Hans Renata

Maximum Entropy Production Principle

Baran Group Meeting
02/13/2010

A Brief Review of Thermodynamics Laws

The first law of thermodynamics/ the law of conservation of energy:

"The heat dQ, which is put into a system, is consumed for the work dW done by the system over external bodies and the change of the internal energy of the system dU"

$$dQ = dW + dU$$

The second law of thermodynamics:

"The entropy of an isolated system increases in the course of a spontaneous change"

$$\Delta S_{tot} > 0$$
$$T\,dS = dQ$$

Alternative formulations of the second law:

"It is impossible to convert heat completely into work in a cyclic process"

"In the neighborhood of any given state of any closed system, there exist states which are inaccessible from it along any adiabatic path, reversible or irreversible"

Hatsopoulos and Keenan's formulation:

"When an isolated system performs a process after the removal of a series of internal constraints, it will reach a unique state of equilibrium: this state of equilibrium is independent of the order in which the constraints are removed."

Statistical thermodynamics definition of entropy:

$$S = -k_B \Sigma\, p_i \ln p_i \quad \text{or} \quad S = k_B \ln W$$

Note that this definition bears strong resemblance to the term "Shannon entropy" in information theory

Interesting quotes regarding thermodynamics:

"It is the only physical theory of universal content, which I am convinced, that within the fraomework of applicability of its basic concepts will never be overthrown." - Einstein

"But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation." - Eddington

Some Metaphysical Ruminations...

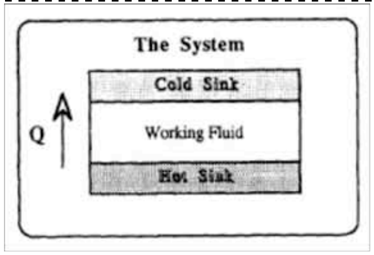
Recall Descartes' *Meditations on First Philosophy:*
- "Clear and distinct idea" of mind as thinking thing, and body as an extended, non-thinking thing
- The immaterial mind and the material body, though distinct as they are, causally interact

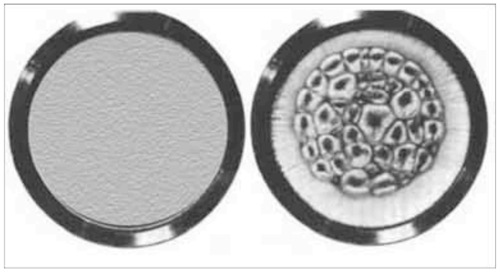
Kant's *Critique of Judgement* also calls for "autonomy of biology" from physics, or the dualism between living things and their environments

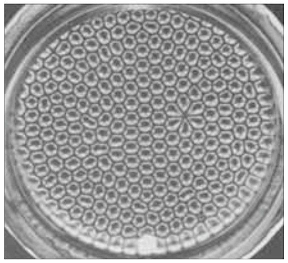
Erwin Schroedinger in "*What is Life?*"

"But, to reconcile the high durability of the hereditary substance with its minute size, we had to evade the tendency todisorder by 'inventing the molecule', in fact, an unusually large molecule which has to be a masterpiece of a highly differentiated order, safeguarded by the conjuring rod of quantum theory... Life seems to be orderly and lawful behavior of matter, not based exclusively on its tendency to go over from order to disorder, but based partly on existing order that is kept up."

Benard Cell Experiment







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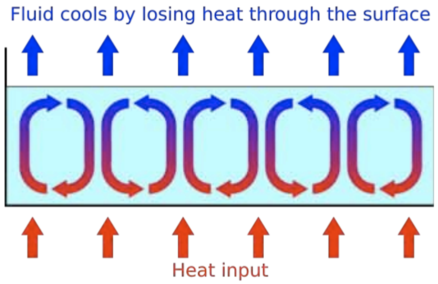
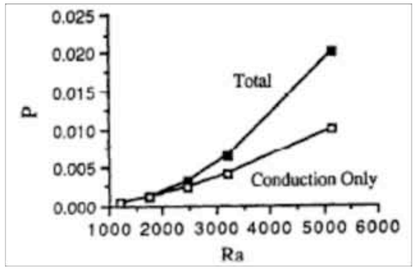
Benard Cell Experiment (Contd...)

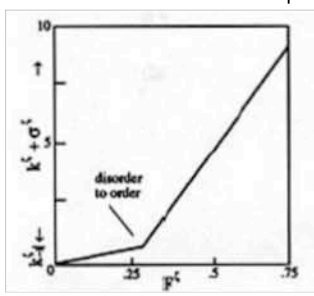




Schroedinger proposed that living systems exist in nonequilibrium thermodynamics and they take energy from outside themselves, and process it to produce a lower entropy state within themselves. In the words of Schneider and Kay, "Life can be viewed as a far from equilibrium dissipative structure that maintains its local level of organization, at the expense of producing entropy in the larger system of which it is part."

Schneider ED, Kay JJ, Mathl. Comput. Modelling, 1994, 19, 25-48

Swenson took a step further by stating "Ordered flow must be more efficient at dissipating potentials than disordered flow."



Maximum Entropy Production Principle

The system will select the path, or assembly of paths, out of otherwise available paths, that minimize the potential or maximize the entropy at the fastest rate given the constraints.

Swenson's 'proof', however, consists of the following thought experiment:

Consider a warm mountain cabin cold, snow-covered woods. With no opening, heat transfer happens mainly via conduction. However, opening a door or a window would provde a new means of transfer via convection and the system will "seize" this opportunity.

"His arguments cannot be viewed as rigorous, but they are sufficiently interesting... One cannot but admire his intuition." (Martyushev LM, Seleznev VD, Phys. Rep. 2006, 426, 1-45)

A Mathematical Take... (Ziegler's Approach)

Employs nonlinear thermodynamics, where thermodynamic forces are expressed as functions of flux densities ie.

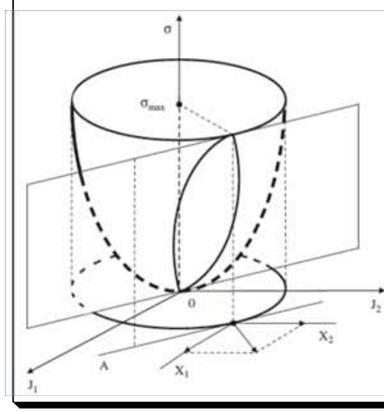
$$\sigma(J_i) = \sum_k X_k(J_i)J_k.$$

Ziegler's proposal:
If irreversible force X is prescribed, the actual flux J, which satisfies the above condition, maximizes the entropy production

Approaches this problem by using Lagrange multipliers method, which gives

$$\delta_J\left[\sigma(J_k) - \mu\left(\sigma(J_k) - \sum_i X_i J_i\right)\right]_X = 0$$

Graphical Interpretation



It can be shown that

$$X_i = \lambda \partial\sigma/\partial J_i$$

$$\lambda = \sigma\left(\sum_i \frac{\partial\sigma}{\partial J_i} J_i\right)^{-1}$$

where $\lambda = (\mu-1)/\mu$. This is known geometrically as orthogonality conditions. Solution obtained thus far, however, is not unique. The case where unique solution exists will correspond to MEP.

Another approach was also developed by Dewar which employed Jaynes' formalism in in information theory, but this seems to apply only to nonlinear stationary states. Furthermore, it has been refuted by several authors due to unjustified assumptions employed.

- Reviewed in Martyushev LM, Seleznev VD, Phys. Rep., 2006, 426, 1-45
- Jaynes ET, Phys. Rev., 1957, 106, 620
- Jaynes ET, Phys. Rev., 1957, 108, 171
- Dewar R, J. Phys. A: Math. Gen., 2003, 36, 631
- Grinstein G, Linker R, J. Phys. A: Math. Theor., 2007, 40, 9717-9720

Note that there exists as well "theorem of minimum entropy production" put forth by Prigogine, but the two should not be mistaken as contradictory principles; MEP applies to all range and appears to be universal, whereas Prigogine's principle only applies to the near equilibrium linear range.

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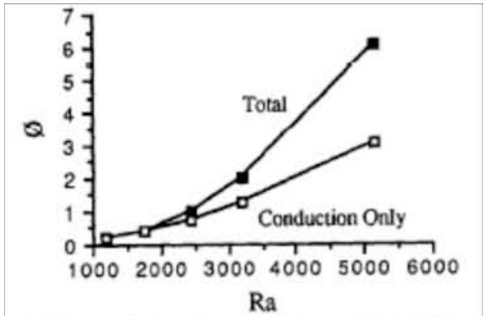
More results from Benard cell experiment



(c) Exergy destruction rate (φ) vs. gradient (Ra).

Schneider and Kay put forth the following proposal:
"The thermodynamic principle which governs the behavior of systems is that, as they are moved away from equilibrium they will utilize all avenues available to counter the applied gradients. As the applied gradients increase, so does the system's ability to oppose further movement from equilibrium."

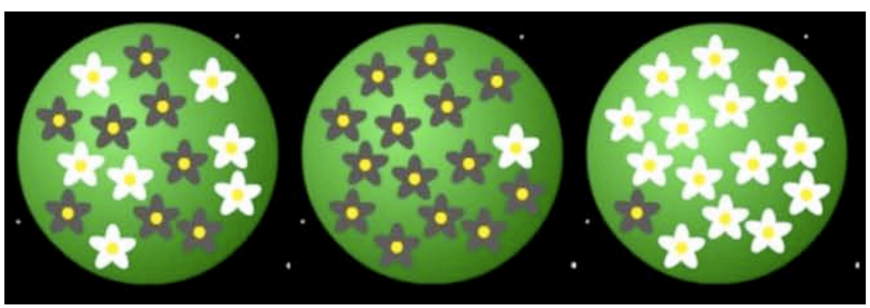
Recall: LeChatelier's principle

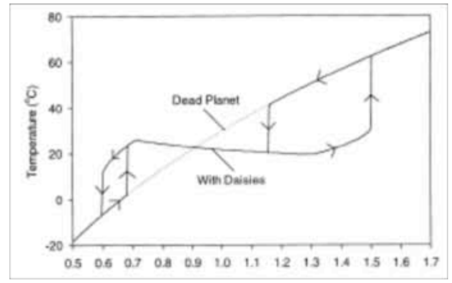
The Gaia Hypothesis (Lovelock, 1972)

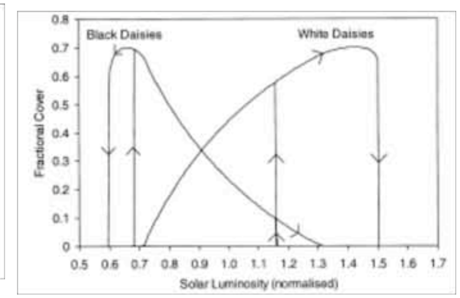
"Life, or the biosphere, regulates or maintains the climate and the atmospheric composition at an optimum for itself."

-Suggesting homeostasis or feedback mechanism
-Criticism of the improbability of altruism on a global scale by Richard Dawkins

Development of Daisyworld (A Numerical Model) (Watson, Lovelock)



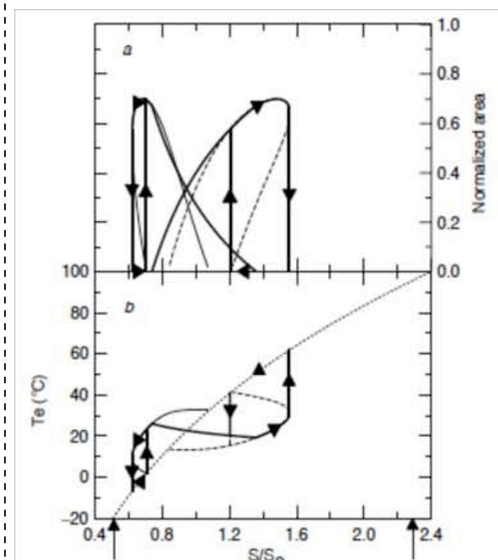




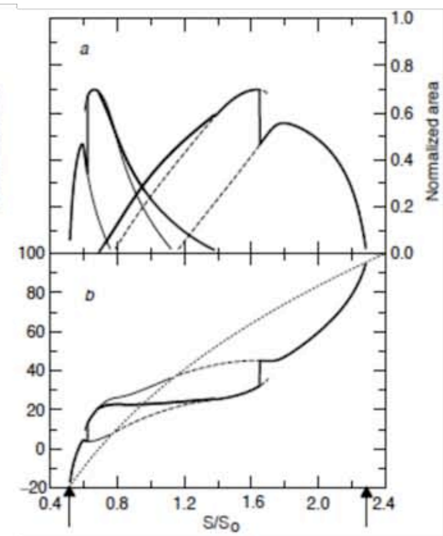
The proposition of the authors: that biosphere works to regulate climate, making it habitable over a certain range of solar luminosity.

Updated models have been developed, which involve rabbits, foxes and other species. They seem to indicate that biodiversity is desirable.

Incorporation of MEP in Daisyworld Simulation
(Pujol T, J. Theor. Biol. 2002, 217, 53-60)



No MEP



With MEP

Application of MEP to Daisyworld predicts:
1. A wider range of solar insolation viable for biota growth
2. A more stable temperature trajectory
3. No hysteresis loop (No bi-stability of the system)

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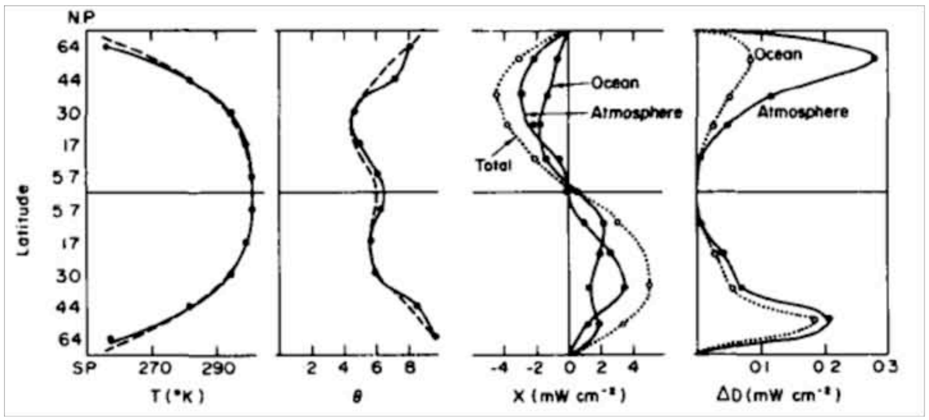
Paltridge's Explanation of the Global State of the Present Climate by MEP Principle

States that the earth should have such an average annual climate that the thermodynamic dissipation is a maximum (or among the great variety of states, the system will choose the one with the maximum entropy production)

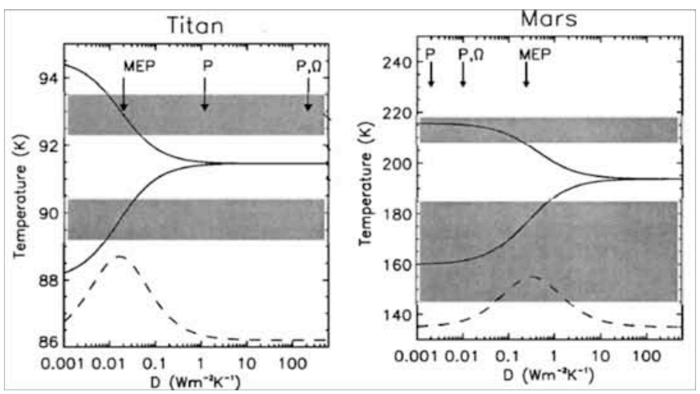
Working model:
- Set up a simple 10-box model for the entire globe
- Assume an energy balance condition for each box (for the atmosphere and the ocean)
- Three unknowns variables: temperature (T), cloud cover (θ) and meridional flux F
- Introduce additional constraint:

$\sigma = - \Sigma\, \Delta F_i / \langle T_i \rangle =$ **maximum**

Result



The same tenet has been extended to Titan and Mars (Lorenz et al, Geophys. Res. Lett., 2001, 28, 415-418



A 2-Dimensional Model of Climatic States Employing MEP
(Pujol T, Llebot JE, Tellus, 2000, 52A, 422-439)

Working model:
- 1024 boxes that cover the entire globe, with 32 latitudinal and 32 longitudinal divisions
- Subdivided into oceanic and atmospheric regions
- Four free variables: temperature, cloud cover, convective heat fluxes and advective heat fluxes
- Introduce additional constraint of entropy maximization, but optimization procedure differs from Paltridge's method in order to save computational cost*
- Compare results obtained with different types of entropy maximized

*Paltridge has previously done a 20 x 20 2-dimensional box model as an extension of his 1-dim model (Paltridge GW, Q. J. R. Meteorol. Soc., 1978, 104, 927-945)

Variable	Expression extremized			Observations
	σ_p	σ_m	σ_t	
T (K)	286.7	287.0	286.7	288[1]
ϑ	0.583	0.615	0.586	0.622[2]
$LE + H$ (W m^{-2})	99.2	99.3	99.2	99.4[1]
H_{LT} (W m^{-2})	240.2	240.2	240.2	240[3]
α_p	0.300	0.305	0.301	0.300[3]
σ_p (W m^{-2} K^{-1})	0.003	0.004	0.003	0.007[1]
σ_m (W m^{-2} K^{-1})	0.067	0.069	0.067	0.071[1]
σ_t (W m^{-2} K^{-1})	1.207	1.207	1.207	1.23[4]

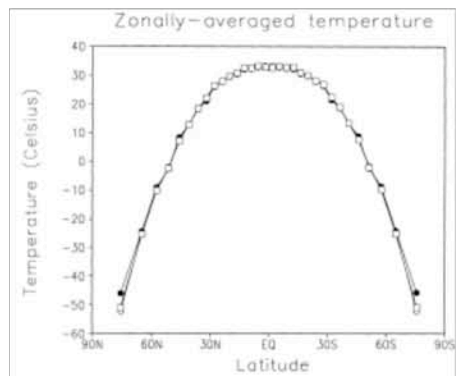


Fig. 3. Zonally-averaged temperature by maximizing σ_p (open circles), σ_m (closed circles) and σ_t (open squares).

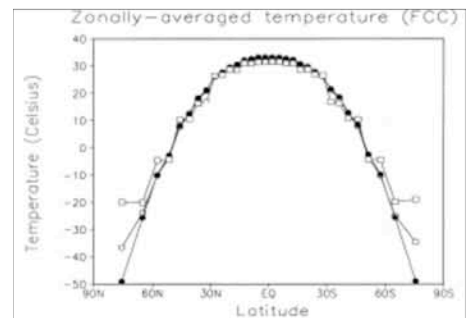


Fig. 7. Zonally-averaged distribution of temperatures with fixed cloud-cover by maximizing σ_p (open circles), σ_m (closed circles) and σ_t (open squares).

The authors also performed several simulations for pre-industrial conditions and possible future scenarios, including both aerosol and greenhouse effects.

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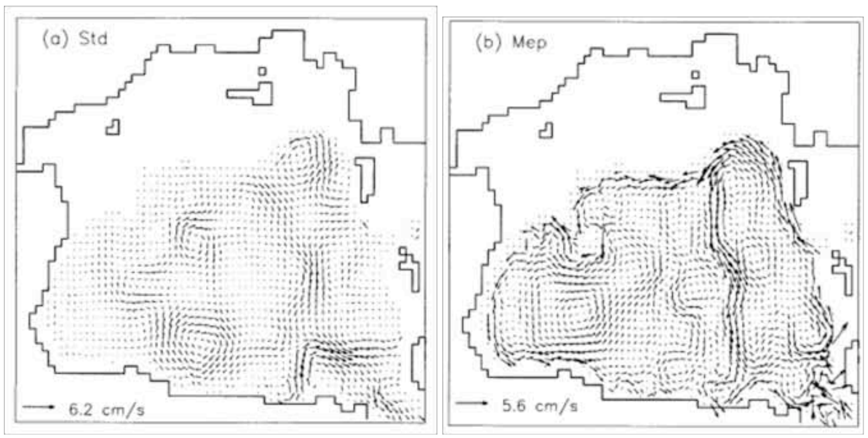
MEP in Oceanography

Attempt of parameterization of eddy fluxes based on MEP principles in inviscid shallow water equations.

Results obtained with MEP better resemble those derived from observation.
Estimates of water transport "fall well into the range given by studies based on observations."

Polyakov I, J. Phys. Oceanogr. 2001, 31, 2255-2270

Ten-Year Mean Ocean Velocity Results



Velocity Observed from Observations

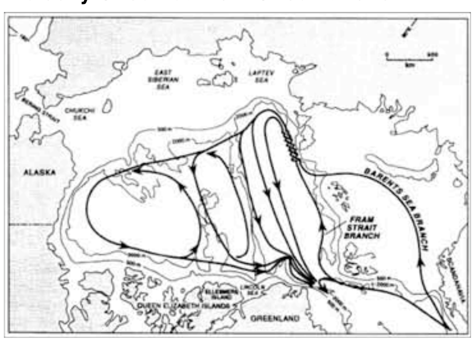
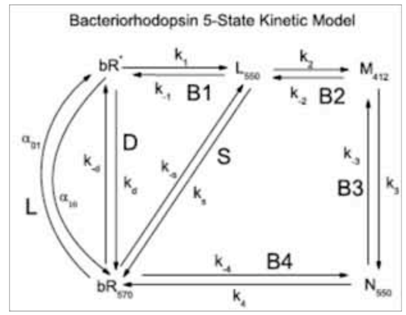


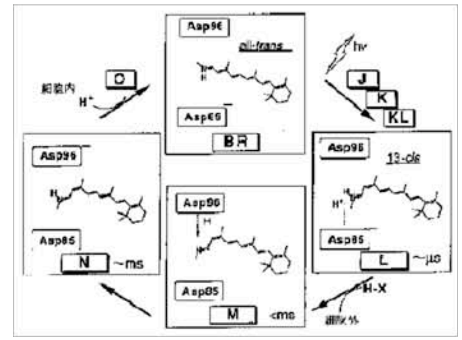
TABLE 2. Water transport (Sv) through Fram Strait.

Author(s)	Inflow	Outflow
From observations		
Shpaikher (1973)	3.6	
Aagaard and Greisman (1975)	7	7
Nikiforov and Shpaikher (1980)	2–5	3
Hanzlick (1983)	5.6	
Rudels (1987)	2	
Heinze et al. (1990)		0.7–1.0
Aagaard et al. (1991)		1.3–2.0
From modeling studies		
Nazarenko et al. (1998)		
without Neptune	1	1
with Neptune	6	6
Zhang et al. (1998)		
without restoring	1.2	2.8
with salinity restoring	1.9	3.3–3.6
Karcher and Oberhuber (1999, manuscript submitted to *J. Geophys. Res.*)	0.4–1.9	
This study		
Std experiment	0.4	3.9
Mep experiment	3.4	2.3

Application of MEP in Photosynthesis Model

- Employs Hill's formalism for cyclic enzymatic reactions with non-equilibrium treatment of light absorption transition
- Optimize forward rate constants in irreversible transitions via iterative procedure: recalculate entropy production maximum and optimal rate constants in each such transition by using optimal values of other rate constants until these values do not change anymore.





Modelling Results

MODELS	VI	VII
OUTPUT		
η_{opt} (%)	10.34	10.52
η_{max} (%)	10.46	10.74
ϕ (%)	93.28	94.90
A/A_{oc} (%)	97.37	97.82
X_L (kJ/mol)	4.36	3.61
J(L) (s^{-1})	71.75	60.07
P_{tot} ($kJmol^{-1}T^{-1}s^{-1}$)	36.66	30.63
P(L)/P(tot) (%)	2.86	2.38
k_1 (optimal) (s^{-1})	4.73×10^9	3.22×10^9
k_2 (optimal) (s^{-1})	2.01×10^4	4590
k_3 (optimal) (s^{-1})	1000	812
k_4 (optimal) (s^{-1})	1060	425
INPUT		
α_{01} (s^{-1})	100	100
K(B1)	10^8	10^8
K(B2)	10^{11}	10^{15}
K(B4)	10^8	10^4
K^0_I/K^0_E	5×10^{-23}	5×10^{-23}
k_s (s^{-1})	1000	100
k_d (s^{-1})	10^8	10^8

Experimental Results

Experiment No.	Quantum yield
1	0.90
2	1.02
3	1.01
4	1.07
5	0.89
mean 0.98 ± 0.036	

Core complex	E_m P/P$^+$ (mV)	EMF = A_ν (meV)	Conversion force ratio from the energy of the photon to A_ν (%)
YM210H	427	200	14.1
YM210	467	220	15.5
YM201F	487	190	13.4
YM210L	493	183	12.9
YM210W	512	166	11.7

Observed experimental rate constants from a similar model:

$$(k_1)_{exp} = 1.67\times10^5 s^{-1} \quad (k_2)_{exp} = 3.03\times10^4 s^{-1}$$
$$(k_3)_{exp} = 556 s^{-1} \quad (k_4)_{exp} = 233 s^{-1}$$

Juretic D, Zupanovic P, Comput. Bio. Chem., 2003, 27, 541-553

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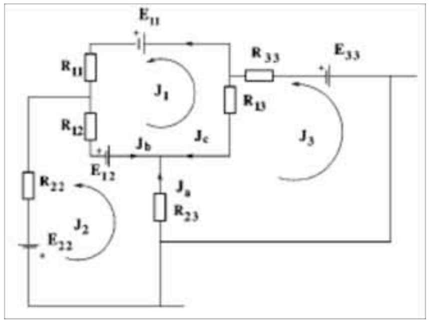
Maximum Entropy Production Principle

MEP and Kirchhoff's Voltage Law

Kirchhoff's Voltage Law states that the algebraic sum of EMFs of the sources is equal to the sum of potential differences in the loop. In summation terms:

$$\sum_j E_{ij} = R_{ii}J_i + \sum_j R_{ij}(J_i - J_j)$$



Procedures taken:
- Express rate of entropy production as a Taylor expansion of current and substitute this to the rate of heat production

$$\frac{dQ}{dt} = \sum_i R_{ii}J_i^2 + \frac{1}{2}\sum_{ij} R_{ij}(J_i - J_j)^2.$$

- Obtain the rate of energy released by EMFs and make use of the first law of thermodynamics

$$\frac{dQ}{dt} - \frac{dW}{dt} = 0$$

to arrive at

$$\sum_i E_{ii}J_i + \frac{1}{2}\sum_{ij} E_{ij}(J_i - J_j) = \sum_i R_{ii}J_i^2 + \frac{1}{2}\sum_{ij} R_{ij}(J_i - J_j)^2$$

- Now the task at hand is to maximize the rate of heat production given the constraint of the first law of thermodynamics
- Employ Lagrange multipliers method to do so
- It can be shown that this approach will lead to

$$\sum_j E_{ij} = R_{ii}J_i + \sum_j R_{ij}(J_i - J_j)$$

Zupanovic P, Juretic D, Phys. Rev. E, 2004, 70, 056108

MEP in Crystal Growth Theory

In 1990, Ben-Jacob and Garik posited the question, "Is there a general principle that allows one to predict the mode of growth for specified conditions from the available morphologies, and thus to explain the morphology diagram?"

They proposed the following criterion: "That the dynamically selected morphology is the fastest growing one."

Ben-Jacob E, Garik P, Nature, 1990, 343, 523

Hill considered a generalized crystal formation with a driving force proportional to either super-saturation, or pressure. Rate of crystallization is expressed as a linear function:

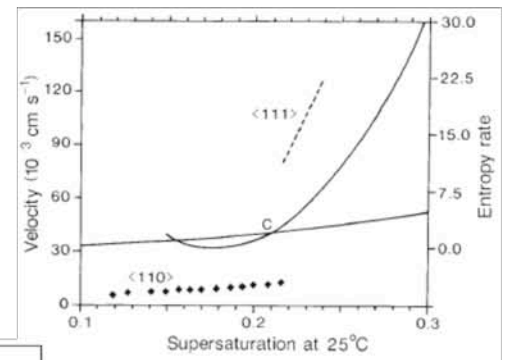
V = L(X-Θ)

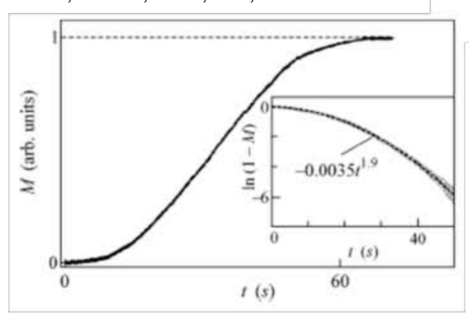
where L = rate coefficient, (X-Θ) = free energy difference

Dissipation is given by
$\phi = \mathbf{L(X\text{-}\Theta)^2}$

Calculation can then be performed on known data from experiments. In this case, it is the change of morphology between <110> and <111> dendritic forms of NH_4Cl. Crossover appears at a supersaturation of 0.21 (Observed discontinuity is at ~0.216)

Hill A, Nature, 1990, 348, 426-428





Martyushev and Axelrod took this observation a step further by positing the question on the relationship between S-shaped growth curve and MEP

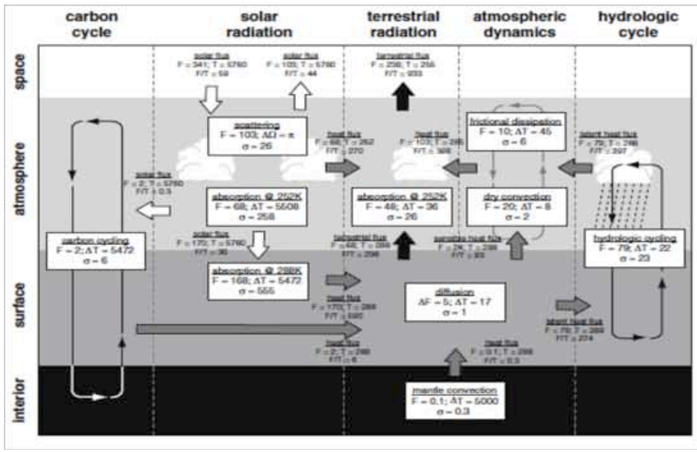
Martyushev LM, Axelrod EG, JETP Lett., 2003, 78, 476-479

Maximum Entropy Production Principle

Recall from Schroedinger's "What is Life?", the idea that life seems to defy the second law of thermodynamics....

As early as 1886, Boltzmann had suggested:

"The general struggle for existence of animate beings is therefore not a struggle for raw materials ... but a struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth... The products of this chemical kitchen constitute the object of struggle of the animal world."



We have earlier seen 'dissipative structures' as gradient dissipators, eg. Benard cell experiment. Tornadoes and hurricanes can also be thought of as performing the same 'function'.

But how about living systems as gradient dissipators?

Lotka, 1922:
"Natural selection tends to make the energy flux through the system a maximum, so far as compatible with the constraints to which the system is subject... The question was raised, whether, in this, man has been unconsciously fulfilling a law of nature, according to which some physical quantity in the system tends toward a maximum."

Schneider and Kay stated the following:

"We suggest that living systems are dynamic dissipative systems with encoded memories, the gene with its DNA, that allow the dissipative processes to continue without having to restart the dissipative process via stochastic events. Living systems are sophisticated mini-tornados, with a memory, (its DNA), whose Aristotelian "final cause" may be the second law of thermodynamics... it represents the emergence of yet another class of processes whose goal is the dissipation of thermodynamic gradients. Life should be viewed as the most sophisticated (until now) end in the continuum of development of natural dissipative structures from physical to chemical to autocatalytic to living systems."

Ulanowicz and Hannon put forth the following propositions in 1987:

1. The second law, in combination with the observed increase in order of living systems, implies that life increases the amount of entropy generated in the universe.
2. Positive feedback, a fundamental element of the life process, serves to augment the total dissipation by a living system.
3. Living systems generate more entropy because they are more effective in utilizing energy than are the ambient physical systems.
4. Living systems generate more entropy than their ambient environment by projecting a lower albedo at shorter electromagnetic wavelengths and generating greater emission at longer wavelengths.

Disclosure from Zotin (the following passage is taken from Martyushev and Seleznev review):

"According to Zotin, the temperature inevitably rises as the energy exchange increases, leading to denaturation of proteins. Nature copes with this problem first by appearance of heat regulation in animals and then by the coming of the man. The man began to use energy sources not only inside, but also outside the organism... Thus, the appearance of the man and the development of the civilization may be viewed as a consequence of Lotka's principle and MEPP. If the man did not appear during the evolution, some species would occupy his place sooner or later."

"Man is condemned to be free"

- Jean-Paul Sartre, "Being and Nothingness", 1943