Optimizing Cooling Processes
-
A Dynamic View on the Third Law

Karl Heinz Hoffmann
TU Chemnitz
Germany

The Third Law

- 1906 Nernst
  1911 Planck

$$\boxed{\lim_{T \to 0} S = 0}$$

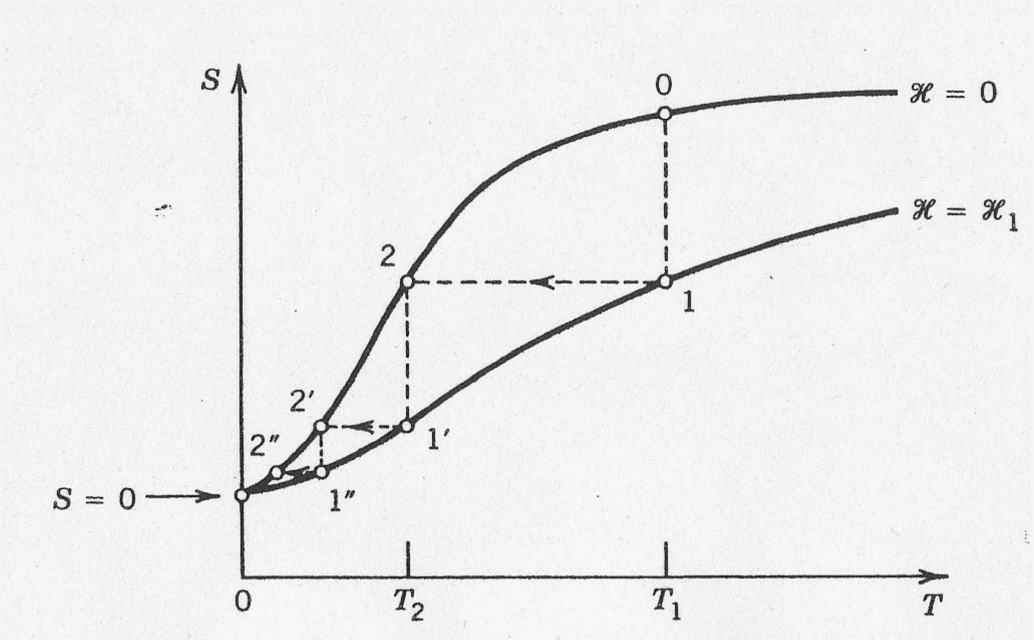
Die interessante Frage, welche Bedeutung dieser Satz für die molekularkinetische Auffassung der Entropie besitzt, kann hier nicht erörtert werden, da wir es hier nur mit der allgemeinen Thermodynamik zu tun haben. Aber die wichtigen Folgerungen, welche er für die Gesetze physikalisch-chemischer Gleichgewichtszustände enthält, müssen hier Besprechung finden.

Zunächst ist leicht einzusehen, daß man, da der Wert der Entropie eine willkürliche additive Konstante enthält, jenen für $T = 0$ eintretenden Wert unbeschadet der Allgemeinheit gleich Null setzen kann, so daß das Nernstsche Wärmetheorem nun lautet: B e i m N u l l p u n k t d e r a b s o l u t e n T e m p e r a t u r b e s i t z t d i e E n t r o p i e e i n e s j e d e n c h e m i s c h h o m o g e n e n f e s t e n o d e r f l ü s s i g e n K ö r p e r s d e n W e r t N u l l. Damit ist über die additive Konstante a der Entropie aller chemisch homogener Substanzen in allen Zuständen eindeutig verfügt, insofern jede Substanz im festen oder flüssigen Aggregatzustand bei der Temperatur Null existenzfähig (wenn auch nicht stabil) ist, und man kann von nun an in diesem Sinne von einem absoluten Wert der Entropie sprechen.

The Third Law

- magnetic refrigeration
- alternate
  - isotherms
  - adiabats
- as

$$\boxed{\lim_{T\to 0} S = 0}$$



No reversible adiabatic process starting at nonzero temperature can possibly bring a system to zero temperature

The Third Law

- consequence: absolute zero is unattainable
- infinite number of steps would be needed to reach absolute zero
- steps are thermodynamic equilibrium steps (infinitely slowly)

What about non-equilibrium processes?

Dynamic View on the Third Law

- Processes in finite time

Finite-Time Thermodynamics
Endoreversible Thermodynamics

- no longer thermodynamic equilibrium branches

- consider a refrigerator

Are there limits on the cooling rate?

Dynamic View on the Third Law

- continuous refrigeration process: entropy production
- the Second Law:

$$\sigma = -\dot{\mathcal{Q}}_c/T_c \; + \; \dot{\mathcal{Q}}_h/T_h > 0$$

$$\mathcal{R}_c = \dot{\mathcal{Q}}_c < \frac{\dot{\mathcal{Q}}_h}{T_h}\, T_c$$

- What exponent δ does apply in $\boxed{\mathcal{R}_c \propto T_c^{\delta}}$?

A Quantum Refrigerator

- working medium:
  an ensemble of quantum harmonic oscillators

$$\hat{\mathbf{H}} = \frac{1}{2m}\hat{\mathbf{P}}^2 + \frac{m\,\omega(t)^2}{2}\hat{\mathbf{Q}}^2$$

- description by density operator

- the work parameter:
  the frequency instead of the volume

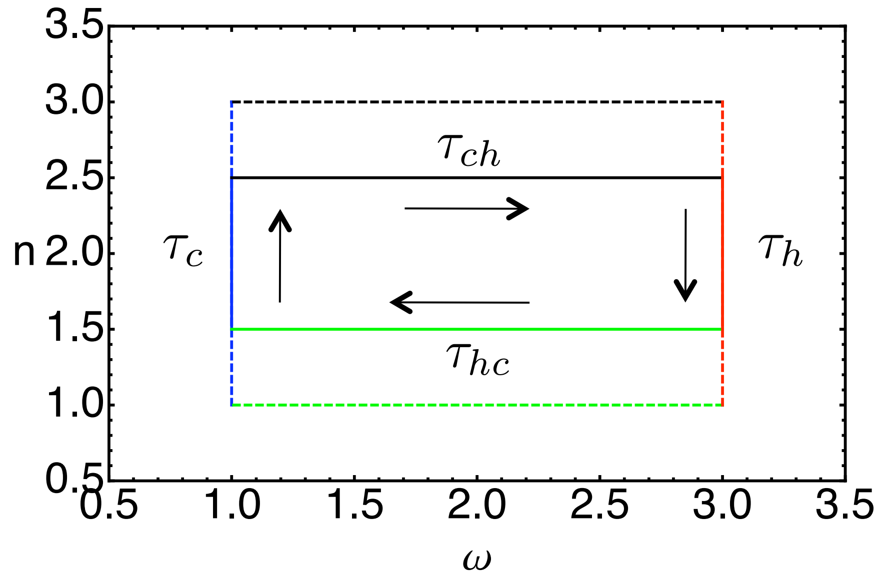
A Quantum Refrigerator: Average Cooling Rate

- for a cyclic refrigerator the cooling rate is the heat up-take per cycle time

$$\mathcal{R}_c = \frac{\mathcal{Q}_c}{\tau} = \frac{\mathcal{Q}_c}{\tau_{hc} + \tau_c + \tau_{ch} + \tau_h}$$

- expectation:

For given T_c one needs to choose optimal $\omega_c, \tau_{hc}, \tau_c, \tau_{ch}, \tau_h$



$$\boxed{\begin{array}{c} \mathcal{Q}_c(\ \omega_c(\ T_c\ )\ ) \\ \tau(\ \omega_c(\ T_c\ )\ ) \end{array}}$$

The Dynamics of a Quantum Working Fluid

- Adiabats: externally driven Hamiltonian $\hat{\mathbf{H}}(\omega(t))$

$$\frac{d\hat{\mathbf{O}}(t)}{dt} = \frac{i}{\hbar}[\hat{\mathbf{H}}(t), \hat{\mathbf{O}}(t)] + \frac{\partial \hat{\mathbf{O}}(t)}{\partial t}$$

- contact to heat bath, fixed frequency: dissipative Lindblad dynamics

$$\frac{d\hat{\mathbf{O}}(t)}{dt} = \mathcal{L}^*(\hat{\mathbf{O}}) = \frac{i}{\hbar}[\hat{\mathbf{H}}, \hat{\mathbf{O}}] + \mathcal{L}_D^*(\hat{\mathbf{O}})$$

- Lindblad term establishes thermal equilibrium to a bath

Simplified Dynamics

- There exists a set of operators which is invariant under the dynamics

$$\hat{\mathbf{H}}, \hat{\mathbf{L}}, \hat{\mathbf{C}}$$

- These are the Hamiltonian, the Lagrangian, and the Correlation

$$\hat{\mathbf{H}} = \frac{1}{2m}\hat{\mathbf{P}}^2 + \frac{m\,\omega(t)^2}{2}\hat{\mathbf{Q}}^2$$

$$\hat{\mathbf{L}} = \frac{1}{2m}\hat{\mathbf{P}}^2 - \frac{m\,\omega(t)^2}{2}\hat{\mathbf{Q}}^2$$

$$\hat{\mathbf{C}} = \omega(t)\frac{1}{2}(\hat{\mathbf{Q}}\hat{\mathbf{P}} + \hat{\mathbf{P}}\hat{\mathbf{Q}})$$

Entropies

- von Neumann entropy

$$S_{\mathrm{vN}} = -k_{\mathrm{B}} \mathrm{Tr}(\hat{\boldsymbol{\rho}} \; \ln \hat{\boldsymbol{\rho}})$$

- energy entropy

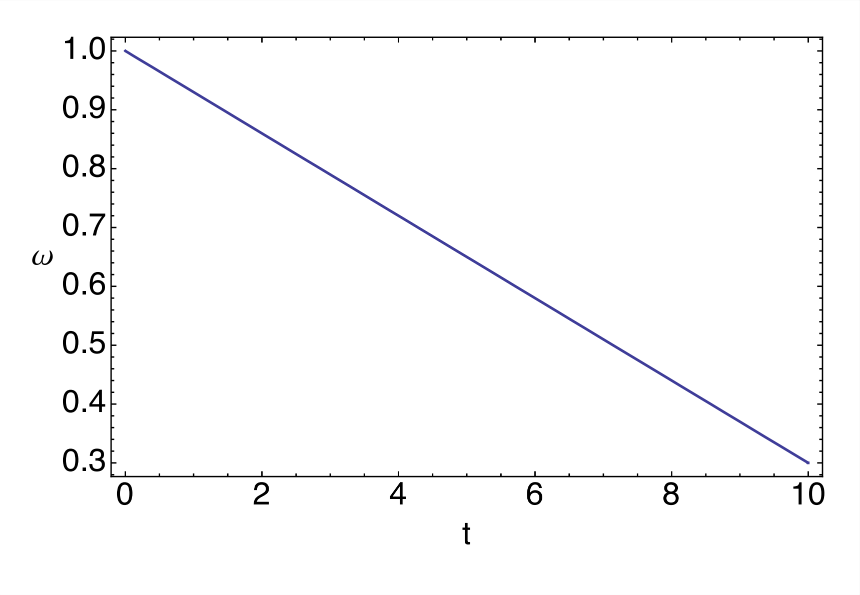
$$S_{\mathrm{E}} = -k_{\mathrm{B}} \sum_n p_n \ln p_n$$

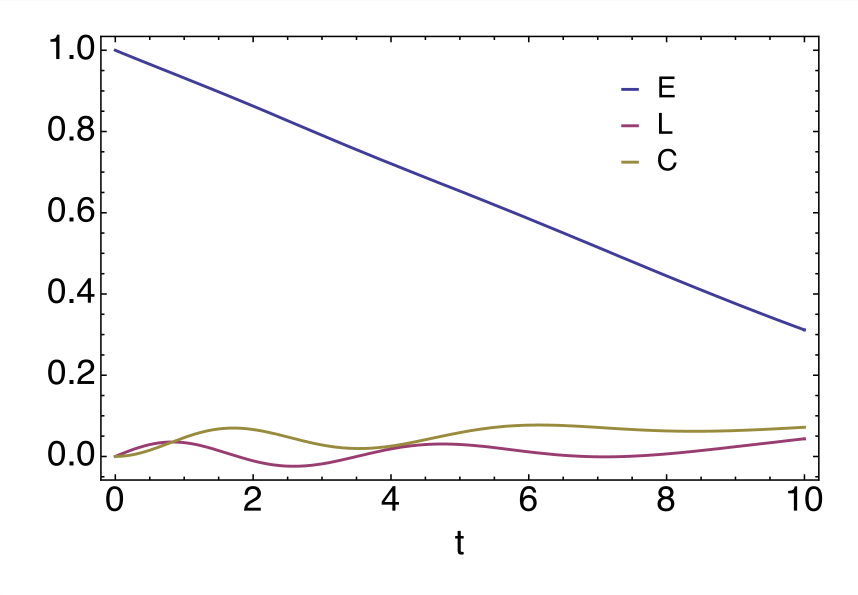
with $p_n = \langle \, n \, |\rho(\hat{\mathbf{H}}, \hat{\mathbf{L}}, \hat{\mathbf{C}})| \, n \, \rangle$ expectation values in energy eigen states

- in equilibrium $S_{\mathrm{vN}} = S_{\mathrm{E}}$

Adiabat Dynamics

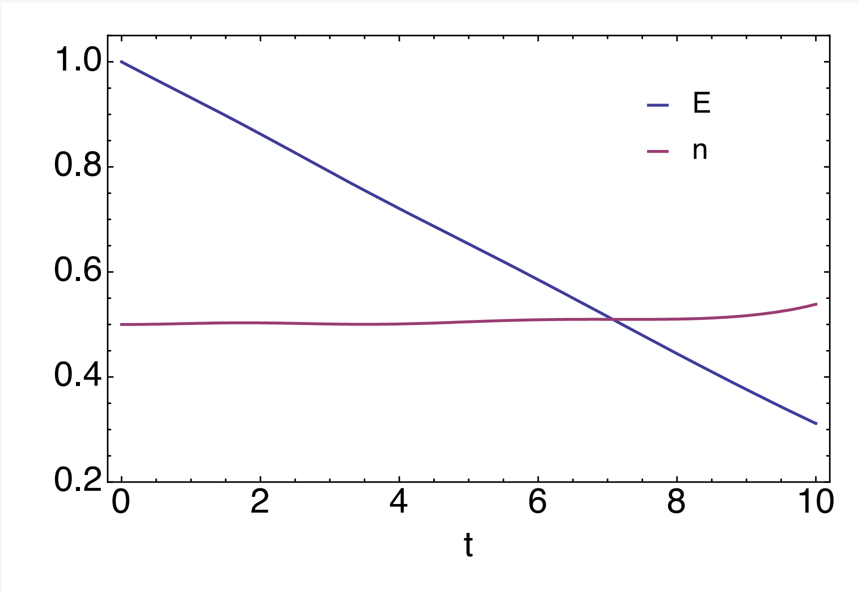
- frequency changing linear in time [0,10] from 1 to 0.3

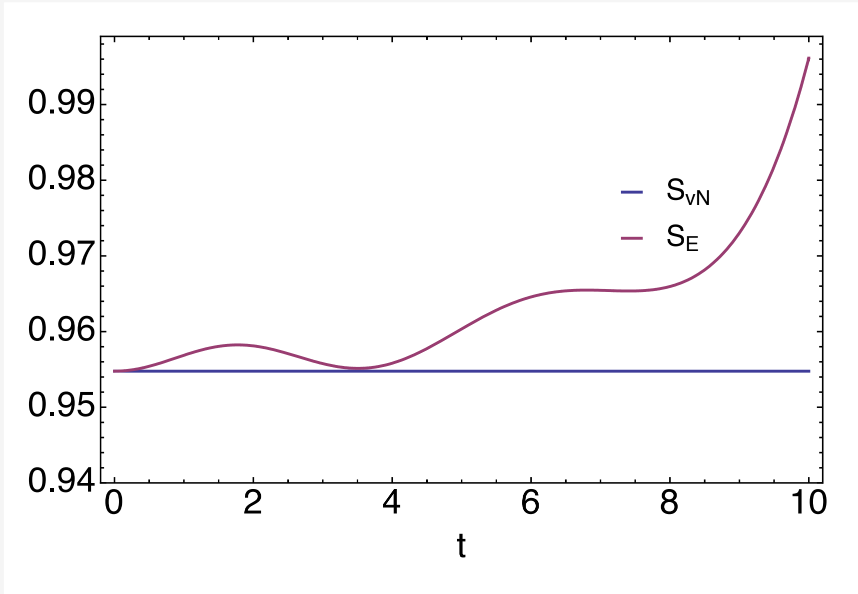




Adiabat Dynamics

- frequency changing linear in time [0,10] from 1 to 0.3



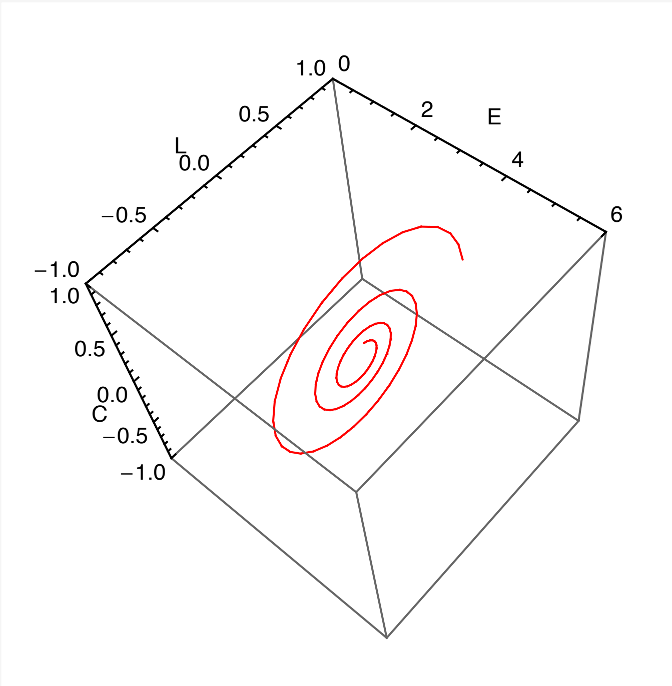


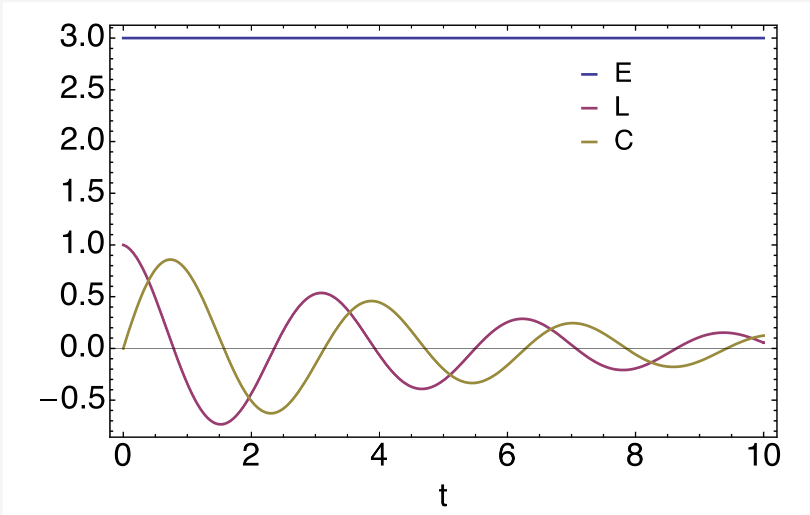
- the mean occupation number n is not constant: **quantum friction**

Heat Bath Contact

- fixed frequency and coupling to a bath with the contact temperature

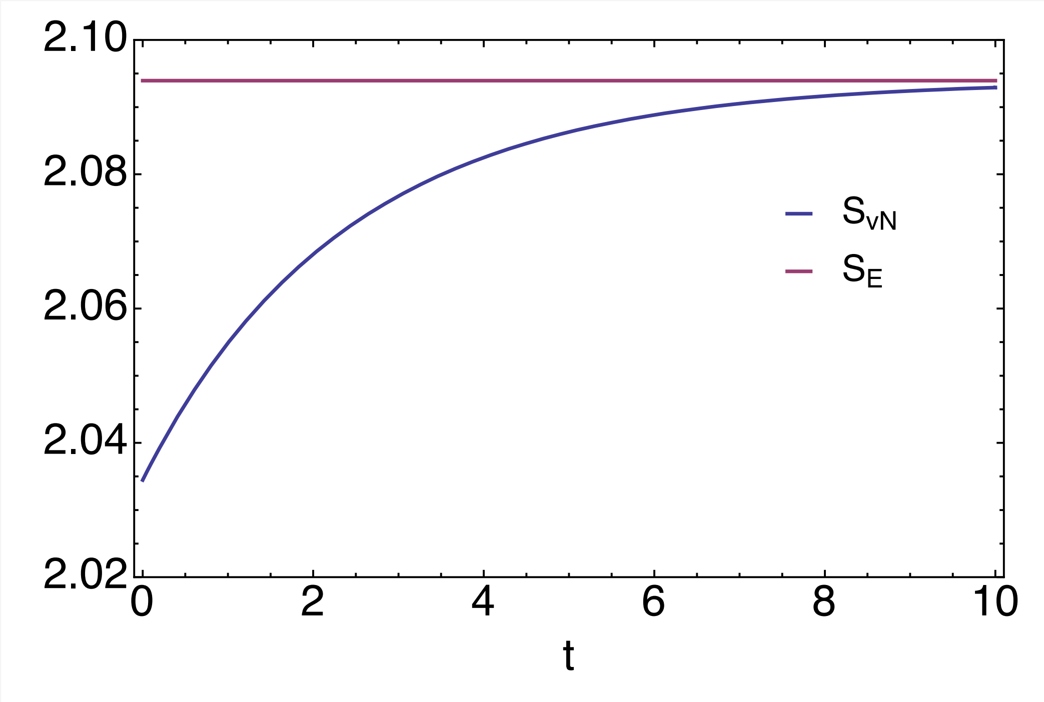
W. Muschik, G. Brunk





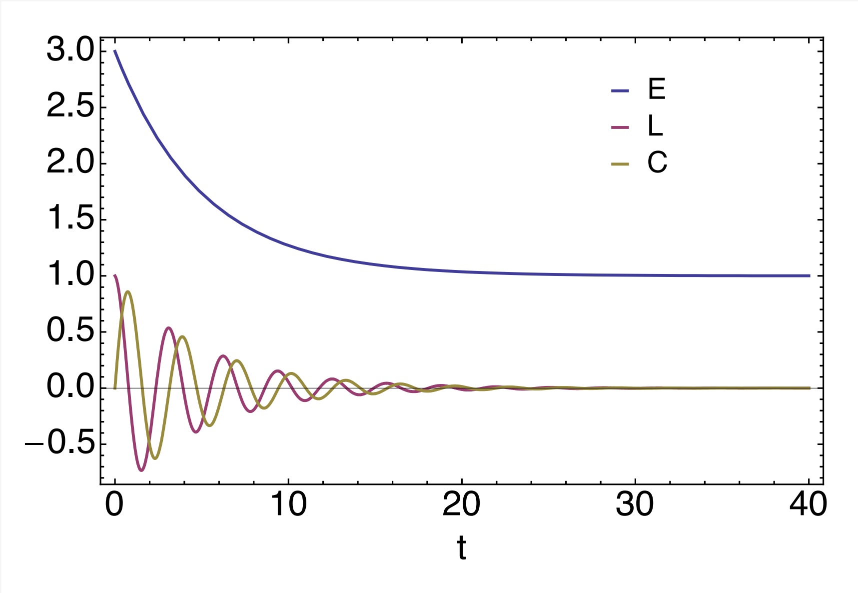
Heat Bath Contact

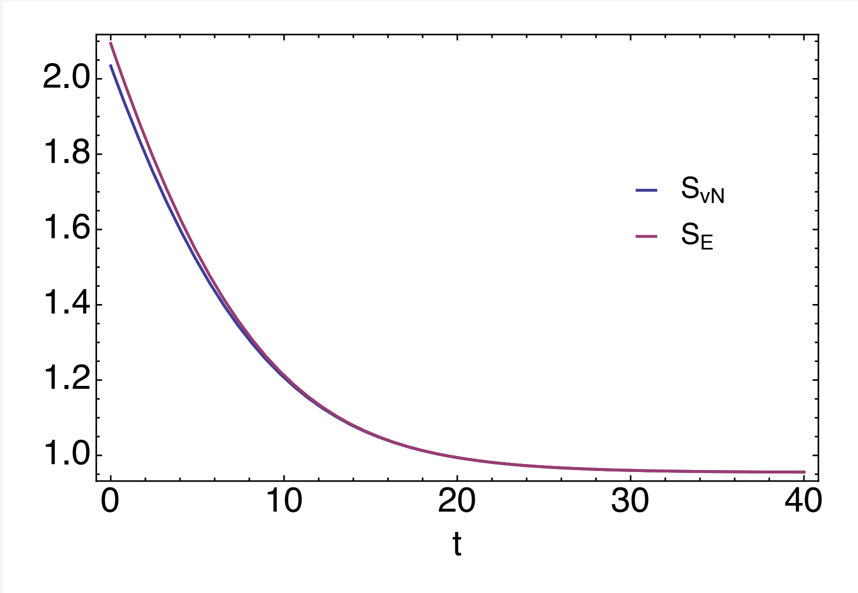
- fixed frequency and coupling to a bath with the contact temperature



Heat Bath Contact

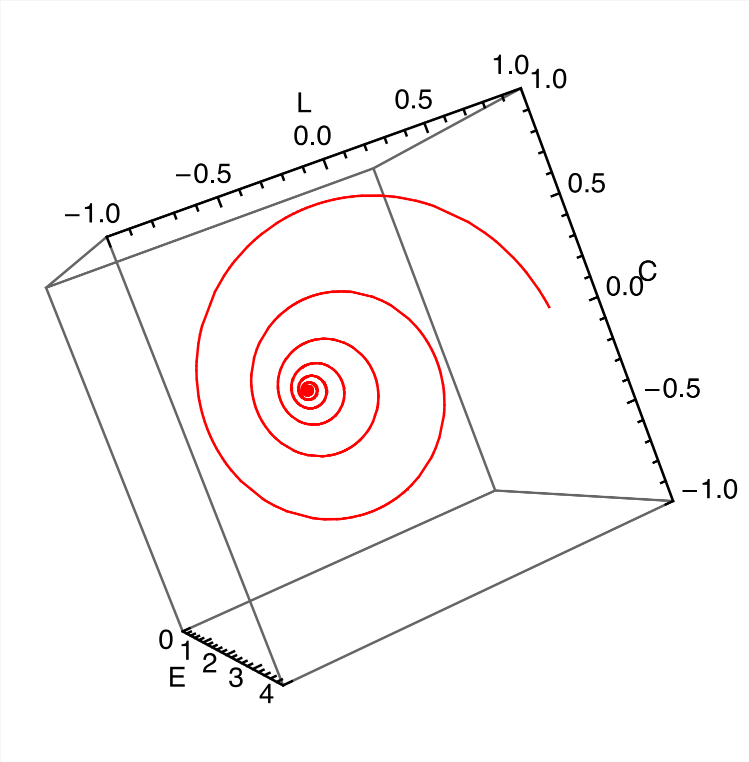
- fixed frequency and coupling to a bath with a different temperature

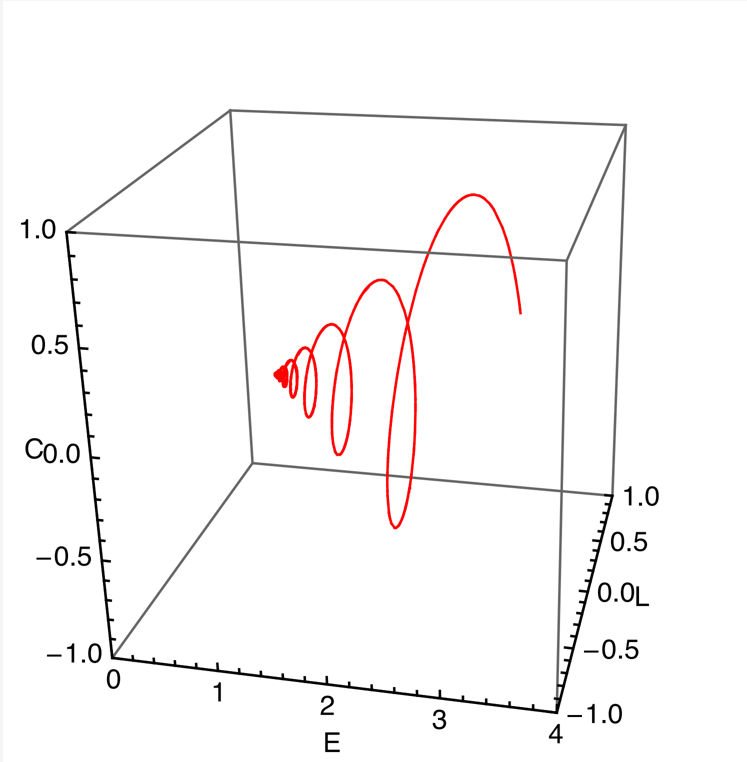




Heat Bath Contact

- fixed frequency and coupling to a bath with a different temperature





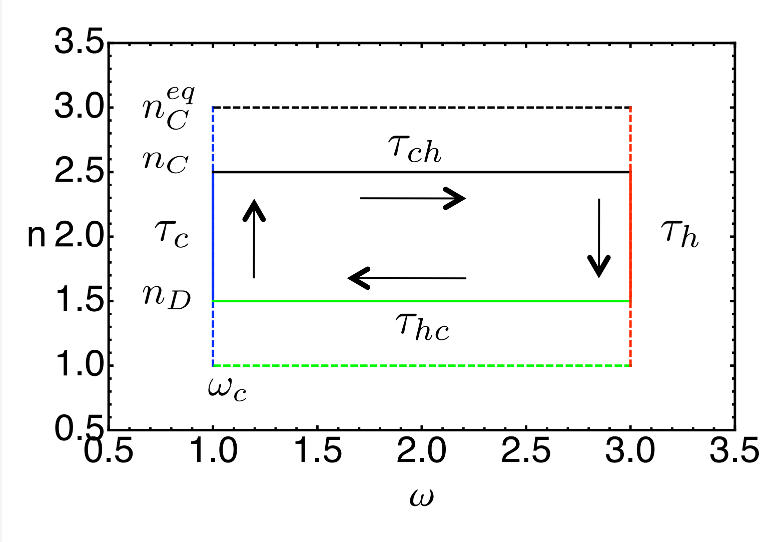
The Cooling Rate

- the cooling rate $$\mathcal{R}_c = \frac{1}{\tau_{hc} + \tau_c + \tau_{ch} + \tau_h} \hbar\omega_c (n_C - n_D)$$

- given the time needed for the adiabats:
  optimize for relative time allocation on the isotherms (isofrequencies)
  optimize for time allocation between isotherms and adiabats

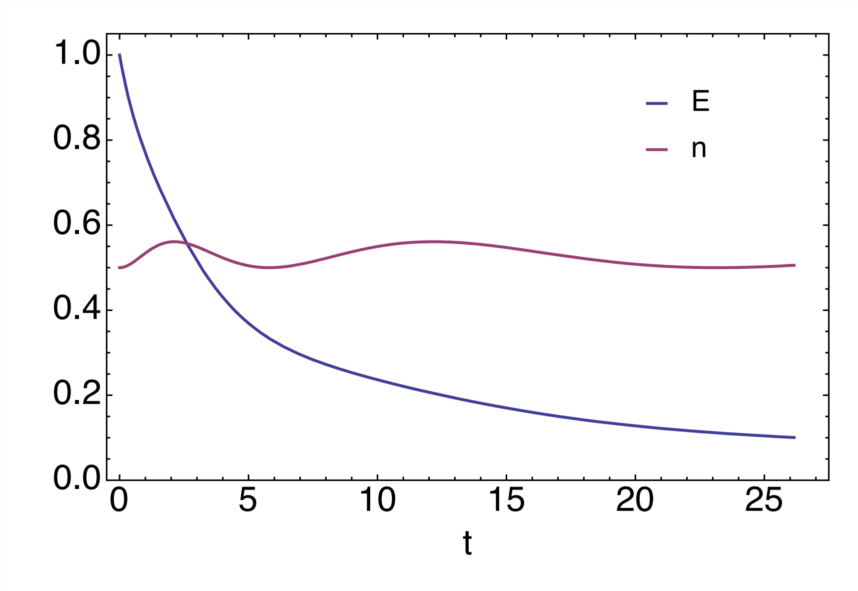
$$\tau_{hc} = \tau_{ch} \qquad \tau_h = \tau_c$$

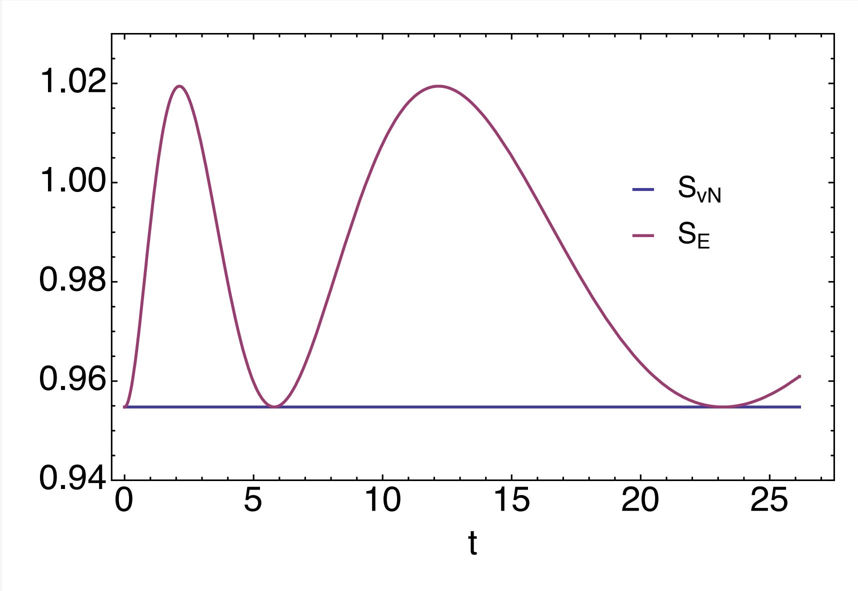
$$\mathcal{R}_c^{\text{opt}} \approx \frac{\hbar\omega_c n_c^{eq}}{\tau_{hc}}$$



Adiabat Dynamics: the 1TURN Process

- special frequency protocol $\mu = \frac{\dot{\omega}}{\omega^2} = \text{const}$





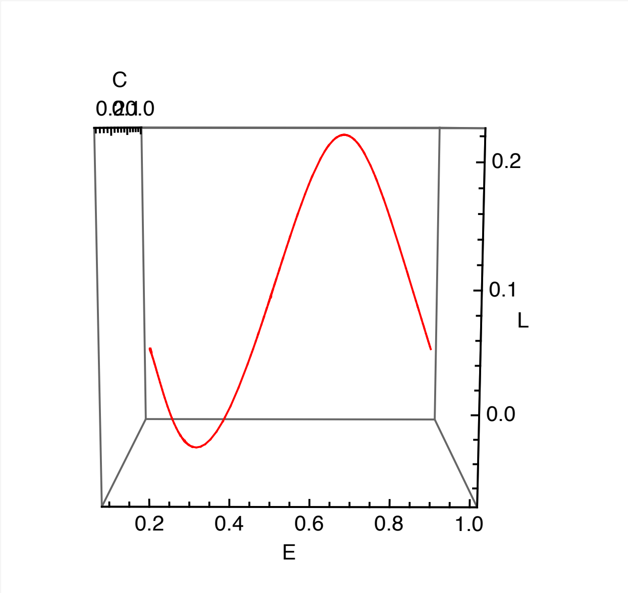
- the optimal time from hot to cold

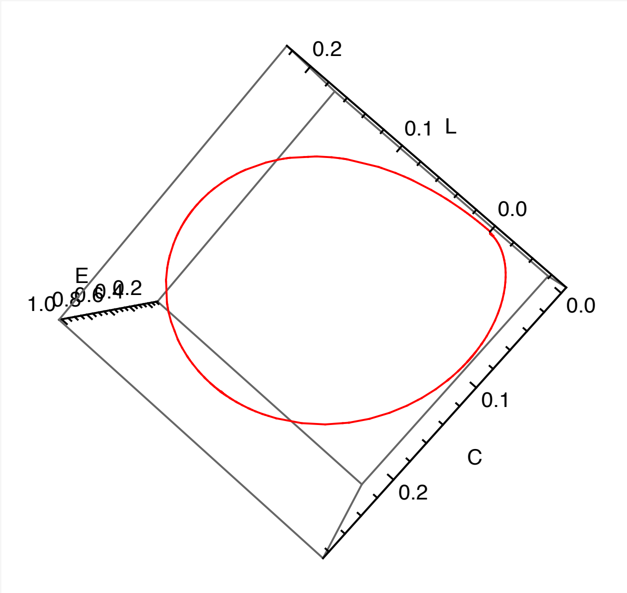
$$\boxed{\tau_{hc}^{*} = \frac{1}{2}\omega_c^{-1}}$$

Time needed for IR Adiabats: the 1TURN Process

- for given ω_c, ω_h choose proper speed and time

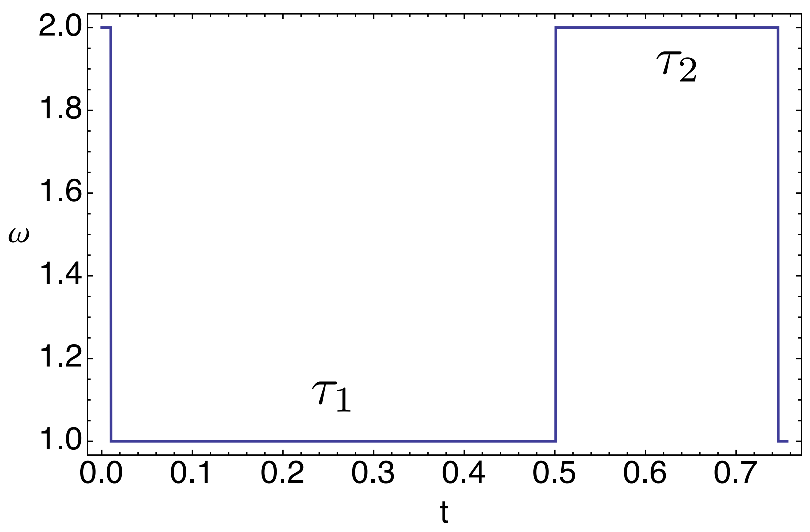
$$\boxed{\tau_{hc}^{*} = \frac{1}{2}\omega_c^{-1}} \longrightarrow \boxed{\mathcal{R}_c^{\mathrm{opt}} < \mathrm{const.}\quad T_c^2}$$

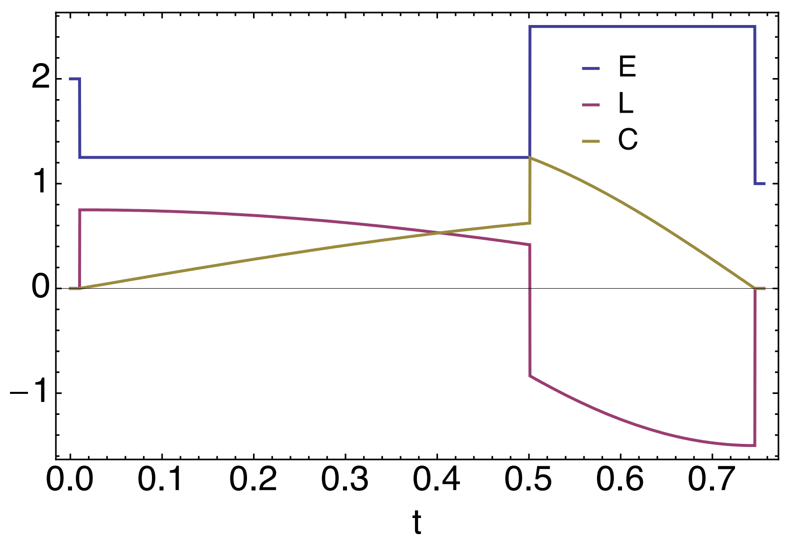




Adiabat Dynamics: 3JUMP Process

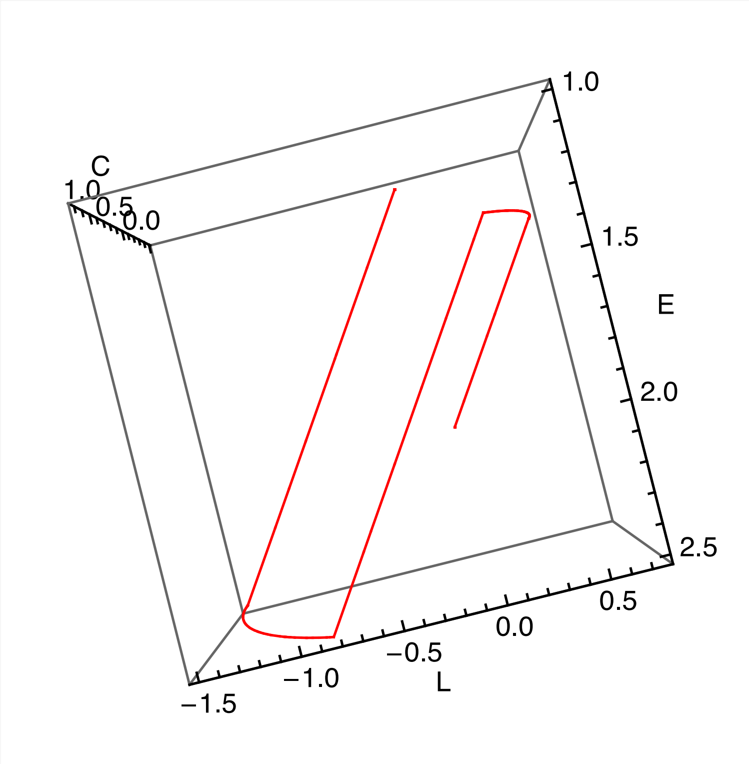
- three frequency jumps between given frequencies

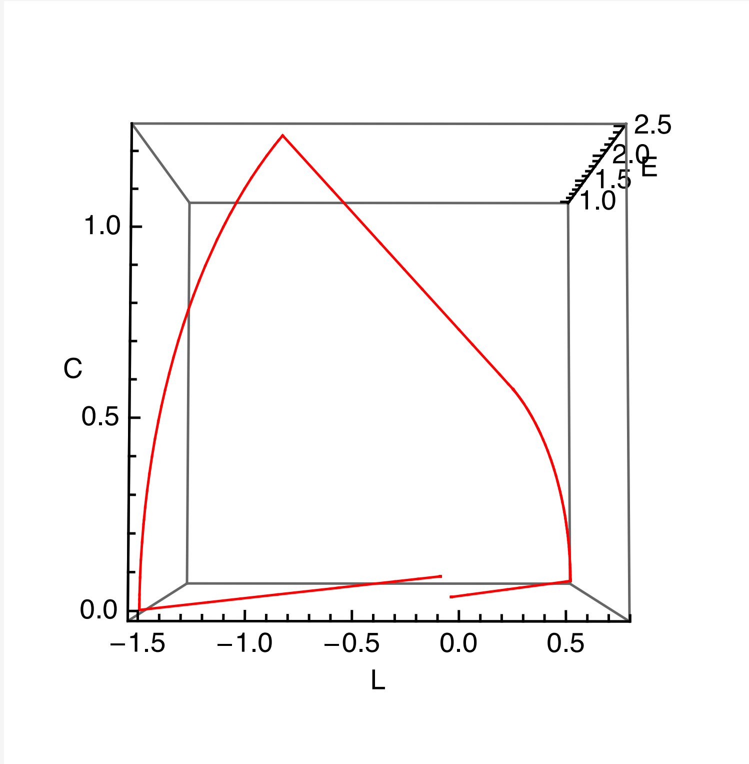




Adiabat Dynamics: 3JUMP Process

- three frequency jumps between given frequencies





Shortest Time needed for Adiabats

- If frequency is confined between ω_c and ω_h

3JUMP Processes are the adiabats
which lead in the shortest time
from equilibrium to equilibrium

- proof on the basis of control theory, very technical

$$\boxed{\tau^*_{hc} = \frac{1}{\sqrt{\omega_h}} \omega_c^{-\frac{1}{2}}} \longrightarrow \boxed{\mathcal{R}_c^{\mathrm{opt}} < \mathrm{const.} \quad T_c^{\frac{3}{2}}}$$

Generalized Dynamics: Finite-Dimensional Lie Algebra

- There exists a set of operators which is invariant under the dynamics

$$\hat{\mathbf{H}}, \hat{\mathbf{L}}, \hat{\mathbf{C}}$$

- More general setting: there exists a set of operators $\mathcal{B}_i$ which form a Lie algebra with

$$[\mathcal{B}_i, \mathcal{B}_j] = \sum_{k=1}^{N} c_{ij}{}^{k} \mathcal{B}_k$$

$$\mathcal{H} = \sum_{i=1}^{N} h^i(t) \mathcal{B}_i$$

Generalized Dynamics: Finite-Dimensional Lie Algebra

- Known constant of the motion:

The Casimir Operator
$$C = \sum_{i,k=1}^{N} g^{ik} \mathcal{B}_k \mathcal{B}_i$$

- There exists a second constant of the motion which is invariant under the dynamics:

The Casimir Companion
$$X = \sum_{i,k=1}^{N} g^{ik} \langle \mathcal{B}_k \rangle \langle \mathcal{B}_i \rangle$$

- The von Neumann entropy – also in non-equilibrium – can always be expressed in terms of the Casimir Companion

Entropies

- von Neumann entropy

$$S_{\mathrm{vN}} = k_{\mathrm{B}} \ln\left(\sqrt{X - \frac{1}{4}}\right) + \sqrt{X}\,\mathrm{arcsinh}\left(\frac{\sqrt{X}}{X - \frac{1}{4}}\right) \qquad X = \frac{E^2 - L^2 - C^2}{\omega^2}$$

- energy entropy

$$S_{\mathrm{E}} = k_{\mathrm{B}} \ln\left(\sqrt{\frac{E^2}{\omega^2} - \frac{1}{4}}\right) + \sqrt{\frac{E^2}{\omega^2}}\,\mathrm{arcsinh}\left(\frac{\sqrt{\frac{E^2}{\omega^2}}}{\frac{E^2}{\omega^2} - \frac{1}{4}}\right) \qquad S_{\mathrm{E}} \geq S_{\mathrm{vN}}$$

- one can define "contact temperature"

$$\frac{1}{T_{\mathrm{contact}}} = \left.\frac{\partial S_{\mathrm{E}}}{\partial E}\right|_{\omega}$$

The Team




Yair Rezek Ronnie Kosloff Peter Salamon Karl Heinz Hoffmann

Fritz Haber Research Center
Hebrew University Jerusalem

San Diego
State University

Tech. Universität
Chemnitz

Summary

- Dynamic view on the Third Law:
  Study temperature dependence of the Cooling Rate
- "Quantum Refrigerator": parametric harmonic oscillators as working medium
- good indicators for non-equilibrium:
  Von Neumann entropy, energy entropy
- Application: Maximum cooling rate of a quantum refrigerator
- There exist adiabatic processes in finite time !!!
- Generalization: Lie algebra dynamics and the Casimir Companion

Selected References 1

- Optimal control in a quantum cooling problem
  Salamon, Peter and Hoffmann, Karl Heinz and Tsirlin, Anatoly
  Applied Mathematics Letters (in press) (2012)

- Time-optimal controls for frictionless cooling in harmonic traps
  Hoffmann, Karl Heinz and Salamon, Peter and Rezek, Yair and Kosloff, Ronnie
  Europhysics Letters 96(6): 60015-1--6 (2011)

- Optimal control of the parametric oscillator
  Andresen, Bjarne and Hoffmann, Karl Heinz and Nulton, James and Tsirlin, Anatoly and Salamon, Peter
  European Journal of Physics 32(3): 827--843 (2011) ; ISSN 0143-0807

- The quantum refrigerator: The quest for absolute zero
  Rezek, Y. and Salamon, P. and Hoffmann, K. H. and Kosloff, R.
  Europhysics Letters 85: 1--5 (2009)

- Maximum work in minimum time from a conservative quantum system
  Salamon, P. and Hoffmann, K. H. and Rezek, Y. and Kosloff, R.
  Physical Chemistry Chemical Physics11: 1027--1032 (2009)

Selected References 2

- Optimal Process Paths for Endoreversible Systems
  Hoffmann, K. H. and Burzler, J. and Fischer, A. and Schaller, M. and Schubert, S.
  Journal of Non-Equilibrium Thermodynamics 28(3): 233--268 (2003)

- Recent Developments in Finite Time Thermodynamics
  Hoffmann, K. H.
  Technische Mechanik 22(1): 14--25 (2002)

- Endoreversible Thermodynamics
  Hoffmann, K. H. and Burzler, J. M. and Schubert, S.
  Journal of Non-Equilibrium Thermodynamics 22(4): 311--355 (1997)