



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

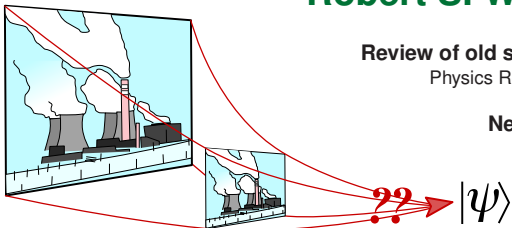
Non-Markovian Quantum Thermodynamics

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



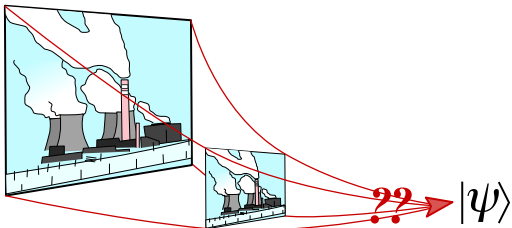
OVERVIEW

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



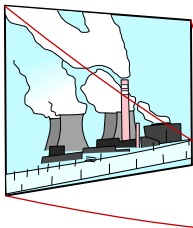
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[i] Experimental examples

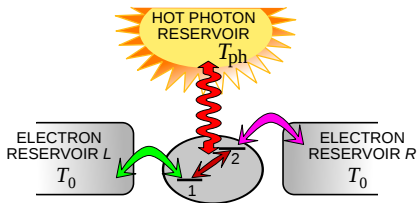
[ii] Irreversibility & Fluctuation theorems

⇒ stochastic thermodynamics (classical)

[iii] Keldysh method: quantum & strong coupling

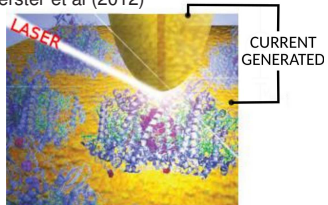
?? → $|\psi\rangle$

HAMILTONIAN

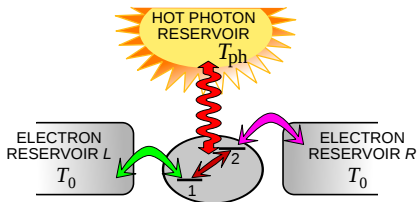


Experiment: photosynthetic molecule

Gerster et al (2012)



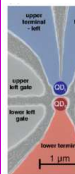
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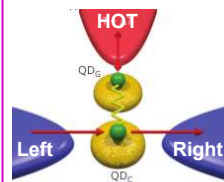
Glattli group (2015)



Worschech group (2015)

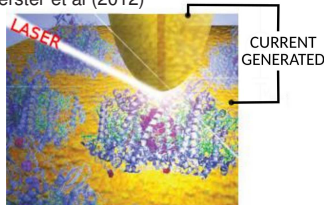


Molenkamp group (2015)



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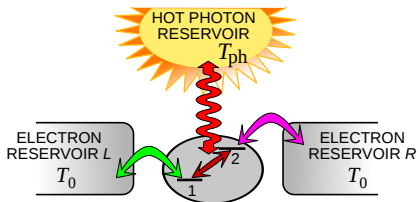
Theory (weak-coupling or linear-response)

Sánchez & Büttiker (2011)

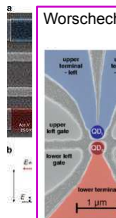
Entin-Wohlmann et al (2011-2015)

Strasberg-Schaller-Brandes-Esposito (2013)

HAMILTONIAN

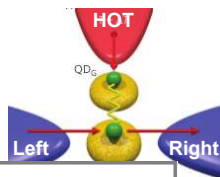


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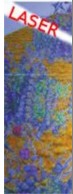


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Experiment
Gerster et al.



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

Reservoir α : $H_{\alpha} = \sum_k E_{\alpha k} \hat{c}_{\alpha k}^{\dagger} \hat{c}_{\alpha k} \quad \leftarrow \text{non-interacting}$

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

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

HAMILTONIAN NOT ENOUGH!!

(15)

(13)

NEED TO DEFINE IRREVERSIBILITY

CLASSICAL: Boltzmann postulated

loss of ALL microscopic info \implies THERMODYNAMICS

♣ Example: Fast relaxation to local thermal state

\implies Boltzmann's PROOF of 2nd law

♣ Counter-example: *Maxwell's demon*



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QUANTUM: Assume *no Maxwell demons* in reservoirs

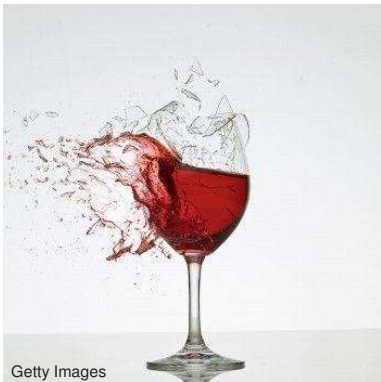
- Quantum system: all info available
- Reservoirs: microscopic info = LOST

\implies system-reservoir correlations/entanglement = LOST

\implies Entropy change $\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{res}}$ (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:

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

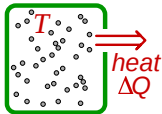
$$S_{\text{bad}} = \ln [\text{N}^\circ \text{ of "bad" states}]$$

A fluctuation theorem:

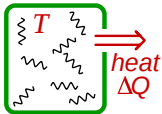
$$P_{\text{bad} \rightarrow \text{good}} = P_{\text{good} \rightarrow \text{bad}} \times \exp \left[- \Delta S_{\text{good} \rightarrow \text{bad}} \right]$$

FLUCTUATION THEOREMS & 2nd LAW

electrons

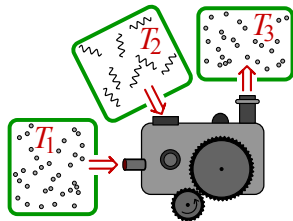


photons/phonons



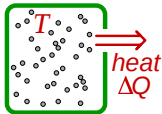
Any large reservoir
at thermal equilibrium

$$\Delta S = \frac{\Delta Q}{k_B T}$$

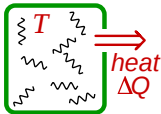


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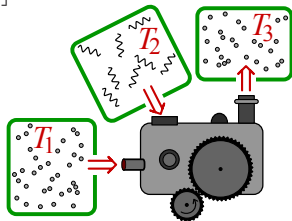
$$\Delta S = \frac{\Delta Q}{k_B T}$$

Fluctuation theorems:

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

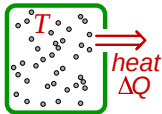
$$\overline{P(-\Delta S)} = P(\Delta S) \exp[-\Delta S]$$

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

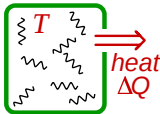


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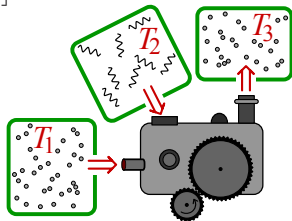
$$\overline{P(-\Delta S)} = P(\Delta S) \exp[-\Delta S]$$

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

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

- Other relations: Jarzynski (1997), etc

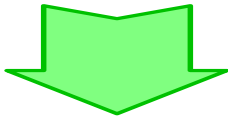
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STOCHASTIC THERMODYNAMICS

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 $\langle E_{\text{coupling}} \rangle$

REAL-TIME TRANSPORT THEORY

quantum + non-markov + interactions + far from equilibrium

Schoeller-Schön (1994)

Keldysh in system's many-body basis

exactly diagonalize H_{sys} including interactions

with NON-INTERACTING reservoirs in free-particle basis

PRICE TO PAY: system-reservoir interactions \implies NON-TRIVIAL

♣ Assumption: initial state is product state

Example Hamiltonian =

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

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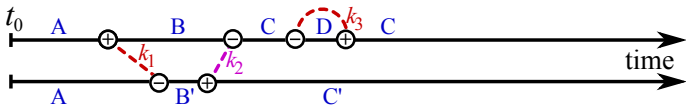
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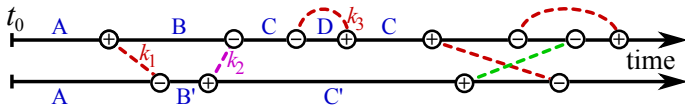
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ENERGY CONSERVATION

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

Having defined:

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



ENERGY CONSERVATION

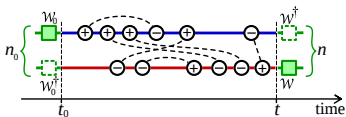
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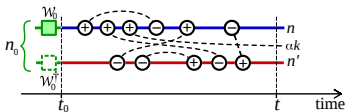
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TECHNICAL DETAILS:

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 \Rightarrow FLUCTUATION THEOREMS

Assume no Maxwell demon

(no microscopic knowledge of reservoirs)

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

◇ Reservoir α ; $\Delta S_{\alpha} = \Delta Q_{\alpha}/T_{\alpha}$ (Clausius)



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◇ System = non-equilib \Rightarrow von Neumann

Initial system state \Rightarrow its diagonal basis

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

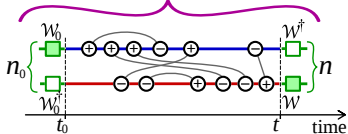
& *final* (reduced) system state \Rightarrow its diagonal basis \leftarrow diagonal $\hat{\mathbf{p}}^{(\text{final})}$

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

TIME REVERSING TRAJECTORIES

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

Ingredient ONE: $n_0 \left\{ \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \right\} n \times e^{-\Delta S_{\text{res}}}(\text{---}) = \bar{n}_0 \left\{ \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \right\} \bar{n}$

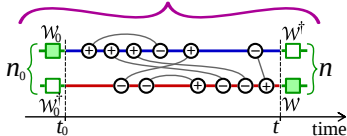


\bar{n} is time-reverse of n
[Messiah textbook]

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

algebra

similar \Rightarrow
stochastic
thermodyn

FLUCTUATION THEOREMS

$$\langle \exp[-\Delta S] \rangle = 1 \Rightarrow$$

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

⇒ Fluctuation theorems ⇒ no violation of 2nd LAW



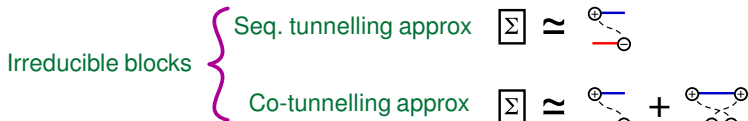
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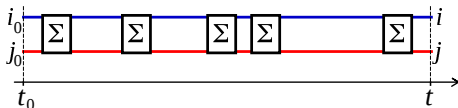
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WORKS FOR STANDARD APPROXIMATION:



& sum to all orders



Non-factorizable initial state

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

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

$$P(\Delta S_2) \equiv \int d(\Delta S_1) Q(\Delta S_2 - \Delta S_1) P(\Delta S_1)$$



$$\langle \exp [- \Delta S_{1 \rightarrow 2}] \rangle = 1 \quad \text{with average being over } Q(\Delta S_{1 \rightarrow 2})$$

$$\Rightarrow \text{2nd LAW} \quad \langle \Delta S_{1 \rightarrow 2} \rangle \geq 0$$

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

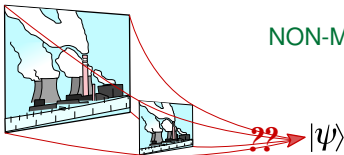
\Rightarrow protocol with multiple identical set-ups

CONCLUSIONS

NON-MARKOVIAN TRAJECTORIES

from all-orders PERTURBATION THEORY

perturbation = sys-reservoir coupling

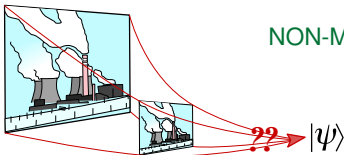


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♣ get FLUCTUATION THEOREMS for *arbitrary* quantum machine

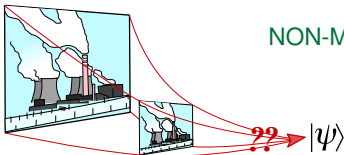
↑ ↑
stochastic thermodyn, 2ND LAW, etc

↑ ↑
strong-coupling, interacting, t-dependent, etc

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New stuff – R.W. arXiv:1611.00670

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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

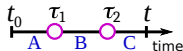
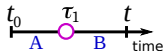
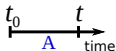
$$U(t; t_0) = \hat{\mathcal{T}} \exp \left[-i \int_{t_0}^t d\tau (\hat{H}_{\text{sys}}(\tau) + \hat{H}_{\text{res}} + \hat{V}(\tau)) \right]$$

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

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

$$\text{with } \hat{U}(\tau; t_0) = \hat{\mathcal{T}} \exp \left[-i \int_{t_0}^{\tau} d\tau' (\hat{H}_{\text{sys}} + \hat{H}_{\text{res}}) \right]$$

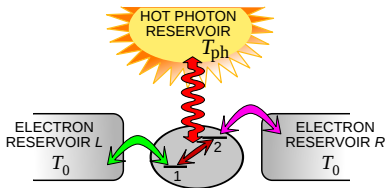
$$= 1 - i \int_{t_0}^t d\tau_1 \hat{V}(\tau_1) - \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \hat{V}(\tau_2) \hat{V}(\tau_1) + \dots$$



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

$$\implies \text{Entropy change } \Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{res}}$$

[drop correlations]



WANT same thing with **QUANTUM** (superpositions/entanglement)
and **STRONG COUPLING** (non-Markovian)

Change of system entropy

Standard thermodynamics :

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

with Shannon entropy

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

Classical “Stochastic thermodynamics”:

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

Seifert (2005)

$$\Delta S_{\text{sys}}^{i_0 \rightarrow i} = - [\ln p_i(t) - \ln p_{i_0}(t_0)]$$

which means $\exp[-\Delta S_{\text{sys}}^{i_0 \rightarrow i}] = \frac{p_i(t)}{p_{i_0}(t_0)}$

← 2nd ingredient
for fluct. theorem



ENTROPY CHANGE IN QUANTUM SYSTEM

$$\Delta S_{\text{sys}} = S_{\text{sys}}(t) - S_{\text{sys}}(t_0) \quad \text{with von Neumann}$$
$$S_{\text{sys}}(\tau) = -\text{Tr} \left[\hat{\rho}_{\text{sys}}(\tau) \ln \left(\hat{\rho}_{\text{sys}}(\tau) \right) \right]$$

ΔS_{sys} for initial/final *QUANTUM* state

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

- *Initial* system density-matrix

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

- *Final* (reduced) system density-matrix

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

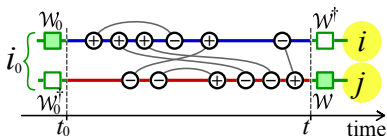
Take double trajectories as going from one *diag. basis* to the other

$$\Delta S_{\text{sys}}^{i_0 \rightarrow i} = \ln p_{i_0}^{(\text{initial})} - \ln p_i^{(\text{final})}$$



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*

