







Quantum Thermodynamics

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Introduction

Heat engine in the 19th century:



Heat engine in the 21th century:



<u>Outline</u>

- 1) Phenomenological thermodynamics
- 2) Stochastic Thermodynamics
- 3) A Hamiltonian formulation
- 4) Born-Markov-Secular Quantum Master Equation (QME)
- 5) Landau-Zener QME
- 6) Repeated interactions
- 7) Strong coupling
- 8) Conclusions

1) Phenomenological Nonequilibrium Thermodynamics



Zeroth law:

System dynamics with an equilibrium

1st law:

$$\dot{\Sigma} = d_t S - \frac{\dot{Q}}{T} \ge 0$$

 $d_t E = \dot{W} + \dot{Q}$

 $d_t S \approx \frac{Q}{T}$

Slow transformation

2nd law:

Entropy production (dissipation)

2) Stochastic Thermodynamics

Esposito and Van den Broeck, Phys. Rev. E **82**, 011143 (2010) Esposito, Phys. Rev. E **85**, 041125 (2012)

Dynamics

Markovian master equation:

$$d_{t}p_{i} = \sum_{j} W_{ij}p_{j} = \sum_{j} \left(W_{ij}p_{j} - W_{ji}p_{i} \right)$$

$$W_{ij} = \sum_{\nu} W_{ij}^{(\nu)} \cdot \cdot \cdot \cdot$$

$$W_{ij} = \sum_{\nu} W_{ij}^{(\nu)}p_{j}(\epsilon_{i} - \epsilon_{j})$$

$$I_{M}^{(\nu)} = \sum_{i,j} W_{ij}^{(\nu)}p_{j}(n_{i} - n_{j})$$

$$Different reservoirs T^{(\nu)} \mu^{(\nu)}$$

Local detailed balance:

$$\frac{W_{ij}^{(\nu)}}{W_{ji}^{(\nu)}} = \exp\left(-\frac{(\epsilon_i - \epsilon_j) - \mu^{(\nu)}(n_i - n_j)}{k_b T^{(\nu)}}\right)$$

Driving

 $n_i \epsilon_i$

Average Thermodynamics



Fluctuating Thermodynamics



Detailed FT for entropy production

$$\ln \frac{P(\sigma)}{\tilde{P}(-\sigma)} = \sigma$$

Involution if $\sigma [\Gamma | \lambda] = -\tilde{\sigma} [\bar{\Gamma} | \lambda]$ Seifert, PRL **95** 040602 (2005)



Most general formulation: Rao & Esposito, NJP 20, 023007 (2018)

Isothermal example: driven junction

Bulnes Cuetara, Esposito, Imparato, PRE 89, 052119 (2014)



3) Hamiltonian formulation



 $H_{\text{tot}}(t) = H_X(t) + H_R + H_{XR}(t)$ Assumption 1: $\rho_{XR}(0) = \rho_X(0)\rho_\beta^R \qquad \rho_\beta^R \equiv \frac{e^{-\beta H_R}}{Z_R}$

$$E_X(t) \equiv \operatorname{tr}_{XR}\{[H_X(t) + H_{XR}(t)]\rho_{XR}(t)\}$$

1st law:
$$d_t E_X(t) = \dot{W}(t) + \dot{Q}(t)$$

 $\dot{W}(t) = d_t E_{XY}(t)$
 $\dot{Q}(t) \equiv -\text{tr}_R \{H_R d_t \rho_R(t)\}$

2nd law: $\Sigma(t) \equiv \Delta S_X(t) - \beta Q(t) = D[\rho_{XR}(t)||\rho_X(t)\rho_\beta^R]$ = $D[\rho_R(t)||\rho_\beta^R] + I_{X:R}(t) \ge 0$

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[Esposito, Lindenberg, & Van den Broeck, NJP 12, 013013 (2010)]

4) Born-Markov-Secular QME

$$H_{\text{tot}}(t) = H_X(t) + H_R + \sum_k A_k \otimes B_k$$

Closed description for the dynamics of the system

$$d_{t}\rho_{X}(t) = -i[H_{X}(t), \rho_{X}(t)] + \mathcal{L}_{\beta}(t)\rho_{X}(t) \equiv \mathcal{L}_{X}(t)\rho_{X}(t),$$
$$\mathcal{L}_{\beta}(t)\rho(t) = \sum_{\omega} \sum_{k,\ell} \gamma_{k\ell}(\omega) \left(A_{\ell}(\omega)\rho(t)A_{k}^{\dagger}(\omega) - \frac{1}{2}\{A_{k}^{\dagger}(\omega)A_{\ell}(\omega),\rho(t)\}\right)$$
$$A_{k}(\omega) \equiv \sum_{\epsilon-\epsilon'=\omega} \prod_{\epsilon} A_{k}\prod_{\epsilon'} \gamma_{k\ell}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \operatorname{tr}_{R}\{B_{k}(t)B_{\ell}(0)\rho_{\beta}^{R}\}$$

Local detailed balance $\gamma_{k\ell}(-\omega) = e^{-\beta\omega}\gamma_{\ell k}(\omega)$ $\mathcal{L}_{\beta}(t)\rho_{\beta}^{X}(t) = 0, \quad \rho_{\beta}^{X}(t) = \frac{e^{-\beta H_{X}(t)}}{Z_{X}(t)}$

Validity:
$$\tau_{th} = \hbar\beta < \tau_{rel} \sim \gamma < \tau_H = \hbar d$$

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[Redfield 65, Agarwal 69, Lindblad 76, Gorini-Frigerio-Verri-Kossakowki-Sudarshan 78]

Closed description for the **thermodynamics** of the system Energy: $E_X(t) = -\text{tr}_X \{ H_X(t) \rho_X(t) \}$ Entropy: $S_X(t) = -\operatorname{tr}_X \{\rho_X(t) \ln \rho_X(t)\}$ 1st law: $d_t E_X(t) = \dot{W}(t) + \dot{Q}(t)$ $\dot{W}(t) = \operatorname{tr}_{X} \left\{ \rho_{X}(t) d_{t} H_{X}(t) \right\}$ $\dot{Q}(t) = \operatorname{tr}_X \left\{ H_X(t) d_t \rho_X(t) \right\} = \operatorname{tr}_X \left\{ H_X(t) \mathcal{L}_X(t) \rho_X(t) \right\}$ 2nd law: $\dot{\Sigma}(t) = d_t S_X(t) - \beta \dot{Q}(t)$ $= -\operatorname{tr}\{[\mathcal{L}_X(t)\rho_X(t)][\ln \rho_X(t) - \ln \rho_\beta^X(t)]\} \ge 0$ [Spohn 77, Spohn-Lebowitz 78, Alicki 79] Reviews: [Kosloff, Entropy 15, 2100 (2013)] [Gelbwaser &co, Adv.At.Mol.Opt.Phys. 64, 329 (2015)] Non-degenerate states: Stochastic thermodynamics With Degenerate states: [Bulnes-Cuetara, Esposito & Schaller, Entropy 18, 447 (2016)] fluctuations Fast periodic driving (Floquet): [Bulnes-Cuetara, Engel & Esposito, NJP 18, 447 (2016)]



[Esposito, Lindenberg, & Van den Broeck, NJP 12, 013013 (2010)]



[Pucci, Esposito & Peliti, J. Stat. Mech. (2013) P04005]

5) A Landau-Zener approach



[Barra & Esposito, PRE 93, 062118 (2016)]

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Effective dynamics



Thermodynamics



[Barra & Esposito, PRE 93, 062118 (2016)]

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Work fluctuations

Jarzynski and Crooks fluctuation relation

m

System initially at equilibrium

$$\frac{P(w^{\mathrm{m}})}{\tilde{P}(-w^{\mathrm{m}})} = \exp\left\{\beta(w^{\mathrm{m}} - \Delta\Omega^{\mathrm{eq}})\right\}$$



[Barra & Esposito, PRE 93, 062118 (2016)]

6) Repeated interactions





[Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)] ¹⁹ [Deffner & Jarzynski, PRX **3**, 041003 (2013)]

"Classical" vs "Quantum" Resource

$$-W \le -\Delta F_U = F_U(0) - F_U(\tau)$$



Assume a quantum state $ho_{
m QM}$ minimizing $F_U(au)$

Build the corresponding classical state
$$\rho_{cl} = \sum_{n} \langle n | \rho_{QM} | n \rangle \langle n |$$

 $E(\rho_{QM}) = E(\rho_{cl}) \qquad S(\rho_{QM}) < S(\rho_{cl}) \longrightarrow F(\rho_{cl}) < F(\rho_{QM})$

Classical resource wins!

[Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)]

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Poisson interaction QME



Closed description for the dynamics of the system

Effect of a kick: $U = e^{-iV_{SU}}$ $\mathcal{J}_S \rho_S(t) \equiv \operatorname{tr}_U \{ U \rho_S(t) \otimes \rho_U U^{\dagger} \}$ $\mathcal{J}_U \rho_U \equiv \operatorname{tr}_S \{ U \rho_S(t) \otimes \rho_U U^{\dagger} \}$

$$d_t \rho_S(t) = -i[H_S(t), \rho_S(t)] + \mathcal{L}_\beta \rho_S(t) + \mathcal{L}_{\text{new}} \rho_S(t)$$

$$\mathcal{L}_{\text{new}}\rho_S(t) \equiv \gamma(\mathcal{J}_S - 1)\rho_S(t)$$

Closed description for the thermodynamics of the system

 1^{st} la

$$\begin{aligned} \text{aw} \qquad d_t E_S(t) &= \dot{W}_S(t) + \dot{W}_{\text{sw}}(t) + \dot{Q}(t) - d_t E_U(t) \\ \dot{W}_S &= \text{tr}_S\{\rho_S(t)d_t H_S(t)\} \\ \dot{W}_{\text{sw}} &= \gamma \text{tr}_{SU}\{[H_S(t) + H_U][U\rho_S(t)\rho_U U^{\dagger} - \rho_S(t)\rho_U]\} \\ &= \gamma \text{tr}_S\{H_S(t)(\mathcal{J}_S - 1)\rho_S(t)\} + \gamma \text{tr}_U\{H_U(\mathcal{J}_U - 1)\rho_U\} \\ \dot{Q}(t) &= \text{tr}_S\{H_S(t)\mathcal{L}_\beta\rho_S(t)\} \\ d_t E_U(t) &= \gamma \text{tr}_U\{H_U(\mathcal{J}_U - 1)\rho_U\} \end{aligned}$$

 $\dot{\Sigma}_{S}(t) = d_{t}S_{S}(t) + d_{t}S_{U}(t) - \beta \dot{Q} > 0$

 $\neq -\mathrm{tr}\{[\mathcal{L}_0\rho_S(t)][\ln\rho_S(t) - \ln\rho_\beta^S(t)]\} - \mathrm{tr}\{[\mathcal{L}_{\mathrm{new}}\rho_S(t)][\ln\rho_S(t) - \ln\bar{\rho}_{\mathrm{new}}]\}$

thermodynamics cannot always be deduced from dynamics alone !!!

Repeated interaction QME



Sequential interactions:
$$H_{SU}(t) = \sum_{n} \Theta(t - n\delta t) \Theta(n\delta t + \delta t - t) \frac{\tilde{V}}{\sqrt{\delta t}}$$

Frequent Poisson interactions *E*

$$H_{SU}(t) = \sum_{n} \delta(t - t_n) \sqrt{\epsilon} \tilde{V}$$

$$w(\tau) = \gamma e^{-\gamma \tau} \qquad 1/\gamma = \epsilon \to 0$$

Closed description for the **dynamics** of the system $\tilde{V} = \sum_{k} A_k \otimes B_k$

$$d_t \rho_S(t) = -i[H_S(t), \rho_S(t)] + \sum_{k,l} \langle B_l B_k \rangle_U \left(A_k \rho_S(t) A_l - \frac{1}{2} \{ A_l A_k, \rho_S(t) \} \right)$$
$$= \mathcal{L}_S \rho_S(t)$$

Closed description for the thermodynamics of the system

$$\begin{aligned} \mathbf{1}^{\text{st}} & \text{law} \qquad d_t E_S(t) = \dot{W}_{\text{sw}}(t) + d_t E_U(t) & \text{heat} \\ & \downarrow \\ \mathbf{2}^{\text{nd}} & \text{law} \qquad \dot{\Sigma}_S(t) = d_t I_{S:U}(t) = d_t S_S(t) + \beta' d_t E_U(t) - \gamma D(\mathcal{J}_U \rho_U \| \rho_U) \ge 0 \end{aligned}$$

Is it like a normal reservoir? No $\mathcal{L}_S e^{-\beta H_U} \neq 0$ due to switching work

[Barra, Scientific Reports 5, 14873 (2015)] [Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)]

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Units entropy changes

Approach 1:
$$ho_U(t) = \mathcal{J}_U
ho_U$$

$$d_t S_U(t) = \gamma(-\operatorname{tr}_U\{(\mathcal{J}_U \rho_U) \ln(\mathcal{J}_U \rho_U)\} + \operatorname{tr}_U\{\rho_U \ln \rho_U\})$$

Approach 2:

$$\bar{\rho}_U(t) = \frac{n_t}{N} \mathcal{J}_U \rho_U + \frac{N - n_t}{N} \rho_U$$

$$d_t \bar{S}_U(t) = -d_t \operatorname{tr}_U \{ \bar{\rho}_U(t) \ln \bar{\rho}_U(t) \} = -\gamma \operatorname{tr}_U \{ [(\mathcal{J}_U - 1)\rho_U] \ln \rho_U \}$$

Different by $d_t \bar{S}_U(t) - d_t S_U(t) = \gamma D(\mathcal{J}_U \rho_U \| \rho_U)$ "mixing" contribution

Thermal units
$$\rho_U = \rho_{\beta'}^U \begin{cases} d_t S_U(t) = \beta' d_t E_U(t) - \gamma D(\mathcal{J}_U \rho_{\beta'}^U \| \rho_{\beta'}^U) \\ d_t \bar{S}_U(t) = \beta' d_t \bar{E}_U(t) & \text{ideal reservoir} \end{cases}$$

7) <u>Strong coupling</u>

Strong coupling using Nonequilibrium Green's functions (not for fluctuations!): [Esposito, Ochoa & Galperin, PRL **114**, 080602 (2015)] [Esposito, Ochoa & Galperin, PRB **92**, 235440 (2015)] [Haughian, Esposito & Schmidt, PRB **97**, 085435 (2018)]

Classical strong coupling using time scale separation (including fluctuations): [Strasberg & Esposito, Phys. Rev. E **95**, 062101 (2017)]

Quantum version is an open problem!!!

Only works in some cases: polaron transformation and QME (including fluctuations): [Krause, Brandes, Esposito & Schaller, JCP **142**, 134106 (2015)] [Schaller, Krause, Brandes & Esposito, NJP **15**, 033032 (2013)]

8) <u>Conclusions</u>

Stochastic thermodynamics is the canonical formulation of nonequilibrium thermodynamics

Exact Hamiltonian identity: Entropy production as system-reservoir correlations

For practical use and EP rate > 0, we use it to build thermodynamics on top of system's kinetics

- Born-Markov-Secular QME: (with or without Floquet)	Weak coupling, dense reservoir
- Landau-Zener QME:	Weak coupling, sparse reservoir
- Repeated interactions:	Importance of the switching work Thermo can't always be deduced from dynamics Fluctuations not explored yet

Strong coupling, quite clear now for classical systems, but not yet for quantum systems!

