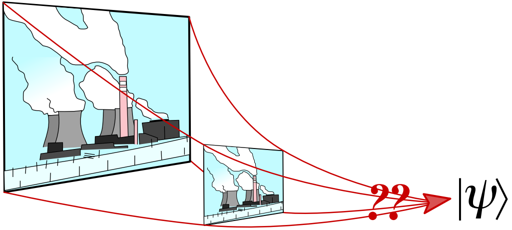
W. & E. Heraeus Seminar – Bad Honnef, 12 April 2017

OVERVIEW

arXiv:1611.00670

Quantum machine: *heat* $\Rightarrow$ *electrical power*

$\Longrightarrow$ Objective : 2nd law of thermodynamics + fluctuation theorems



OVERVIEW

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Quantum machine: *heat* $\Rightarrow$ *electrical power*

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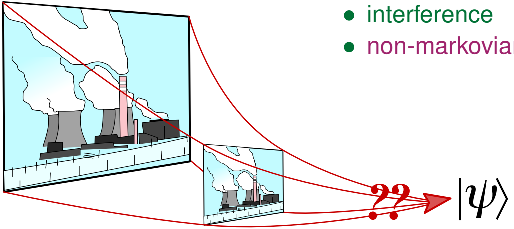
♣ TRAJECTORIES from perturbation theory (all orders) in coupling

Real-time Keldysh for density matrix

- interference
- non-markovian = strong coupling

(cotunneling, Kondo, etc)



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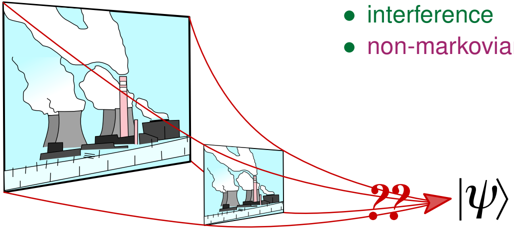

♣ Symmetry relation: *TRAJECTORY* $\Leftrightarrow$ *TIME-REVERSE*

♣ Families of approximations which respect 2nd law (& fluct. theorems)

INTRODUCTION

TRAJECTORIES

$\Downarrow \qquad \Downarrow$

SECOND LAW of THERMODYNAMICS

& FLUCTUATION THEOREMS

classical rate equations $\longrightarrow$ fluctuation theorems

FLUCTUATION THEOREMS & 2$^{\text{nd}}$ LAW

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

Entropy:

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

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

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

FLUCTUATION THEOREMS & 2nd LAW

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

Entropy:

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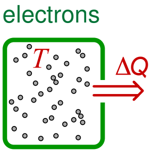
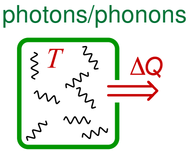
$$S_{\rm bad} = \ln \left[\text{N}^\circ \text{ of "bad" states} \right]$$

$$P_{\rm bad \to good} \; = \; P_{\rm good \to bad} \; \times \; \exp \Big[- \Delta S_{\rm good \to bad} \Big]$$

Dissipative dynamics: need ΔS of fluid $\Leftarrow$ trajectory of system

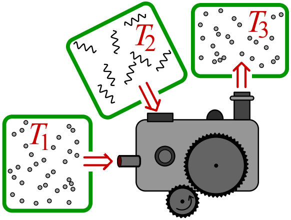
FLUCTUATION THEOREMS & 2nd LAW



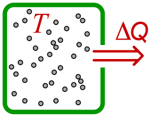


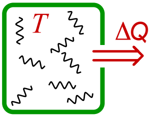
Any large reservoir
at thermal equilibrium

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



FLUCTUATION THEOREMS & 2nd LAW





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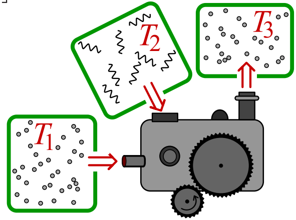
Fluctuation theorems:

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

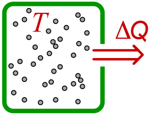
$$\overline{P}(-\Delta S) \;=\; P(\Delta S)\;\exp\left[\,-\Delta S\,\right]$$



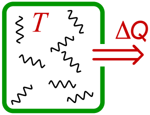
$\Rightarrow$ 2nd law *on average* $\langle \Delta S \rangle \;\geq\; 0$

FLUCTUATION THEOREMS & 2nd LAW

electrons



photons/phonons



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Fluctuation theorems:

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

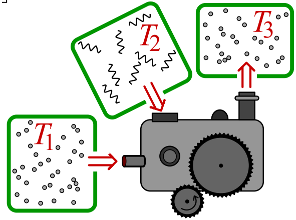
$$\overline{P}(-\Delta S) \;=\; P(\Delta S)\; \exp\left[\,-\Delta S\,\right]$$

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

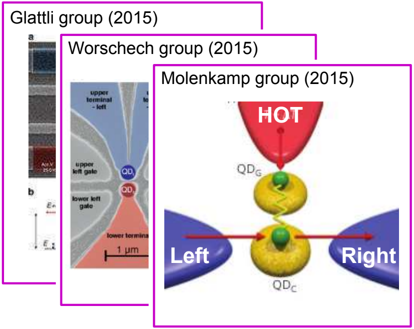
$$\left\langle \exp\left[\,-\Delta S\,\right] \right\rangle \;=\; 1$$

- Other relations: Jarzynski (1997), etc

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



EXAMPLES: EXISTING NANOSCALE MACHINES



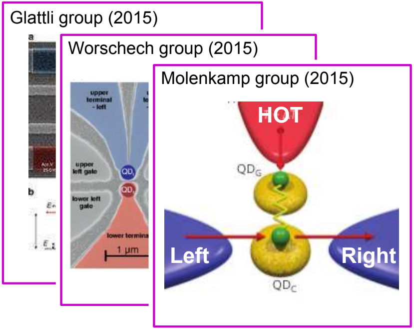
Theory:

Sánchez & Büttiker(2011)

Entin-Wohlmann et al (2011-2015)

Strasberg-Schaller-Brandes-Esposito (2013)

EXAMPLES: EXISTING NANOSCALE MACHINES



Theory:

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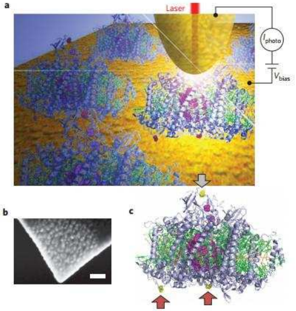
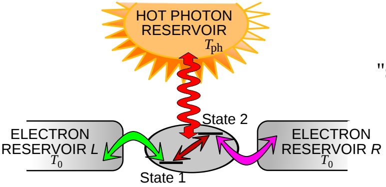
Strasberg-Schaller-Brandes-Esposito (2013)

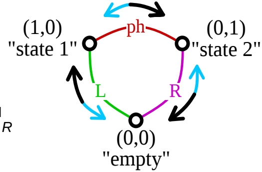
Single photosynthetic molecule

Gerster et al (2012)



TRAJECTORIES for STOCHASTIC THERMODYNAMICS





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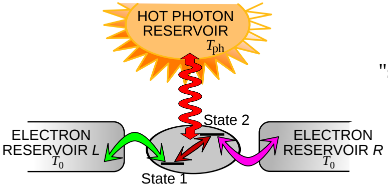
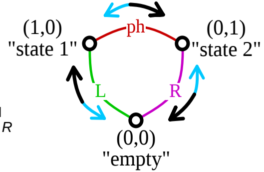




Rate equation (markovian master equation)

$$\frac{\mathrm{d}}{\mathrm{d}t} P_b(t) \; = \; \sum_a \Big(\Gamma_{ba}\, P_a(t) \; - \; \Gamma_{ab}\, P_b(t) \Big)$$

where P_b = prob. system is in state b

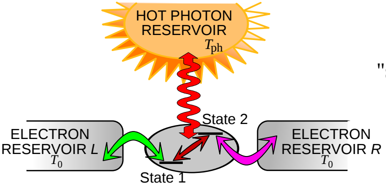
& Γ_{ba} = rate $a \to b$

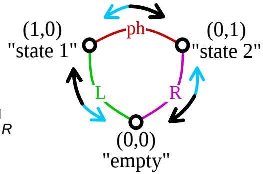
$$\left.\begin{array}{l} \text{Rate}\big[(0,0) \to (1,0)\big] \propto \text{Fermi} \\ \text{Rate}\big[(1,0) \leftarrow (0,0)\big] \propto 1-\text{Fermi} \end{array}\right\} \Rightarrow$$

LOCAL DETAILED BALLANCE

$$\Gamma_{ab} = \Gamma_{ba} \exp\big[-\Delta S_{ba} \big]$$

TRAJECTORIES for STOCHASTIC THERMODYNAMICS

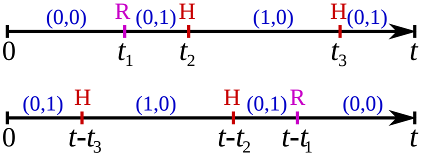




Stochastic thermodynamics Seifert (2005), Schmeidl-Seifert (2007)

Trajectory ζ =

time-reverse $\bar{\zeta}$ =



Prob. of $\bar{\zeta}$ = $\big($ Prob. of ζ $\big) \times \exp\Big[-\Delta S_{\rm res}(\zeta) \Big]$ $\Longrightarrow$ Fluctuation theorem

Beyond simple rate equations ...

completely

quantum

including SUPERPOSITIONS, ENTANGLEMENT, etc

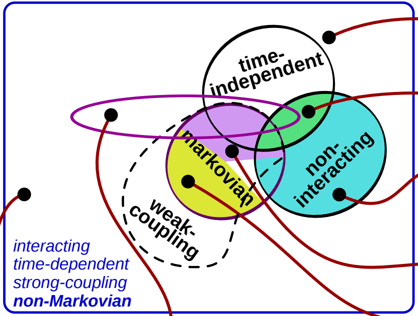
GENERAL : Strong-coupling = non-Markovian

Time-dependent external drive

SUITABLE for CALCULATION:

Currents, heat flows, thermodynamic efficiencies, ...

Previous proofs of 2nd law for quantum machines



Keldysh (adiababtic driving)
Ludovico et al (2016)

Landauer scattering theory
Nenciu (2007), RW (2013)

Keldysh (non-interacting)
Ludovico et al (2014)
Esposito, Ochoa, Galperin (2015)
Bruch et al (2016)

Rate equations
Schmeidl-Seifert (2007)

Lindblad equation
Alicki (1979) & others
reviewed by Kosloff (2013)

Single reservoir systems
including fluct. theorems
Cohen-Imry (2012)

Formal proofs for ALL cases (by taking sys+res as closed system)
including fluct. theorems reviewed by Campisi, Talkner, Hanggi (2011)

PERTURBATION THEORY as TRAJECTORIES

PERTURBATION THEORY as TRAJECTORIES

PERTURBATION
sys-reservoir coupling
$\Downarrow$

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

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

for interaction picture

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

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

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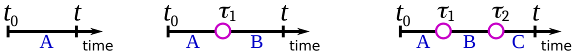
$$= \quad 1 \quad - \mathrm{i}\int_{t_0}^{t} \mathrm{d}\tau_1\, \hat{\mathcal{V}}(\tau_1) \; - \int_{t_0}^{t} \mathrm{d}\tau_2 \int_{t_0}^{\tau_2} \mathrm{d}\tau_1\, \hat{\mathcal{V}}(\tau_2)\, \hat{\mathcal{V}}(\tau_1) \; + \cdots$$



REAL-TIME KELDYSH APPROACH

quantum + non-markov + interactions + far from equilibrium

Schoeller-Schön (1994) + Konig + Gefen

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quantum + non-markov + interactions + far from equilibrium

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BIG simplifications:

- interactions in system but NOT in reservoirs

  $\Longrightarrow$ many-body eigenbasis for system

  $\Longrightarrow$ free-particle eigenbasis for reservoirs

- infinite N° of reservoir modes k

  $\Longrightarrow$ coupling to lowest (2nd) order for each k

- Assumption: initial state is product state

Example Hamiltonian =

$$\underbrace{\hat{\mathcal{H}}_{\text{sys}}\left(\hat{d}_n^\dagger, \hat{d}_n, t\right)}_{\text{interacting system}} + \sum_k \underbrace{V_{nk}\left(\hat{d}_n^\dagger \hat{c}_k + \hat{d}_n \hat{c}_k^\dagger\right)}_{\text{coupling}} + \underbrace{\sum_k E_k \hat{c}_k^\dagger \hat{c}_k}_{\text{electron reservoirs}} + \text{ photon terms}$$

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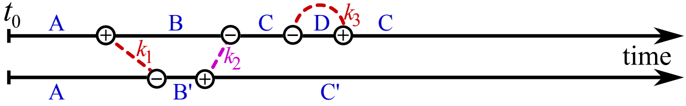
Evolution as function of time :



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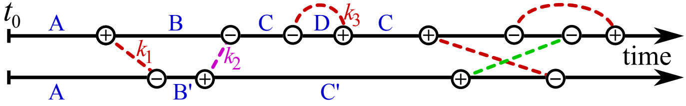


TIME-REVERSE OF TRAJECTORIES

◇ time-reverse Hamiltonian

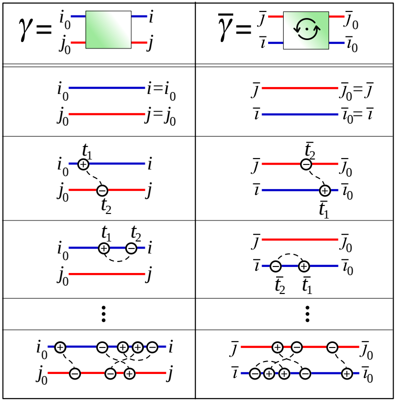
$$\overline{H}(\tau, B) = H(t + t_0 - \tau, -B)$$

◇ time-reverse *states*

$\overline{\imath}$ $=$ time-reverse of state i

momentum of $\overline{\imath}$ opposite to i

(for spins see Messiah's book)



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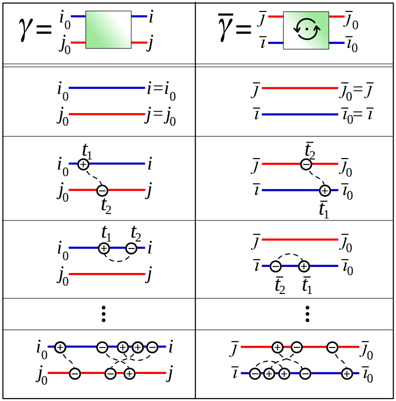
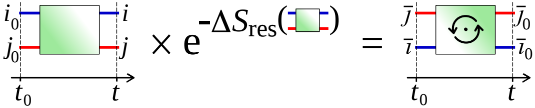
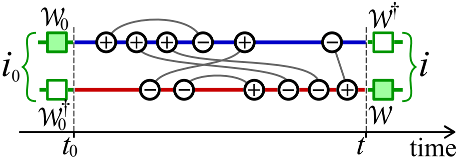


RESULT:

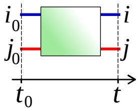


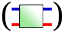
Trajectories from system *diagonal* basis to *diagonal* basis

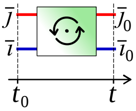
Diagonalize system state with *rotations* $\mathcal{W}_0$ & $\mathcal{W}$ at beginning and end



With rotations we still have:



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



algebra same as for rate equations $\Longrightarrow$ *ALL CLASSICAL FLUCTUATION THEOREMS*

Crook's, Jarzynski, Kawasaki, etc

$\Longrightarrow$ 2nd LAW

Fluctuation theorems in APPROXIMATE theories

Any approximation which:

(1) contains a time-reverse for every trajectory

(2) conserves probability

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

Fluctuation theorems in APPROXIMATE theories

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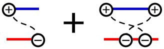
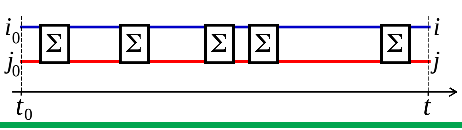
WORKS FOR STANDARD APPROXIMATION:

Irreducible blocks

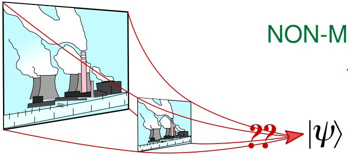
- Seq. tunnelling approx $\boxed{\Sigma} \simeq$ 
- Co-tunnelling approx $\boxed{\Sigma} \simeq$ 

& sum to all orders



CONCLUSIONS

arXiv:1611.00670



NON-MARKOVIAN TRAJECTORIES

from all-orders PERTURBATION THEORY

perturbation = sys-reservoir coupling

CONCLUSIONS

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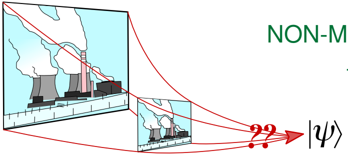

NON-MARKOVIAN TRAJECTORIES

from all-orders PERTURBATION THEORY

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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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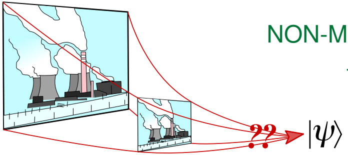

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♣ *for FAMILIES OF APPROXIMATIONS*

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

— EXTRAS —

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

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

Subtlety of sum over stochastic trajectories

Let $\langle \cdots \rangle$ be average by summing over all stochastic trajectories

& let $\ll \cdots \gg$ be *normal* average

$\Longrightarrow$ One has $\langle\, \Delta S_{\rm res} + \Delta S_{\rm sys}\, \rangle \;=\; \ll \Delta S_{\rm res} \gg + \ll \Delta S_{\rm sys} \gg$

However $\langle\, [\Delta S_{\rm res} + \Delta S_{\rm sys}]^n\, \rangle$ seems to contain

some correlations between $\Delta S_{\rm res}$ and $\Delta S_{\rm sys}$, but not *ALL* of them!

i.e. it seems to be between

$$\ll [\Delta S_{\rm res} + \Delta S_{\rm sys}]^n \gg$$

and $\ll [\Delta S_{\rm sys}]^n \gg \;\times\; \ll [\Delta S_{\rm res}]^n \gg$

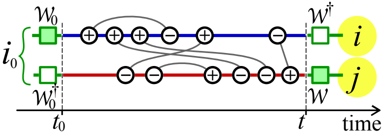
??

Physics hidden here!

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*