Laboratoire de Physique et Modélisation des Milieux Condensés
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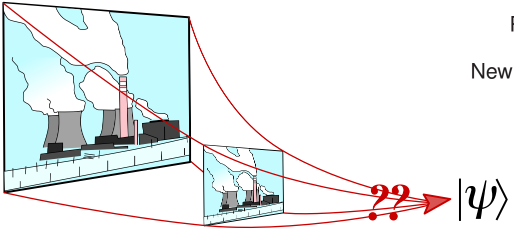
The laws of thermodynamics at the nanoscale

Robert S. Whitney

REVIEW ARTICLE: Benenti, Casati, Saito, R.W.
Physics Reports 694, 1 (2017)

New work: R.W. arXiv:1611.00670



Les Houches, 20 Sept 2017

OVERVIEW

♣ QUANTUM ⇔ THERMODYNAMICS

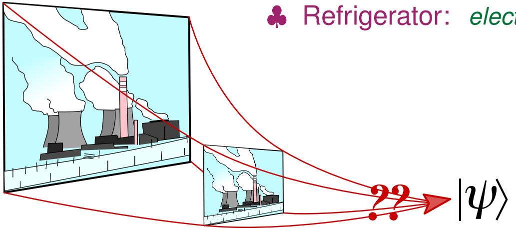
Role of *entropy* in quantum technology

♣ Quantum Technologies :

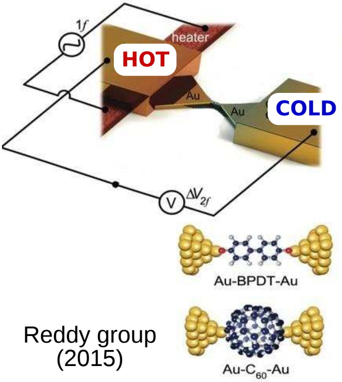
- Computing: *electrical power* ⇒ *information*
- Motor: *electrical power* ⇒ *motion*

♣ Power source: *heat* ⇒ *electrical power*

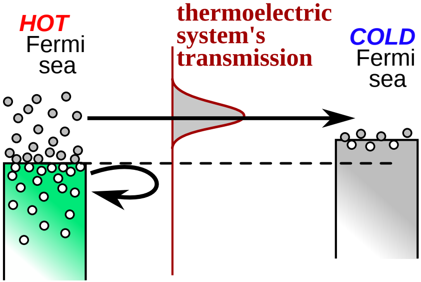
♣ Refrigerator: *electrical power* ⇒ *heat*



EXAMPLES: EXISTING NANOSCALE MACHINES

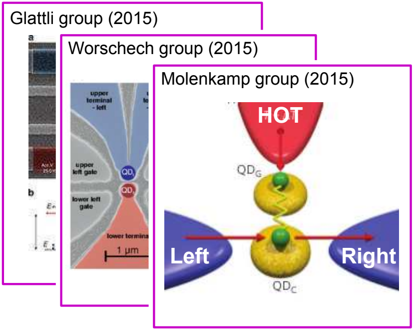


Reddy group
(2015)



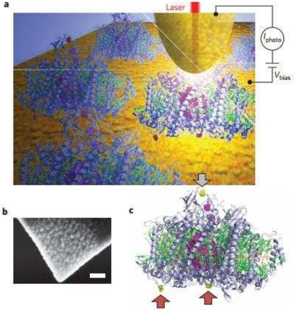
Theory - Sivan-Imry (1986)

EXAMPLES: EXISTING NANOSCALE MACHINES



Single photosynthetic molecule

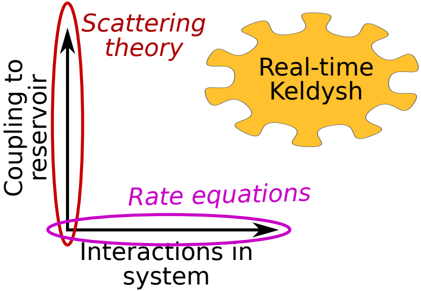
Gerster et al (2012)



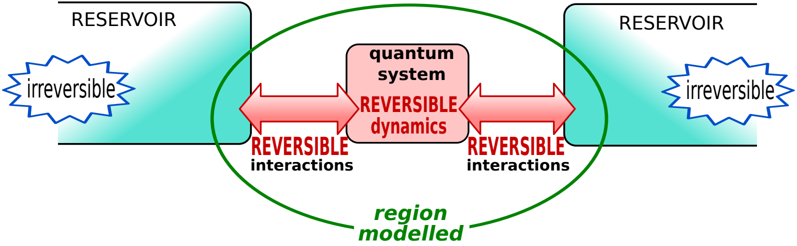
Theory:

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

MODELLING METHODS



MODELLING METHODS



REVERSIBLE or NOT?

- Where is *entropy produced?*
- 2nd law of thermodynamics*?*

PART 1 : SCATTERING THEORY

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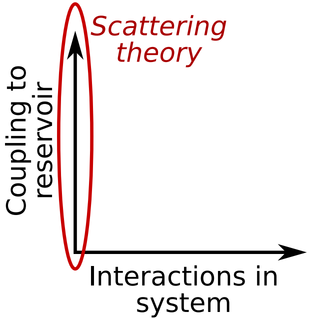
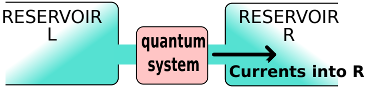
see Chapters 4-6 of our review: Physics Reports, 694, 1 (2017)

arXiv:1608.05595



LANDAUER SCATTERING THEORY

(TWO TERMINALS)



Particle current into R $\equiv \frac{\mathrm{d}}{\mathrm{d}t} N_R = \int \mathrm{d}E \quad \mathcal{T}(E) \left[f\left(\frac{E-\mu_L}{T_L}\right) - f\left(\frac{E-\mu_R}{T_R}\right) \right]$

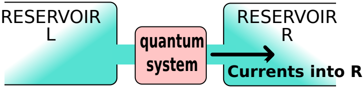
Energy current into R $\equiv \frac{\mathrm{d}}{\mathrm{d}t} E_R = \int \mathrm{d}E \; E \; \mathcal{T}(E) \left[f\left(\frac{E-\mu_L}{T_L}\right) - f\left(\frac{E-\mu_R}{T_R}\right) \right]$

UNITS: $\hbar = k_\mathrm{B} = 1$

- Electric current into R $= e \frac{\mathrm{d}}{\mathrm{d}t} N_R$
- Work into R $= \mu_R \frac{\mathrm{d}}{\mathrm{d}t} N_R \quad \Longrightarrow$ power generated $=$ sum L & R $= (\mu_R - \mu_L) \frac{\mathrm{d}}{\mathrm{d}t} N_R$
- Heat current into R $= \frac{\mathrm{d}}{\mathrm{d}t} E_R - \mu_R \frac{\mathrm{d}}{\mathrm{d}t} N_R$
- Entropy current into R $=$ Heat current$\big/ T_R$ $\quad \Leftarrow$ CLAUSIUS LAW (1855)

LANDAUER SCATTERING THEORY

(TWO TERMINALS)



or see section 6.4 of our review
arXiv:1608.05595

- Rate of change of entropy $\frac{\mathrm{d}}{\mathrm{d}t}S$

  = (Entropy current into L) + (Entropy current into R) $\geq \ 0$

  $\Rightarrow$ 2nd law proven for all situations (all $\mathcal{T}(E)$, all T_L, T_R, ...)

  Nenciu (2007) = proof for N reservoirs

- Carnot efficient system : reversible $\frac{\mathrm{d}}{\mathrm{d}t}S = 0$

  requires transmission is only non-zero at $\frac{E-\mu_L}{T_L} = \frac{E-\mu_R}{T_R}$

  Humphrey, Newbury, Taylor, Linke (2002)

PART 2 : RATE EQUATIONS

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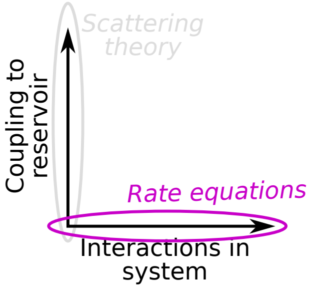
see Chapters 8 & 9 of our review: Physics Reports, 694, 1 (2017)

arXiv:1608.05595



FLUCTUATION THEOREMS $\Longrightarrow$ Second Law

FLUCTUATION THEOREMS & 2nd LAW

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

Entropy:

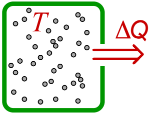
$$S_{\rm good} = \ln\left[\,\text{N° of "good" states}\,\right]$$

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

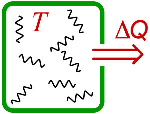
$$P_{\rm bad\to good} \;=\; P_{\rm good\to bad} \;\times\; \exp\left[-\Delta S_{\rm good\to bad}\right]$$

FLUCTUATION THEOREMS & 2nd LAW

electrons



photons/phonons



Any large reservoir
at thermal equilibrium

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

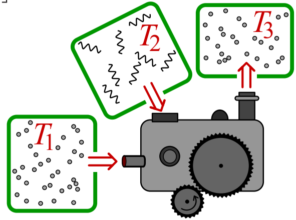
Fluctuation theorems:

- 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)

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

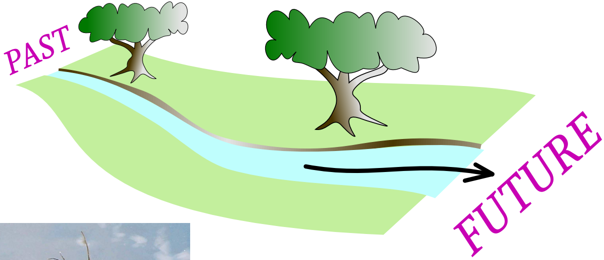


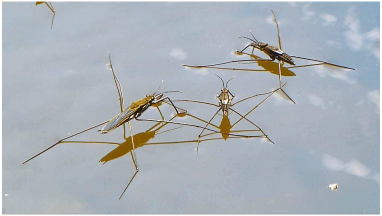
$\Rightarrow$ 2nd law *on average* $\langle \Delta S \rangle \;\geq\; 0$

THE FLUCTUATING ARROW OF TIME

"Arrow of time" $\equiv$ 2nd law thermodynamics

defined in Eddington's popular science book on thermodynamics (1927)





We skate back and forth in time,
as we drift into the future.

THE FLUCTUATING ARROW OF TIME

Probability that time *reverses* for me; $\Longleftarrow$ I talk *backwards!!*

i.e. probability that all chemical transitions in my body go in “wrong direction”

My body's $\Delta S/k_{\mathrm{B}}$ per second $\simeq \dfrac{\text{food eaten per day}}{\text{(seconds in day)} \times k_{\mathrm{B}}T} \sim 10^{24}$

Prob. that I go *back in time* for time τ

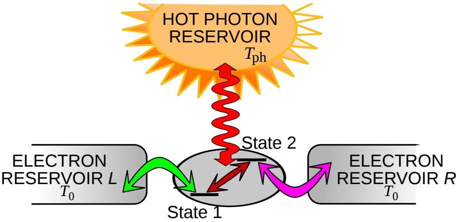
$= \text{(prob. of normal time flow)} \times \mathrm{e}^{-\Delta S(\tau)/k_{\mathrm{B}}} \simeq \mathrm{e}^{-\Delta S(\tau)/k_{\mathrm{B}}}$

$\Rightarrow$ I go back in time continuously on scale of a yoctosecond (10^{-24}s)

but only go back in time for 50 yoctosecond

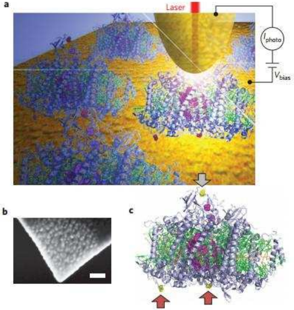
once in age of universe

EXAMPLE: EXISTING NANOSCALE MACHINE



Single photosynthetic molecule

Gerster et al (2012)



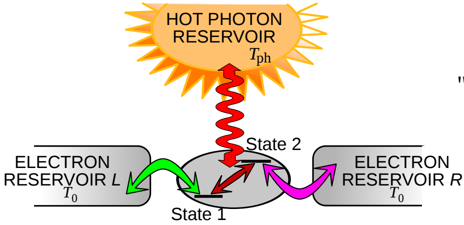
RULE OF THUMB for when fluctuations important or not

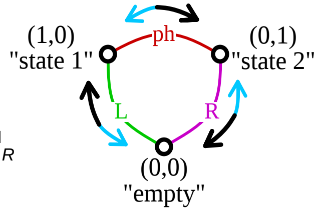
Forget fluctuations (only consider average) for $\langle \Delta S \rangle \gg k_{\rm B}$

$\simeq$ Work output $\gg k_{\rm B}T \sim 10^{-21}$ Joules

e.g. moving 100 electrons across 1V

NANOSCALE PHOTOVOLTAIC





Rate $\left[(0,0) \rightarrow (1,0)\right] \propto$ Fermi

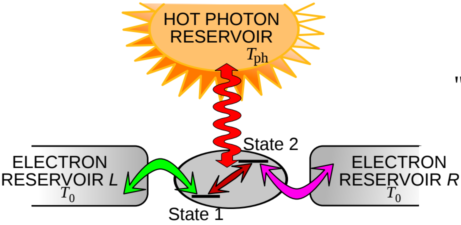
Rate $\left[(1,0) \leftarrow (0,0)\right] \propto 1-$Fermi

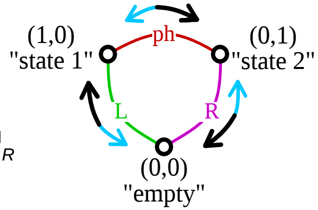
$\Rightarrow$ local detailed balance

$\Rightarrow$ Rate $[x \leftarrow y]$ = Rate $[x \rightarrow y]$ $\times \exp\left[-\Delta S_{\text{res}}(x \rightarrow y)\right]$

$\Delta S_{\text{res}} =$ entropy change in reservoir

NANOSCALE PHOTOVOLTAIC





Set of coupled equations for system evolution:

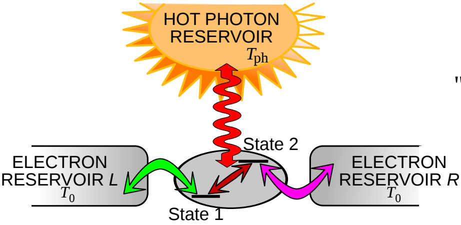
$$\frac{\mathrm{d}}{\mathrm{d}t}P_b(t) = \sum_a \Big(\Gamma_{ba}\,P_a(t) - \Gamma_{ab}\,P_b(t)\Big)$$

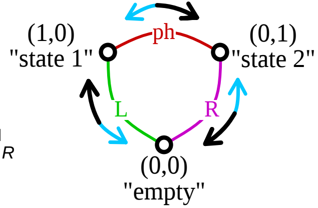
where P_b = prob. system is in state b

& Γ_{ba} = rate $a \rightarrow b$

or see section 9.3 of our review

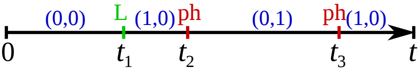
NANOSCALE PHOTOVOLTAIC



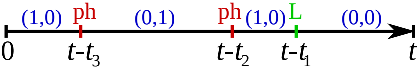


Evolution with time "stochastic thermodynamics" Seifert (2005) :

Trajectory ζ =



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



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

CONCLUSION : RATE EQUATIONS $\Longrightarrow$ FLUCTUATION THEOREMS

$\Longrightarrow$ 2ND LAW of THERMODYNAMICS

(on average)

WARNING : My handwaving neglected system entropy change $\Delta S_{\rm sys}$

Correct fluctuation theorems are for $\Delta S = \Delta S_{\rm sys} + \Delta S_{\rm res}$

to add $\Delta S_{\rm sys}$ to analysis see section 8.10 of our review

arXiv:1608.05595

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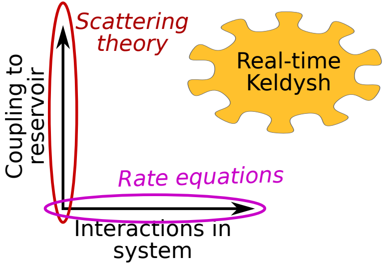
e.g. moving 100 electrons across 1V

PART 3: REAL TIME KELDYSH METHOD

Method: Schoeller-Schön (1994) + Konig

Recent: Splettstösser and Wegewijs's teams

Thermodynamics: Whitney (arXiv:1611.00670)



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Recent: Splettstösser and Wegewijs's teams

Thermodynamics: Whitney (arXiv:1611.00670)

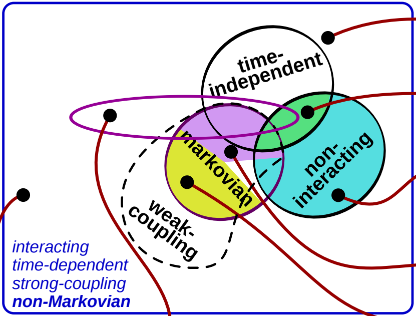
including SUPERPOSITIONS, ENTANGLEMENT, etc

GENERAL : Multiple reservoirs at different Ts
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
sys-reservoir coupling
⇓

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

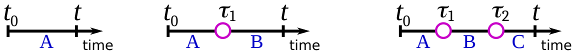
$$= \hat{\mathcal{T}} \exp\left[-\mathrm{i}\int_{t_0}^{t} \mathrm{d}\tau \; \hat{\mathcal{V}}(\tau)\right]$$

for interaction picture

$$\hat{\mathcal{V}}(\tau) = \hat{U}_0(\tau;t_0)\, \hat{V}(\tau)\, \hat{U}_0^{\dagger}(\tau;t_0)$$

with $\hat{U}_0(\tau;t_0) = \hat{\mathcal{T}} \exp\left[-\mathrm{i}\int_{t_0}^{t} \mathrm{d}\tau (\hat{H}_{\mathrm{sys}} + \hat{H}_{\mathrm{res}})\right]$

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



REAL-TIME KELDYSH APPROACH

quantum + non-markov + interactions + far from equilibrium

Schoeller-Schön (1994) + Konig

BIG simplifications:

- interactions in system but NOT in reservoirs

  $\Longrightarrow$ many-body eigenbasis for system

  $\Longrightarrow$ free-particle eigenbasis for reservoirs

- infinite N$^\circ$ of reservoir modes k

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

- Assumption: initial state is product state

Example Hamiltonian =

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

REAL-TIME KELDYSH APPROACH

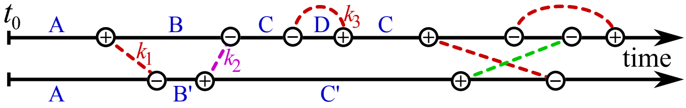
quantum + non-markov + interactions + far from equilibrium

Schoeller-Schön (1994) + Konig

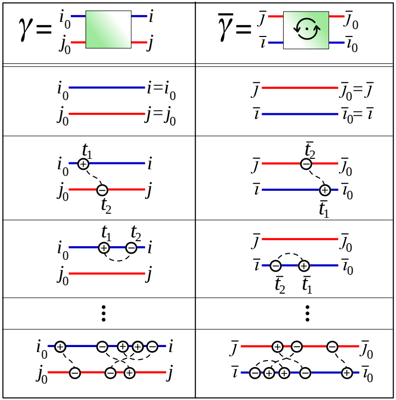
BIG simplifications:

- interactions in system but NOT in reservoirs
  - $\Longrightarrow$ many-body eigenbasis for system
  - $\Longrightarrow$ free-particle eigenbasis for reservoirs
- infinite N$^\circ$ of reservoir modes k
  - $\Longrightarrow$ coupling to lowest (2nd) order for each k
- Assumption: initial state is product state

Evolution as function of time :



TIME-REVERSE OF TRAJECTORIES



◇ time-reverse Hamiltonian

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

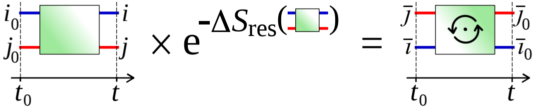
◇ time-reverse *states*

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

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

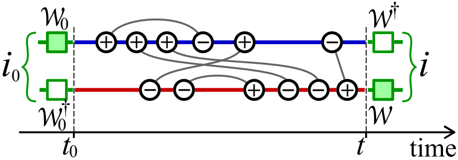
(for spins see Messiah's book)

RESULT:

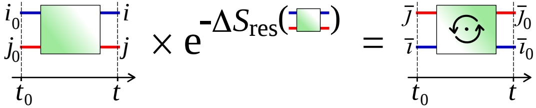


Trajectories from system *diagonal* basis to *diagonal* basis

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



With rotations we still have:



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

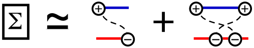
$\Longrightarrow$ Fluctuation theorems $\Longrightarrow$ no violation of 2nd LAW

WORKS FOR STANDARD APPROXIMATION:

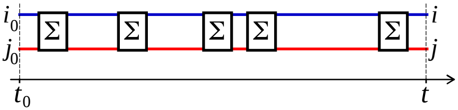
Irreducible blocks

- Seq. tunnelling approx

- Co-tunnelling approx



& sum to all orders



CONCLUSIONS FOR REAL-TIME KELDYSH

R.W. arXiv:1611.00670

♣ get FLUCTUATION THEOREMS for *arbitrary* quantum machine

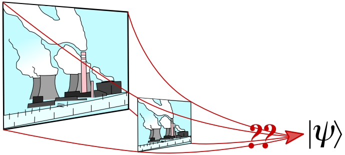
$\Uparrow \quad \Uparrow \qquad\qquad \Uparrow \quad \Uparrow$

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

♣ *for FAMILIES OF APPROXIMATIONS* {

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

TAKE-HOME MESSAGE



Three theories:

(1) scattering theory

(2) rate equations

(3) real-time Keldysh

$\Longrightarrow$ Laws of thermodynamics (on average)

♣ No perpetual motion machines

♣ Efficiency $\leq$ Carnot (on average)

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$\simeq$ Work output $\gg k_{\rm B}T \sim 10^{-21}$ Joules

e.g. moving 100 electrons across 1V