Finite-time optimization of chemical and unrelated reactions

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Finite-Time Thermodynamics

- Effect of finite time
- Effect of finite size
- Optimize what

rev. thermo	irrev. thermo		extended irrev. thermo	kinetics
0 →				
equilibrium	min. entropy production	max. power		chaos

Finite-Time Thermodynamic idea

Reversible thermo. procedures
+ simple rate processes
+ finite total duration

Macroscopic modeling
Generic
Any objective function

Finite-Time Thermodynamic concepts

- Bounds for finite time
- Generalized exergy for finite time
- Generalized thermo. potentials incorporating constraints
- Constant rate of entropy production for linear transfer laws
- What is being optimized?
- Optimal path
- Thermodynamic geometry
- …

Entropy survives

Entropy applies equally in the chemistry lab, to the quantum computer, and to black holes.

Albert Einstein: "*classical thermodynamics ... is the only physical theory of universal content that, within the framework of applicability of its basic concepts, will never be overthrown*".

Cooling of atomic systems is not a question of removing the last bit of energy but entropy.

Entropy governs everything

Some basics

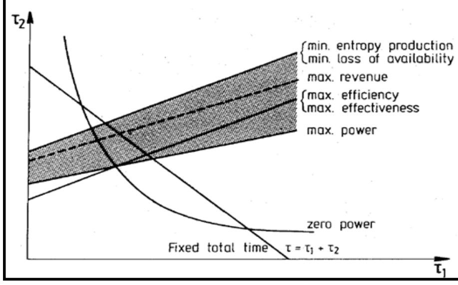
There are many ways to slice a kiwi

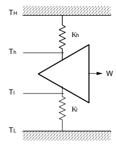
What makes you happy?

- you are in a hurry
- you want to conserve
- you want profit
- you have ulterior motives

Criteria of performance

Every person has his own objective: max. power, max. efficiency, max. profit, ...
They all correspond to *different bounds* and *different optimal paths*.



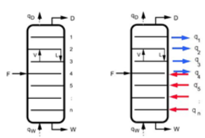


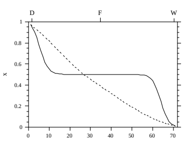
Controls are needed

The operator, not Nature, decides.

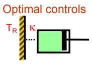
All optimization requires controls to steer the process in the desired direction.

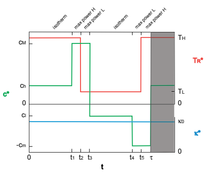
Diabatic distillation

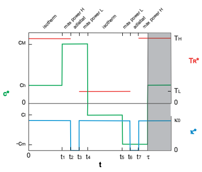




Optimal controls







Simulated annealing

Annealing schedule $\frac{dT}{dt} = -\frac{vT}{\varepsilon\sqrt{C}}$

M. H. Rubin, Phys. Rev. A **19**, 1277-1289 (1979)

Constraints

- you cannot use freeways
- you cannot drive at night
- you must meet district heating demands
- you have no use for waste heat
- limitations of your machinery
- purity of products

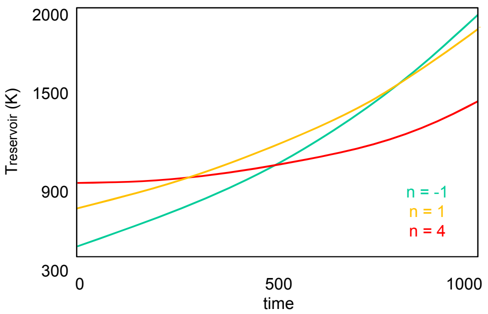
- fix production / consumption / duration

Optimal heating sequence

min ΔS^u

$q \propto \Delta(T^n)$

system 300 → 900 K



Bose/Fermi work per cycle

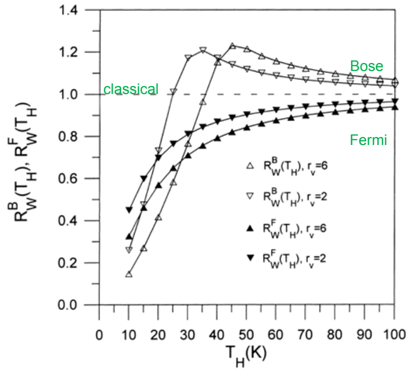
$T_L/T_H=0.4$

$r_v=V_H/V_L$

$P=nkT\times$ quantum factor

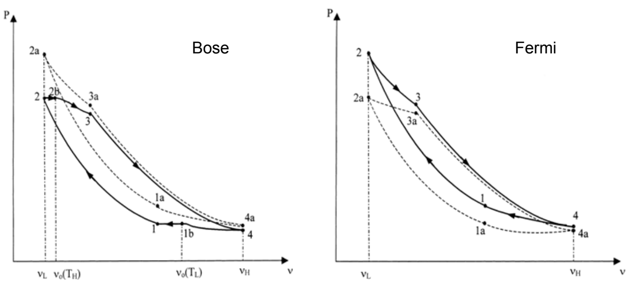
For all

$\eta_C=1-T_L/T_H$



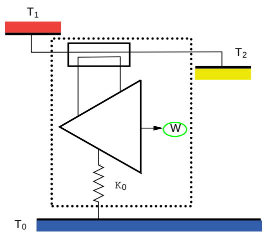
A. Sisman, H. Saygin, Applied Energy, **68**, 367-376 (2001)

Carnot cycles



A. Sisman, H. Saygin, Applied Energy, **68**, 367-376 (2001)

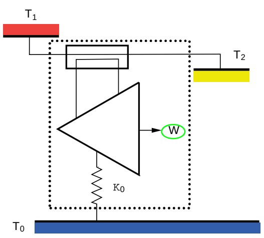
System boundary



max W <> min ΔS^u

$= \sigma^{system}$?

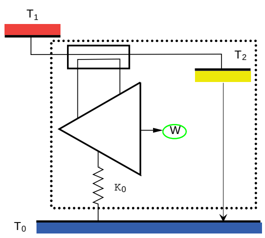
System boundary



max W <> min ΔS^u

$= \sigma^{system}$?

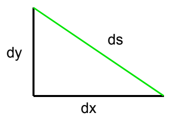
or



max W = min ΔS^u

Thermodynamic geometry

Length



$$ds = \sqrt{dx^2 + dy^2}$$

$$L = \int \sqrt{dx^2 + dy^2} = \int \sqrt{1 + \left(\frac{dy}{dx}\right)^2}\, dx = \int \sqrt{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2}\, dt$$

In general $\quad L = \int \sqrt{(dx, dy)(\mathbf{M})\begin{pmatrix} dx \\ dy \end{pmatrix}}$

e.g. $\quad L = \int_i^f \sqrt{(dx, dy)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} dx \\ dy \end{pmatrix}} = \int_i^f \sqrt{(dr, d\theta)\begin{pmatrix} 1 & 0 \\ 0 & r^2 \end{pmatrix}\begin{pmatrix} dr \\ d\theta \end{pmatrix}}$

Thermodynamic metric

Length: $L = \int \sqrt{d\mathbf{X}^t \mathbf{M}\, d\mathbf{X}}$ $\quad$ conjugate: $Y_i = \left(\frac{\partial P}{\partial X_i}\right)$

Entropy picture: $S(\mathbf{X}), \quad \mathbf{X} = (U, V, N_1, \ldots), \quad \mathbf{Y} = \left(\frac{1}{T}, \frac{p}{T}, -\frac{\mu}{T}, \ldots\right), \quad \mathbf{M}_S = -\left(\frac{\partial^2 S}{\partial X_i \partial X_j}\right)$

Energy picture: $E(\mathbf{X}), \quad \mathbf{X} = (S, V, N_1, \ldots), \quad \mathbf{Y} = (T, -p, \mu, \ldots), \quad \mathbf{M}_U = \left(\frac{\partial^2 U}{\partial X_i \partial X_j}\right)$

Probability picture: $S(\mathbf{X}) = -\sum p_i \ln p_i, \quad \mathbf{X} = (p_i), \quad \mathbf{Y} = -(\ln p_i + 1), \quad \mathbf{M}_S = \left(\frac{1}{p_i}\right)$

Thermodynamic metric

Ideal gas
$\{U, S, V\}$

$$-D^2 S = -\begin{pmatrix} \frac{\partial^2 S}{\partial U^2} & \frac{\partial^2 S}{\partial U \partial V} \\ \frac{\partial^2 S}{\partial V \partial U} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix} = \begin{pmatrix} \frac{C_v}{U^2} & 0 \\ 0 & \frac{R}{V^2} \end{pmatrix}$$

$$D^2 U = \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} \end{pmatrix} = \begin{pmatrix} \frac{T}{C_v} & -\frac{p}{C_v} \\ -\frac{p}{C_v} & \frac{\gamma p}{V} \end{pmatrix}$$

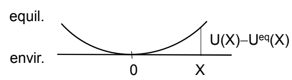
Using: $dU = TdS - pdV$
$PV = RT$
$U = C_v T$
$TS = C_p T$
$R = C_p - C_v$

Curvature

$$U^{eq}(X) = U_0 + \frac{\partial U}{\partial X}\Delta X + \frac{1}{2}\frac{\partial^2 U}{\partial X \partial X}(\Delta X)^2 + \ldots$$

$$U^{env}(X) = U_0 + \frac{\partial U}{\partial X}\Delta X$$

Availability = exergy: $\quad dA = dU - T_e dS + P_e dV$



Thermodynamic metric bounds

Continuous process

FTT bound: $\quad \Delta S^u \geq \frac{L_S^2 \varepsilon}{\tau} \qquad -\Delta A^u \geq \frac{L_U^2 \varepsilon}{\tau}$

Reversible bound: $\quad \Delta S^u \geq 0 \qquad -\Delta A^u \geq 0$

For slow processes $\quad v = \frac{dL}{dt} = \text{const.} \quad \Rightarrow \quad \frac{dT}{dt} = \frac{-vT}{\varepsilon\sqrt{C}}$

Continuous adjustment to a moving target
Curvature ~ interaction strength

e.g. $\sum p_i = 1$
$\Rightarrow$ Gaussian curvature = 4

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Continuous adjustment to a moving target
Curvature ~ interaction strength

e.g. $\sum p_i = 1$
$\Rightarrow$ Gaussian curvature = 4

Step process

$\Delta S^u \geq \frac{L^2}{2N} \qquad \Delta L = \text{const.}$

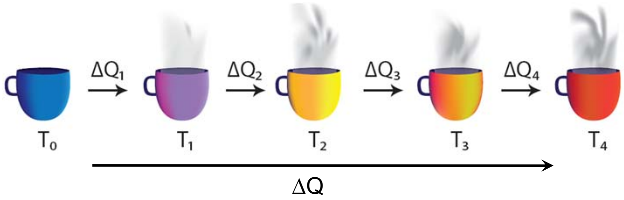
Step processes

- Consecutive heat engines
- Information encoding
- Economic gain
- Distillation column
- Chemical reactions

Horse-Carrot processes

Use thermodynamic geometry to determine optimal operation

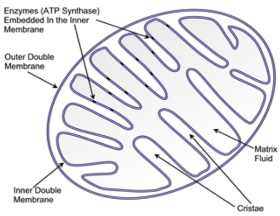
Stepwise heating



$$\Delta Q = \sum_i \Delta Q_i$$

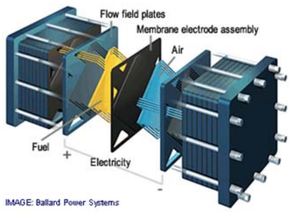
$$\Delta S = \int_{T_0}^{T_4} dQ\left(\frac{1}{T} - \frac{1}{T_4}\right) > \sum_i \Delta S_i = \sum_i \int_{T_{i-1}}^{T_i} dQ\left(\frac{1}{T} - \frac{1}{T_i}\right)$$

Mitochondrion



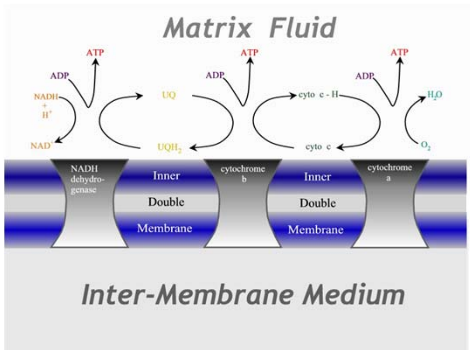
1×10^{-6} m

Fuel cell



1×10^{-1} m

Cytochrome chain



Fuel cell

$$2\,H_2 + O_2 \Leftrightarrow 2\,H_2O + 1.1\ \text{eV}$$

Thermodynamic metric

Length: $L = \int \sqrt{d\mathbf{X}^t\,\mathbf{M}\,d\mathbf{X}}$ conjugate: $Y_i = \left(\frac{\partial P}{\partial X_i}\right)$

Entropy picture: $S(\mathbf{X})$, $\mathbf{X} = (U, V, N_1, \ldots)$, $\mathbf{Y} = \left(\frac{1}{T}, \frac{p}{T}, -\frac{\mu}{T}, \ldots\right)$, $\mathbf{M}_S = -\left(\frac{\partial^2 S}{\partial X_i\,\partial X_j}\right)$

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Energy picture – ideal gas

$U(S,V,n_i)$ derived from:

$$U = NC_vT$$

$$pV = NkT$$

$$\mu_i = kT\left[\ln\frac{n_i}{V} - \frac{C_v}{k}\ln(m_ikT) + a\right]$$

with $T = \frac{\partial U}{\partial S}, p = -\frac{\partial U}{\partial V}, \mu_i = \frac{\partial U}{\partial n_i}, N = \sum_i n_i$

$$U(S,V,n_i) = be^{\frac{S}{NC_v}} N \prod_j \left[\left(\frac{n_j}{V}\right)^{\frac{k}{C_v}} \frac{1}{m_j}\right]^{\frac{n_j}{N}}$$

Energy picture – ideal gas

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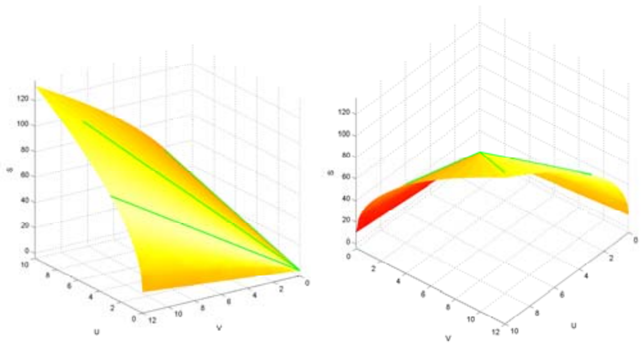
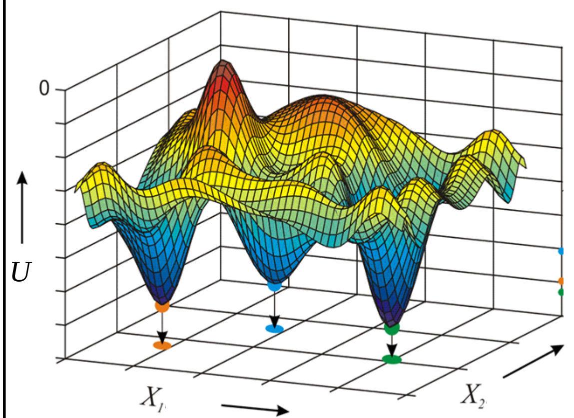
$$\boxed{U(S,V,n_i) = be^{\frac{S}{NC_v}}N\prod_j\left[\left(\frac{n_j}{V}\right)^{\frac{k}{C_v}}\frac{1}{m_j}\right]^{\frac{n_j}{N}}}$$

Ideal gas equilibrium surface



Water equilibrium surface

Gift from James Clerk Maxwell to J. Willard Gibbs 1874.



Metric – ideal gas

$$M_U = \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial n_i} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial V \partial n_i} \\ \frac{\partial^2 U}{\partial n_i \partial S} & \frac{\partial^2 U}{\partial n_i \partial V} & \frac{\partial^2 U}{\partial n_i \partial n_j} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{T}{NC_v} & \frac{-p}{NC_v} & \frac{\mu_i}{NC_v} - \frac{T}{N} \\ \frac{-p}{NC_v} & \left(1+\frac{k}{C_v}\right)\frac{p}{V} & -\frac{k}{C_v}\frac{\mu_i}{V} \\ \frac{\mu_i}{NC_v} - \frac{T}{N} & -\frac{k}{C_v}\frac{\mu_i}{V} & \mu_i\left(\frac{\mu_j}{U} - \frac{1}{N}\right) - \frac{1}{N}\mu_j + \frac{1}{N^2}U + \frac{RT}{N_j}\delta_{ij} \end{pmatrix}$$

Variables

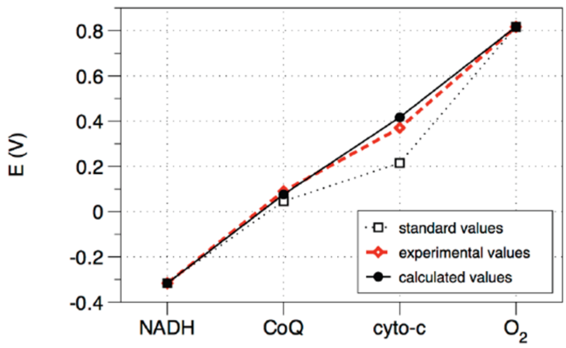
variable		*condition*	
S		T const.	
V		p const.	
N_{H+}		pH const.	
N_P		[P] const.	
N_{ATP}	N_{ADP}	$N_{ATP}+N_{ADP}$ const.	[ATP] const.
N_{NADH}	N_{NAD+}	$N_{NADH}+N_{NAD+}$ const.	[NADH] const.
N_{CoQ}	N_{CoQH_2}	$N_{CoQ}+N_{CoQH_2}$ const.	
$N_{cyto\text{-}c}$	$N_{cyto\text{-}c\text{-}H}$	$N_{cyto\text{-}c}+N_{cyto\text{-}c\text{-}H}$ const.	
N_{H_2O}		$[H_2O]$ const.	
N_{O_2}		$[O_2]$ const.	
	14		12

Dimension reduction

- Many dimensions: S, V, N_1, N_2, …
- Conservation equations and common T, p relate these
- Eventually just one, e.g. ζ or electrochemical potential
- Formally equivalent to distillation column in T

Procedure:
calculate total length L
each step is L_n=L/N
$L_n \Rightarrow \zeta_n$ and thus concentrations

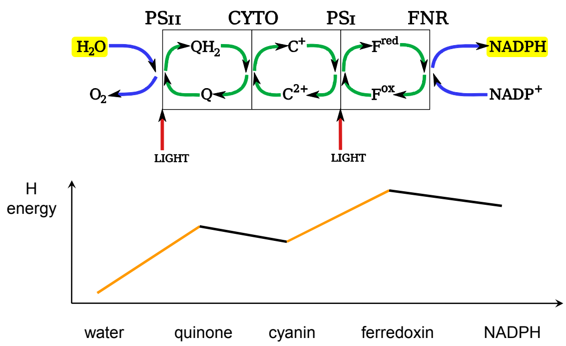
Optimal electrochemical path



Conclusions

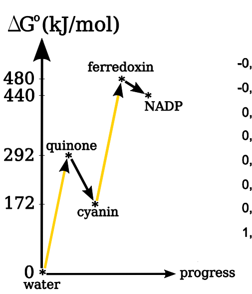
- The cytochrome chain is a step process
- sharing a common medium
- at constant T and pH
- with the electro-chemical potential as the control.
- The sequence is logical, not physical.

Electron transport chain

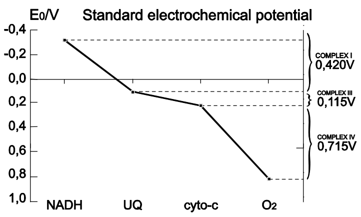


Energy path

photosynthesis



cytochrome chain



How to handle light

A + photon → B

Does the photon count as a reactant?
Is there equilibrium between the 3 components?
How does light interact with matter?

Length elements

length element:

$$(dL)^2 = kT\left[\frac{\tilde{N}_Q}{x_Q(1-x_Q)}dx_Q^2 + \frac{\tilde{N}_C}{x_C(1-x_C)}dx_C^2 + \frac{\tilde{N}_F}{x_F(1-x_F)}dx_F^2\right]$$

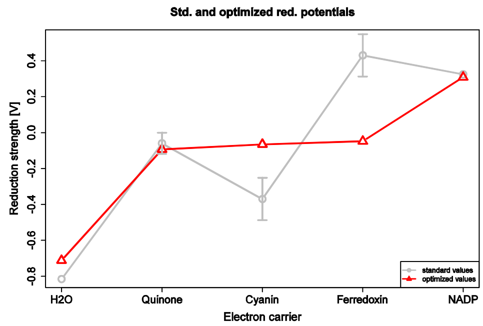
reduction potential:

$$E - E_i^0 = \frac{RT}{n_i F}\ln\frac{[A^i_{red}]}{[A^i_{ox}]} = \frac{kT}{n_i e}\ln\frac{1-x_i}{x_i}$$

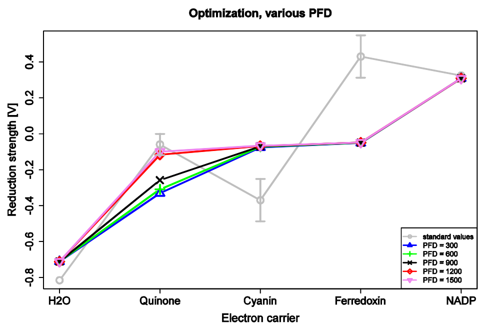
total length:

$$L = \int dL = \int_{E_1}^{E_2}\sqrt{\sum_i \frac{\tilde{N}_i e^2 n_i^2 / kT}{\left[1+e^{(E-E_i^0)en_i/kT}\right]}}\,dE$$

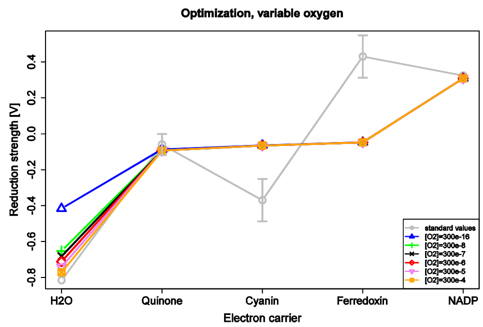
Optimal path



Light intensity



Oxygen partial pressure



Conclusions

- Photosynthesis is a step process
- sharing a common medium
- at constant T and pH
- with the electro-chemical potential as the control.

- Alternating light and dark processes necessary to avoid recombination.
- Sunlight intensity optimal. However …
- Low sensitivity on oxygen pressure.

Chemical reaction

$A \Leftrightarrow B \Leftrightarrow C$

$k_i = s_i e^{-U_i/kT} \qquad u = e^{-1/kT}$

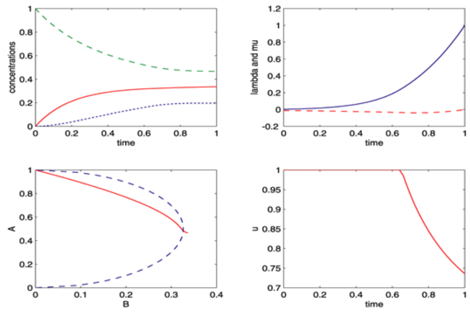
maximize [B] at $t = \tau$

Constraints:

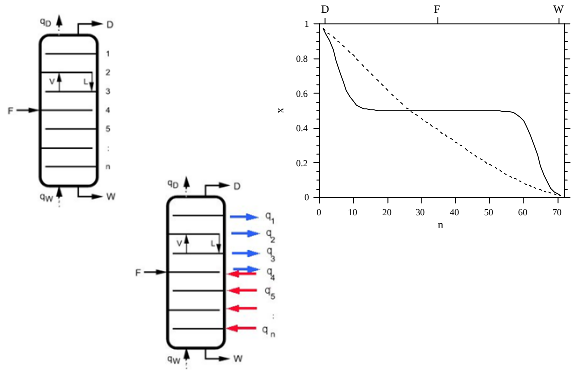
rate equations	$\frac{dA}{dt}, \quad \frac{dB}{dt}$
conjugate	$\lambda, \quad \mu$
initial conds.	$A(0) = 1, \quad B(0) = 0, \quad C(0) = 0$

At final time $\quad \frac{dB^*}{dt} = \left.\frac{dB}{dt}\right|_{t=\tau}$

Chemical reaction optimization



Distillation column



Column optimization

Step process : $\Delta S^u \geq \frac{L^2}{2N}$ $\quad \Delta L = \text{const.}$

$\mathbf{X} = (S_V, V_V, N_{1V}, N_{2V}, S_L, V_L, N_{1L}, N_{2L})$

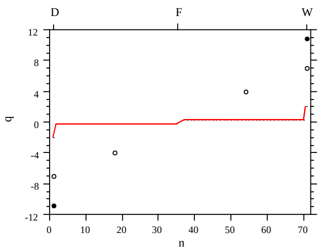
$\mathbf{M}_S = (8 \times 8)$

…but simplifies using equilibium equations to

$L_S = \sum_{k=1}^{N} D_S^k$

$D_S^k = \frac{\sqrt{C_r^k}}{T^k} \Delta T$

Optimum : all D_S^k equal



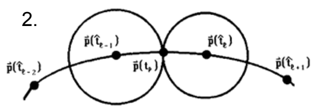
Min losses in adaptive coding

source p(t) → encoder (t) → channel → decoder (t) → receiver

1. How many code changes?
2. When to change?
3. Which code in segment?

3. E.g. Huffman code

2.



1.

$K \propto \sqrt[3]{r\tau L^2}$

$C = \frac{3}{2} C_{\text{switch}} + \frac{1}{3} C_{\text{excess bits}}$

Probabilistic description

Metric : $S(p_i) = -\sum p_i \ln p_i, \quad \mathbf{Y} = -(\ln p_i + 1), \quad \mathbf{M}_S = \left(\frac{1}{p_i}\right)$

Length : $L = \int \sqrt{d\mathbf{p}^t \, \mathbf{M} \, d\mathbf{p}}$

Loss : $R = r \left[\sum_{j=1}^{K} \sum_{i=1}^{m} p_i^j (-\ln \overline{p}_i^j) - \int_0^\tau H(\mathbf{p}(t)) \, dt \right]$

Delayed adjustment in economics

Utility fcn. moves faster than the market

Loss W $\geq$ L^2/T

L total length of change, T duration

Example:

Cobb-Douglas utility fcn. $U(x,y) = x^a y^b$

Geometry flat (spiral) in (r,θ)

$$L[(x_1,y_1),(x_2,y_2)] = \sqrt{(x_2-x_1)^2 + (y_2-y_1)^2} \quad \text{if } |\theta_1 - \theta_2| \leq \pi$$

$$L[(x_1,y_1),(x_2,y_2)] = \sqrt{x_1^2 + y_1^2} + \sqrt{x_2^2 + y_2^2} \quad \text{if } |\theta_1 - \theta_2| > \pi$$

Simulated annealing

State space / universe: $\Omega=\{\omega\}$

Energy / objective function: $E(\omega)$

Neighborhood: $N(\omega)$

Temperature schedule / control: $T(t)$

Metropolis algorithm:

1. choose prospective $\omega' \in N(\omega)$

2. accept ω' with probability $P_{acc} = \begin{cases} 1 & \text{if } \Delta E \le 0 \\ e^{-\Delta E/T} & \text{if } \Delta E > 0 \end{cases}$

Annealing schedule

Originally suggested:

$T(t) = a \exp(-t/b)$

$T(t) = a/(b+t)$

$T(t) = a/\ln(b+t)$

Adaptive schedule: $\frac{dT}{dt} = -\frac{vT}{\varepsilon\sqrt{C}}$ or $\frac{\langle E\rangle - E_{eq}(T)}{\sigma} = v$

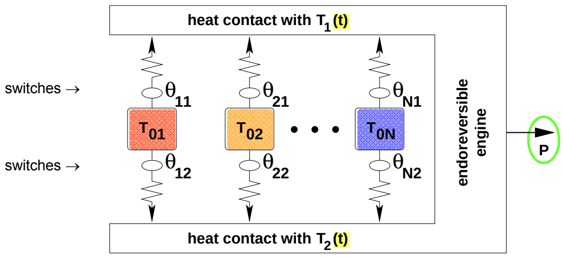
From ensemble

$$Z(T) = \sum_i p_i \exp(-E_i/T)$$

$$E(T) = T^2 \frac{d\ln Z}{dt}$$

$$C(T) = \frac{dE}{dT} = \frac{\langle(\Delta E)^2\rangle}{T^2}$$

Multi-source endoreversible engine



Averaged non-linear optimization

- Optimal controls are piecewise constant fcns. taken from
- m+1 possible values where
- m number of constraints

Thus:

- T_1 and T_2 are time-independent
- m=1 $\Rightarrow$ just 2 possible values for T_1 and T_2 (T_h and T_c) and for $\theta_{i\alpha}$ (0 and 1)

Possible solutions

$\theta_{i\alpha}=1$ if $T_h<T_{0i}$ HOT

$\theta_{i\alpha}=0$ if $T_c<T_{0i}<T_h$ temperate

$\theta_{i\alpha}=1$ if $T_{0i}<T_c$ COLD

i.e. *hot and cold reservoirs are constantly used, temperate ones never*

Recap of some finite-time thermo tools

- Curzon-Ahlborn engine
- Generalized potentials
- Criteria of performance
- Thermodynamic length
- Optimal control
- Averaged non-linear optimization

References

B. Andresen: Current Trends in Finite-Time Thermodynamics; Angew. Chem. Int. Ed. **50**, 2690-2704 (2011).

B. Andresen: Aktuelle Trends in der Thermodynamik in endlicher Zeit; Angew. Chem. **123**, 2742-2757 (2011).

T. A. Bak, P. Salamon, B. Andresen: Optimal behavior of consecutive chemical reactions A<=>B<=>C; J. Phys. Chem. A **106**, 10961-10964 (2002).

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FTT problem

Find the metric matrix $-D^2P = -\frac{\partial^2 S}{\partial X_i \partial X_j}$

in statistical mechanics, i.e. based on

$$S = -\sum_i p_i \ln p_i$$