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Quantum Thermodynamics
A nonequilibrium Green's function approach

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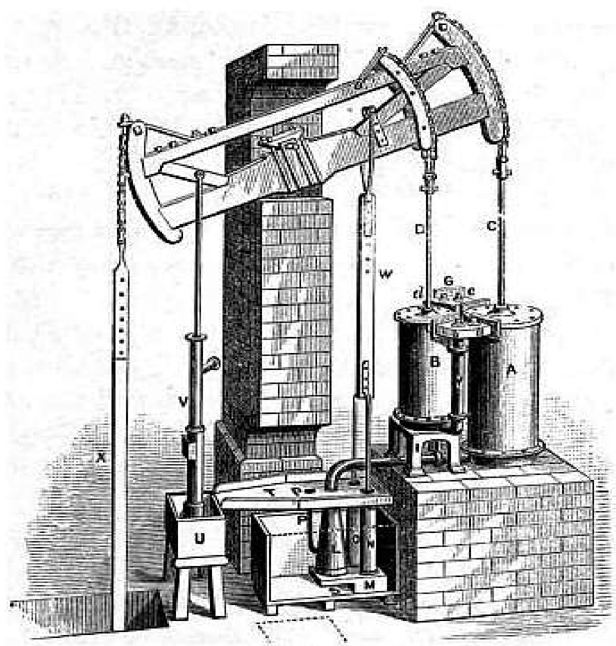
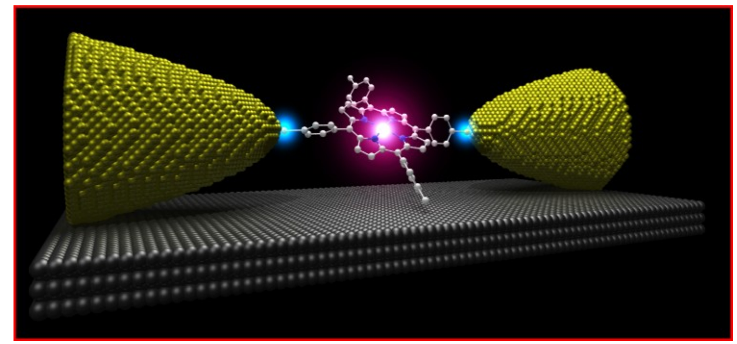
Mallorca, April 24, 2015

Introduction

Thermodynamics in the 19th century:

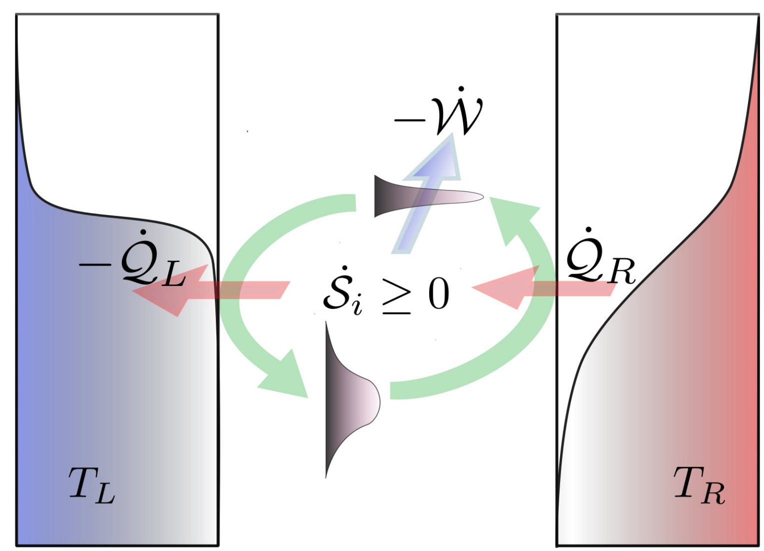


Thermodynamics in the 21th century:



http://www.scm.com/

$$\frac{d}{dt}\mathcal{E} = \sum_\nu \dot{\mathcal{Q}}_\nu + \dot{\mathcal{W}}$$



$$\frac{d}{dt}\mathcal{S} = \sum_\nu \frac{\dot{\mathcal{Q}}_\nu}{T_\nu} + \dot{\mathcal{S}}_i$$

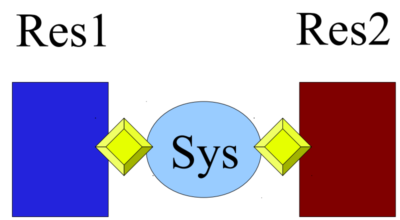
Outline

- Nonequilibrium Thermodynamics: Phenomenology
- Stochastic thermodynamics (weak coupling)
- Strong coupling

    - Exact identity

    - NEGF

Nonequilibrium Thermodynamics: Phenomenology



- Zeroth law: Existence of equilibrium with a well defined temperature
- First law: $$d_t U(t) = \dot{W}(t) + \sum_\nu \dot{Q}_\nu(t)$$
- Second law: $$\dot{S}_i(t) = d_t S(t) - \sum_\nu \beta_\nu \dot{Q}_\nu(t) \geq 0$$
- Third law: $$S^{eq} \to 0 \quad d_t S^{eq} \to 0 \quad \text{when} \quad T \to 0$$

Reversible transformation:
(slow trsf. in contact
with one reservoir)

$$\dot{S}_i(t) = 0 \quad , \quad T d_t S^{eq}(t) = \dot{Q}^{eq}(t)$$

Fundamental relation of equilibrium thermo

$$T d_t S^{eq}(t) = d_t E^{eq}(t) - \dot{W}^{eq}(t)$$

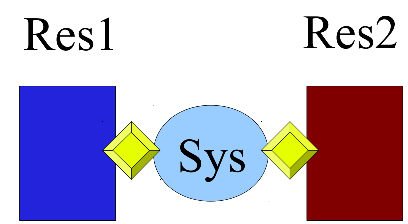
Stochastic Thermodynamics (weak coupling)

Esposito, *Stochastic thermodynamics under coarse-graining*, PRE **85**, 041125 (2012)

Van den Broeck and Esposito, *Ensemble and Trajectory Thermodynamics: A Brief Introduction*, Physica A **418**, 6 (2015)

Bulnes Cuetara, Engel and Esposito, Stochastic thermodynamics of rapidly driven systems, accepted in NJP arXiv:1412.0283

Microscopically derived
Markovian Quantum Master Equation



$$\dot{p}_i = \sum_j W_{ij} p_j = \sum_j \left(W_{ij} p_j - W_{ji} p_i \right)$$

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

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

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

Energy, Particle number, Shannon entropy

$$E = \sum_i \epsilon_i p_i \quad , \quad N = \sum_i n_i p_i \quad , \quad S = \sum_i [-k_b \ln p_i] p_i$$

Matter conservation

$$d_t N = \sum_\nu I_N^{(\nu)}$$

Energy and Matter currents

$$I_E^{(\nu)} = \sum_{i,j} W_{ij}^{(\nu)} p_j (\epsilon_i - \epsilon_j)$$

$$I_M^{(\nu)} = \sum_{i,j} W_{ij}^{(\nu)} p_j (n_i - n_j)$$

1st law: (energy conservation)

- $$d_t E = \dot{\mathcal{W}} + \dot{\mathcal{W}}_c + \sum_\nu \dot{\mathcal{Q}}^{(\nu)}$$

Heat $\dot{\mathcal{Q}}^{(\nu)} = I_E^{(\nu)} - \mu^{(\nu)} I_M^{(\nu)}$

Mechanical work $\dot{\mathcal{W}} = \sum_i p_i d_t \epsilon_i$

Chemical work $\dot{\mathcal{W}}_c = \sum_\nu \mu^{(\nu)} I_M^{(\nu)}$

2nd law: (non-conservation of entropy)

- $$\dot{S}_{\mathbf{i}} = d_t S - \sum_\nu \frac{\dot{Q}_\nu}{T_\nu} \geq 0$$

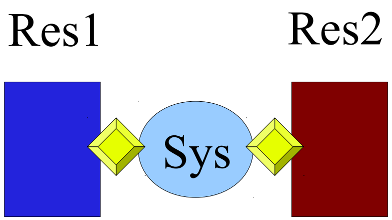
$$\dot{S}_{\mathbf{i}} = \frac{k_b}{2} \sum_{\nu,i,j} \left(W_{ij}^{(\nu)} p_j - W_{ji}^{(\nu)} p_i\right) \ln \frac{W_{ij}^{(\nu)} p_j}{W_{ji}^{(\nu)} p_i} \geq 0$$

- 0th law: $\dot{S}_{\mathbf{i}} = 0$ iff $W_{ij}^{(\nu)} p_j = W_{ji}^{(\nu)} p_i$ (detailed balance = equilibrium)

$$p_i^{eq} = \exp\{-\frac{\epsilon_i - \mu n_i - \Omega^{eq}}{k_b T}\}$$

- 3rd law: $T \to 0$ $S^{eq} \to 0$

An exact identity (strong coupling)



Entropy production as correlation between system and reservoir

Esposito, Lindenberg, Van Den Broeck, New J. Phys. **12**, 013013 (2010)

$$H(t) = H_s(t) + \sum_\nu H_\nu + V(t)$$

Single assumption:
$$\begin{cases} \rho(0) = \rho_s(0) \prod_\nu \rho_\nu^{\text{eq}} \\ \rho_\nu^{\text{eq}} = \exp\big(-\beta_\nu H_\nu\big)/Z_\nu \end{cases}$$

1st law:

$$\Delta U(t) = W(t) + \sum_\nu Q_\nu(t)$$

Energy: $U(t) = \langle \big(H_s(t) + V(t)\big) \rangle_t$

Entropy: $S(t) = -\text{Tr}_s \rho_s(t) \ln \rho_s(t)$

Heat:
$$Q_r(t) = \langle H_r \rangle_0 - \langle H_r \rangle_t = \int_0^t d\tau \text{Tr}\big(H_s(t) + V(t)\big)\dot{\rho}(t)$$

Work:
$$W = \langle H(t) \rangle_t - \langle H(0) \rangle_0 = \int_0^t d\tau \text{Tr}\big(\dot{H}_s(t) + \dot{V}(t)\big)\rho(t)$$

2nd law:

$$\Delta_i S(t) = \Delta S(t) - \sum_\nu \beta_\nu Q_\nu(t) = D[\rho(t)||\rho_s(t) \prod_\nu \rho_\nu^{\text{eq}}] \geq 0$$

$$D[\rho||\rho'] \equiv \text{Tr}\rho \ln \rho - \text{Tr}\rho \ln \rho'$$

Limitations:

$\frac{d}{dt}\Delta_i S$ can be negative

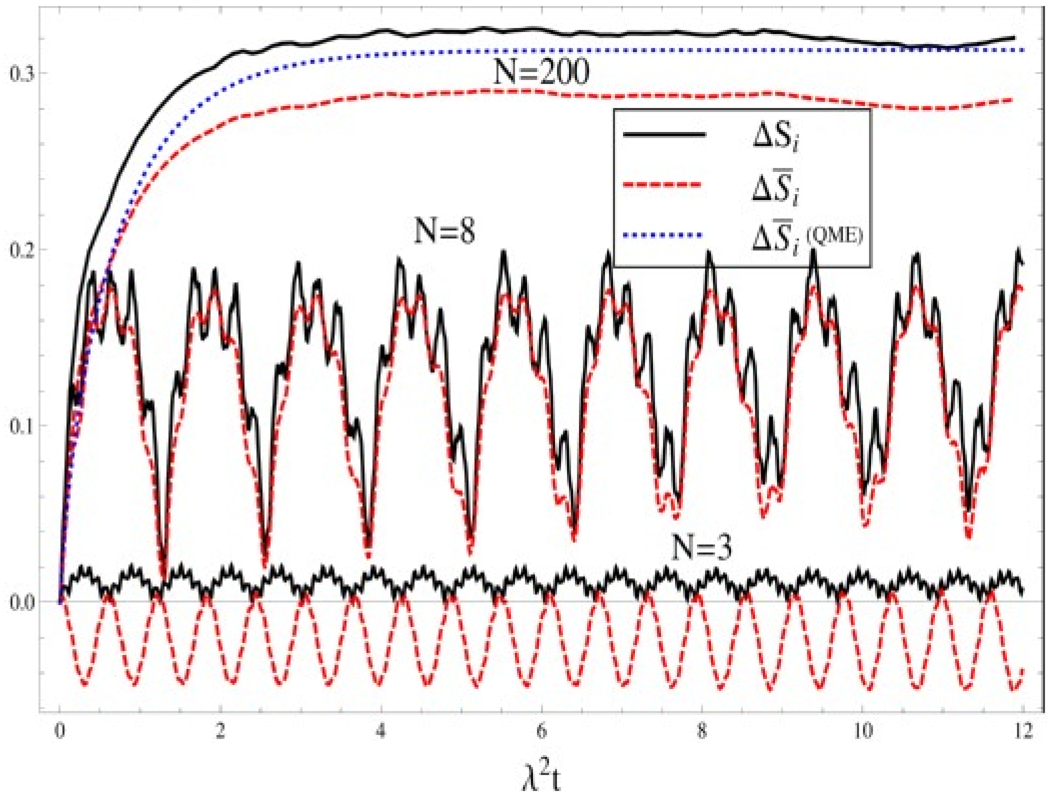
no zeroth law

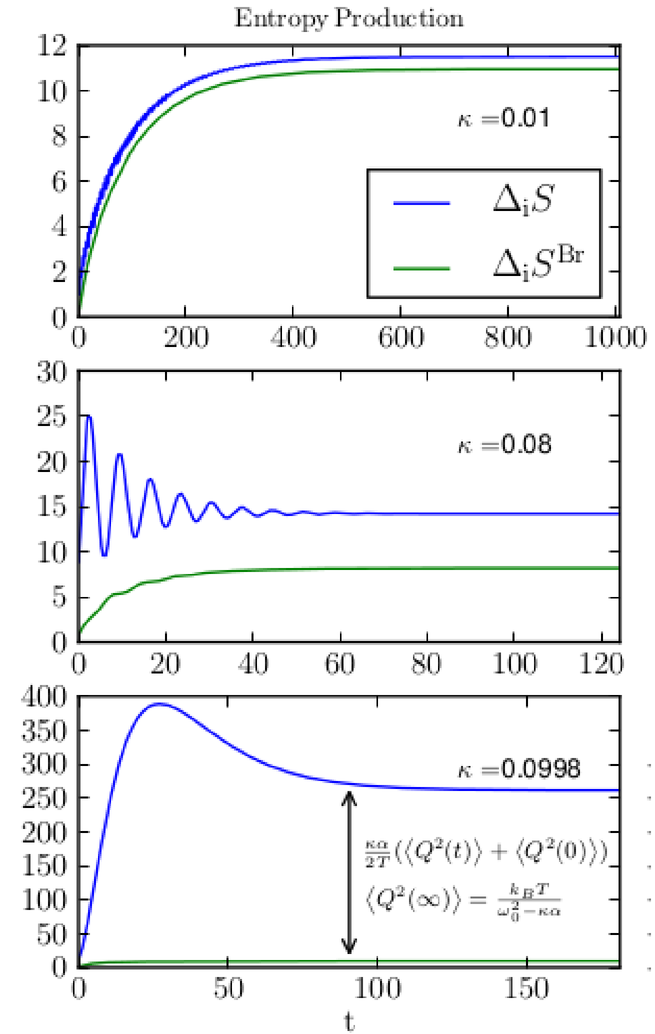
no clear notion of reversible trsf.

See also Reeb & Wolf, New J. Phys. **16**, 103011 (2014)

Entropy Production in Quantum Brownian Motion
Pucci, Esposito and Peliti,
J. Stat. Mech. (2013) P04005

$$H = \frac{\Delta}{2}\sigma_z + H_r + \lambda\sigma_x R$$

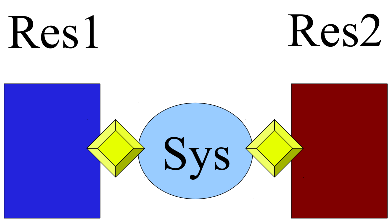


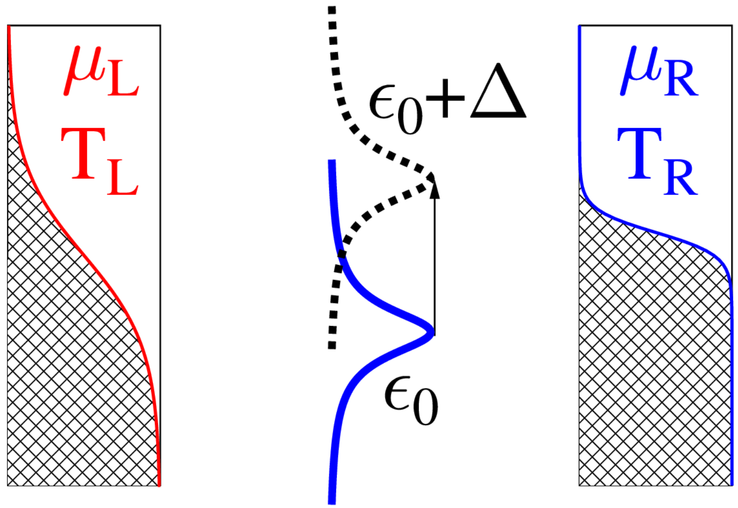


$$\frac{d}{dt}\Delta_i S < 0$$ occurs at finite N as well as at infinite N!

Quantum thermodynamics with NEGF (strong coupling)

M. Esposito, M. A. Ochoa and M. Galperin,
Quantum thermodynamics: A nonequilibrium Green's function approach
Phys. Rev. Lett. **114**, 080602 (2015).





$$\hat{H}(t) = \hat{H}_S(t) + \sum_\nu \hat{H}_\nu + \sum_\nu \hat{V}_\nu(t)$$

$$\hat{H}_S(t) = \varepsilon(t)\hat{d}^\dagger \hat{d} \qquad \hat{H}_\nu = \sum_{k\in\nu} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k \qquad \hat{V}_\nu(t) = \sum_{k\in\nu}\left(V_k^\nu(t)\hat{d}^\dagger \hat{c}_k + \text{H.c.}\right)$$

Contour Green's functions:

$$G(\tau_1,\tau_2) = -i\left\langle T_c\,\hat{d}(\tau_1)\,\hat{d}^\dagger(\tau_2)\right\rangle \longrightarrow \text{Gradient expansion}$$

Equation of motion for the population of the level $\phi(t,E)$:

$$\{E-\varepsilon(t)-\Lambda(t,E); A(t,E)\,\phi(t,E)\} + \{\mathrm{Re}\,G^r(t,E); \Gamma(t,E)\,\phi(t,E)\} = \mathcal{C}(t,E)$$

$$\{f_1; f_2\} \equiv \partial_E f_1 \partial_t f_2 - \partial_t f_1 \partial_E f_2$$

Retarded Green's functions: $G^r(t,E) = [E-\varepsilon(t)-\Sigma^r(t,E)]^{-1}$

Self-energy:

$$\Sigma^r(t,E) = \Lambda(t,E) - i\Gamma(t,E)/2$$

Lamb shift Broadening

$$\Sigma^r(t_1,t_2) = -i \sum_{\nu=L,R} \sum_{k\in\nu} V_k^\nu(t_1)\,\overset{*}{V}{}_k^\nu(t_2)\,\theta(t_1-t_2)e^{-i\varepsilon_k(t_1-t_2)}$$

Spectral function: $A(t,E) = -2\,\mathrm{Im}\,G^r(t,E) = \dfrac{\Gamma(t,E)}{(E-\varepsilon(t)-\Lambda(t,E))^2 + (\Gamma(t,E)/2)^2}$

Energy resolved particle current:

$$\mathcal{C}_\nu(t,E) = \mathcal{C}_\nu^+(t,E) - \mathcal{C}_\nu^-(t,E)$$

$$\begin{cases} \mathcal{C}_\nu^+(t,E) = A(t,E)\Gamma_\nu(t,E) f_\nu(E)\,[1-\phi(t,E)] \\ \mathcal{C}_\nu^-(t,E) = A(t,E)\Gamma_\nu(t,E)\phi(t,E)\,[1-f_\nu(E)] \end{cases}$$

Renormalized spectral function: $\mathcal{A}(t,E) = A(1-\partial_E \Lambda) + \Gamma \partial_E \mathrm{Re} G^r \geq 0$

is positive and normalized

Energy resolved quantities!

$$\mathcal{N}(t) = \int \frac{dE}{2\pi} \mathcal{A}(t,E)\, \phi(t,E)$$

$$\mathcal{E}(t) = \int \frac{dE}{2\pi} \mathcal{A}(t,E)\, E\, \phi(t,E)$$

$$\mathcal{S}(t) = \int \frac{dE}{2\pi} \mathcal{A}(t,E)\, \sigma(t,E)$$

where $\sigma(t,E) = -\phi(t,E) \ln \phi(t,E) - [1-\phi(t,E)] \ln[1-\phi(t,E)]$

Introduced in the context of the quantum Boltzmann equation by

Ivanov, Knoll, and Voskresensky, Nuclear Physics A 672, 313 (2000)

Balance equations:

$$\begin{cases} d_t\mathcal{N}(t) = \sum_\nu \mathcal{I}_\nu(t) \\ d_t\mathcal{E}(t) = \sum_\nu \dot{\mathcal{Q}}_\nu(t) + \dot{\mathcal{W}} + \dot{\mathcal{W}}_c & \text{First law} \\ d_t\mathcal{S}(t) = \dot{\mathcal{S}}_i(t) + \sum_\nu \frac{\dot{\mathcal{Q}}_\nu(t)}{T_\nu} & \text{Second law} \end{cases}$$

Heat $\dot{\mathcal{Q}}_\nu = \mathcal{J}_\nu(t) - \mu_\nu\,\mathcal{I}_\nu(t)$

Particle current $\mathcal{I}_\nu(t) = \int \frac{dE}{2\pi}\,\mathcal{C}_\nu(t,E)$

Chemical work $\dot{\mathcal{W}}_c = \sum_\nu \mu_\nu\,\mathcal{I}_\nu(t)$

Energy current $\mathcal{J}_\nu(t) = \int \frac{dE}{2\pi}\,E\,\mathcal{C}_\nu(t,E)$

Mechanical work $\dot{\mathcal{W}}(t) = \int \frac{dE}{2\pi}\Big(- A\,\phi\,\partial_t(E-\varepsilon(t)-\Lambda) - \Gamma\,\phi\,\partial_t \mathrm{Re}\,G^r\Big)$

Entropy production

$$\boxed{\dot{\mathcal{S}}_i(t) = \sum_\nu \int \frac{dE}{2\pi}\,\big(\mathcal{C}_\nu^+(t,E) - \mathcal{C}_\nu^-(t,E)\big)\ln\frac{\mathcal{C}_\nu^+(t,E)}{\mathcal{C}_\nu^-(t,E)} \geq 0}$$

Equilibrium:

$\forall\nu:\ f_\nu(E) = \phi(t,E)$

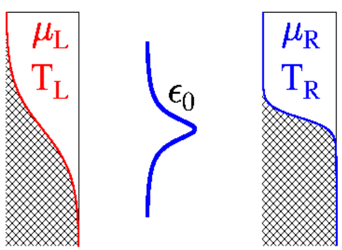
- Weak coupling limit $\xrightarrow[\Lambda \to 0]{\Gamma \to 0}$ we recover stochastic thermodynamics $A, \mathcal{A} \to 2\pi\delta(E-\varepsilon)$

- 0th law: At equilibrium $\phi(t,E) = f(E)$ the Fermi distribution at μ , T

- 3rd law: $T \to 0$ $\quad \sigma^{eq}(E) \to 0$ $\quad \mathcal{S}^{eq} \to 0$

- At nonequilibrium steady state: $\dot{\mathcal{S}}_i(t) = -\sum_\nu \frac{\dot{\mathcal{Q}}_\nu(t)}{T_\nu} \geq 0$

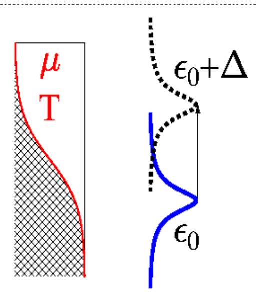
(a)

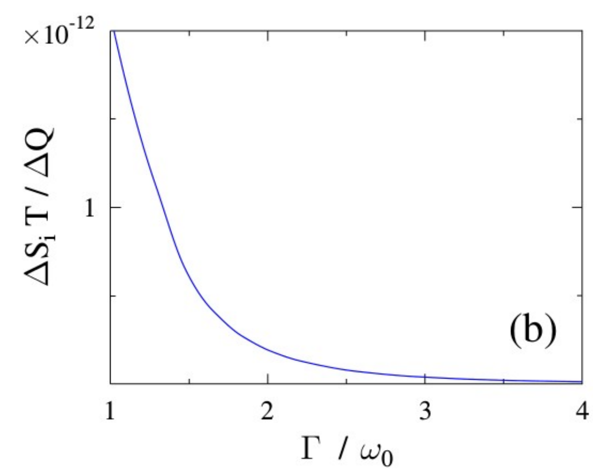


$$\dot{\mathcal{Q}}_\nu = \mathcal{J}_\nu(t) - \mu_\nu \mathcal{I}_\nu(t) \quad \begin{cases} \mathcal{I}_\nu(t) = -\mathrm{Tr}\left[\hat{N}_\nu d_t \hat{\rho}(t)\right] \\ \mathcal{J}_\nu(t) = -\mathrm{Tr}\left[\hat{H}_\nu d_t \hat{\rho}(t)\right] \end{cases}$$

- For reversible transformations: $T d_t \mathcal{S}^{eq}(t) = \dot{\mathcal{Q}}(t)$

(b)





Remark 1

$$\mathcal{C}_\nu(t,E) = C_\nu(t,E) - \{\Lambda_\nu(t,E); A(t,E)\,\phi(t,E)\} - \{\Gamma_\nu(t,E)\,\phi(t,E); \mathrm{Re}\,G^r(t,E)\}$$

$$\mathcal{A}(t,E) = A(1-\partial_E\Lambda) + \Gamma\partial_E\mathrm{Re}G^r \geq 0$$

$$N(t) = \int \frac{dE}{2\pi}\,\boxed{A(t,E)}\,\phi(t,E) \qquad N(t) = \mathrm{Tr}\big[\hat{N}_S\,\hat{\rho}(t)\big]$$

$$E(t) = \int \frac{dE}{2\pi}\,\boxed{A(t,E)}\,E\,\phi(t,E) \qquad E(t) = \mathrm{Tr}\Big[\Big(\hat{H}_S(t) + \sum_\nu \hat{V}_\nu(t)/2\Big)\hat{\rho}(t)\Big]$$

$$S(t) = \int \frac{dE}{2\pi}\,\boxed{A(t,E)}\,\sigma(t,E)$$

$$J_\nu(t) = \int \frac{dE}{2\pi}\,E\,\boxed{C_\nu(t,E)} \qquad J_\nu(t) = -\mathrm{Tr}\Big[\Big(\hat{H}_\nu + \hat{V}_\nu(t)/2\Big)d_t\hat{\rho}(t)\Big] + \frac{1}{2}\mathrm{Tr}\Big[d_t\hat{V}_\nu(t)\hat{\rho}(t)\Big]$$

$$I_\nu(t) = \int \frac{dE}{2\pi}\,\boxed{C_\nu(t,E)} \qquad I_\nu(t) = -\mathrm{Tr}\big[N_\nu d_t\hat{\rho}(t)\big]$$

$$d_t E(t) = \sum_\nu \dot{Q}_\nu(t) + \dot{W} + \dot{W}_c \qquad \begin{cases} \dot{W}(t) = \mathrm{Tr}\left[d_t \hat{H}_S(t) \hat{\rho}(t) \right] \\ \dot{Q}_\nu = J_\nu(t) - \mu_\nu \, I_\nu(t) \end{cases}$$

But no second law!

$$\dot{S}_i(t) \equiv d_t S(t) - \sum_\nu \frac{\dot{Q}_\nu(t)}{T_\nu}$$ can be negative!!!

Special case where it works: 1 level, 1 reservoir, wide band, no driving in coupling

Ludovico, Lim, Moskalets, Arrachea, Sanchez, Phys. Rev. B 89, 161306 (2014)

Remark 2

Why not using the "standard" heat definition?

$$\dot{\tilde{Q}} = \tilde{J}(t) - \mu_\nu \, \tilde{I}(t) \quad \begin{cases} \tilde{J}(t) = -\mathrm{Tr}\left[\hat{H} d_t \hat{\rho}(t)\right] \\ \tilde{I}(t) = -\mathrm{Tr}\left[\hat{N} d_t \hat{\rho}(t)\right] \end{cases}$$

Quasistatic transformation with a single reservoir (reversible transformation):

$$d_t \tilde{S}^{eq} = \frac{\dot{\tilde{Q}}^{eq}(t)}{T} = d_t \left[\int \frac{dE}{2\pi} A(t,E) \left(\sigma^{eq}(t,E) + f(E) \frac{E-\epsilon}{T} \right) \right]$$

$$\sigma^{eq}(t,E) = -f(E) \ln f(E) - [1 - f(E)] \ln[1 - f(E)]$$

When $T \to 0$ $\tilde{S}^{eq} \to \infty$ no third law!!!

Open questions

Generalization to many orbitals and to interacting systems....

Beyond gradient expansion (for faster driving)....

Fluctuations....

Experiments....

Main reference:

M. Esposito, M. A. Ochoa and M. Galperin,
Quantum thermodynamics: A nonequilibrium Green's function approach,
Phys. Rev. Lett. **114**, 080602 (2015)

Advertisement:

M. Esposito, M. A. Ochoa and M. Galperin,
Efficiency fluctuations in quantum thermoelectric devices,
Phys. Rev. B **91**, 115417 (2015)

Thank you for your attention!