Thermodynamics
Past, Present and Future

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Contents

- Historical remarks, foundations of TD,
- How to present the 3 fundamental laws now,
- Key role of TD in the physics of 20th century (quantum theory, low temp.& high energy physics, black holes, BIG BANG etc.),
- TD of selforganization and evolution,
- Evolution principles, entropy and information,
- TD of information and life,
- Exotic applications, Mbar plasmas
- Open problems, Conclusions.

Science in Berlin19th century:

Impact of Hegel in philosophy, Humboldt in natural science, Magnus in physics.

Hegels Grabmal, Dorotheenstädt. Friedhof Berlin

Foundation of the 3 basic laws - Role of schools in Berlin-

- First Law:
- Hermann Helmholtz(1821-1894) studied in B. physiology and physics, was working as a military surgeon in Potsdam, made in free time exp. in Magnus lab with rotting, muscular activity, member of “Berliner Physikalische Gesellschaft”, reported his conclusions 1847.
- Helmholtz (1847): “Über die Erhaltung der Kraft, eine physikalische Abhandlung.”

Überdie Erhaltung derKraft
eine physikalische Abhandlung
Dr.H. Helmholtz

Über die Erhaltung der Kraft,

eine physikalische Abhandlung

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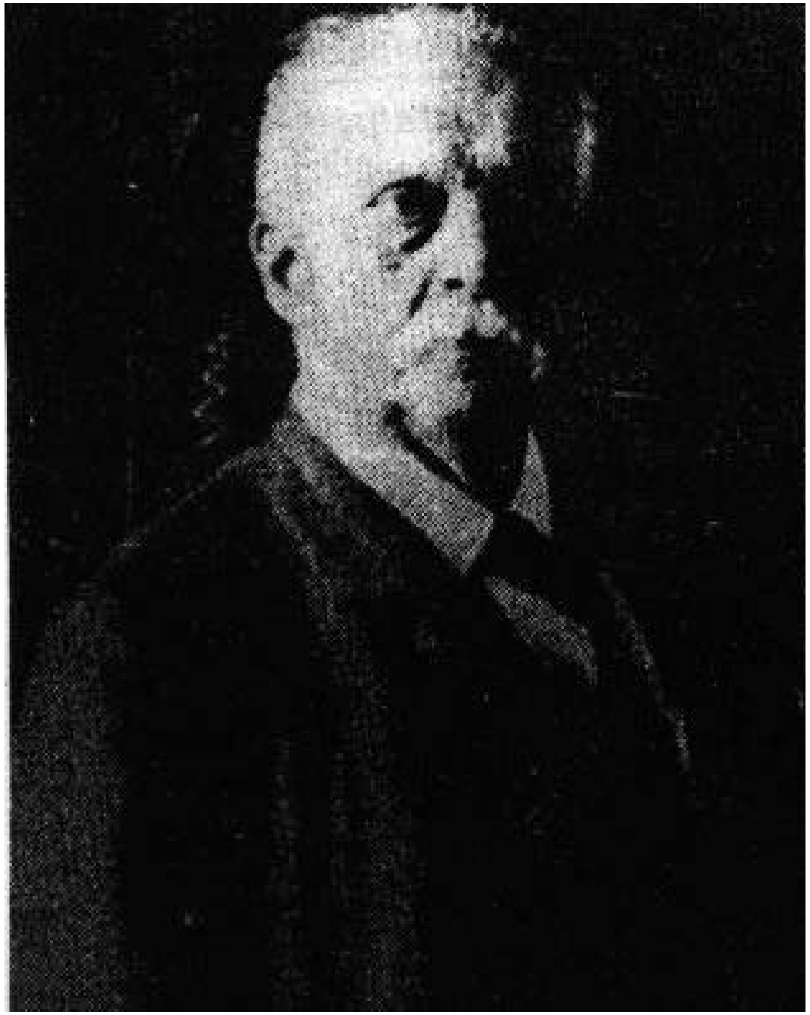
von

Dr. H. Helmholtz.

Helmholtz: founder of a great school in physics 1871-1933



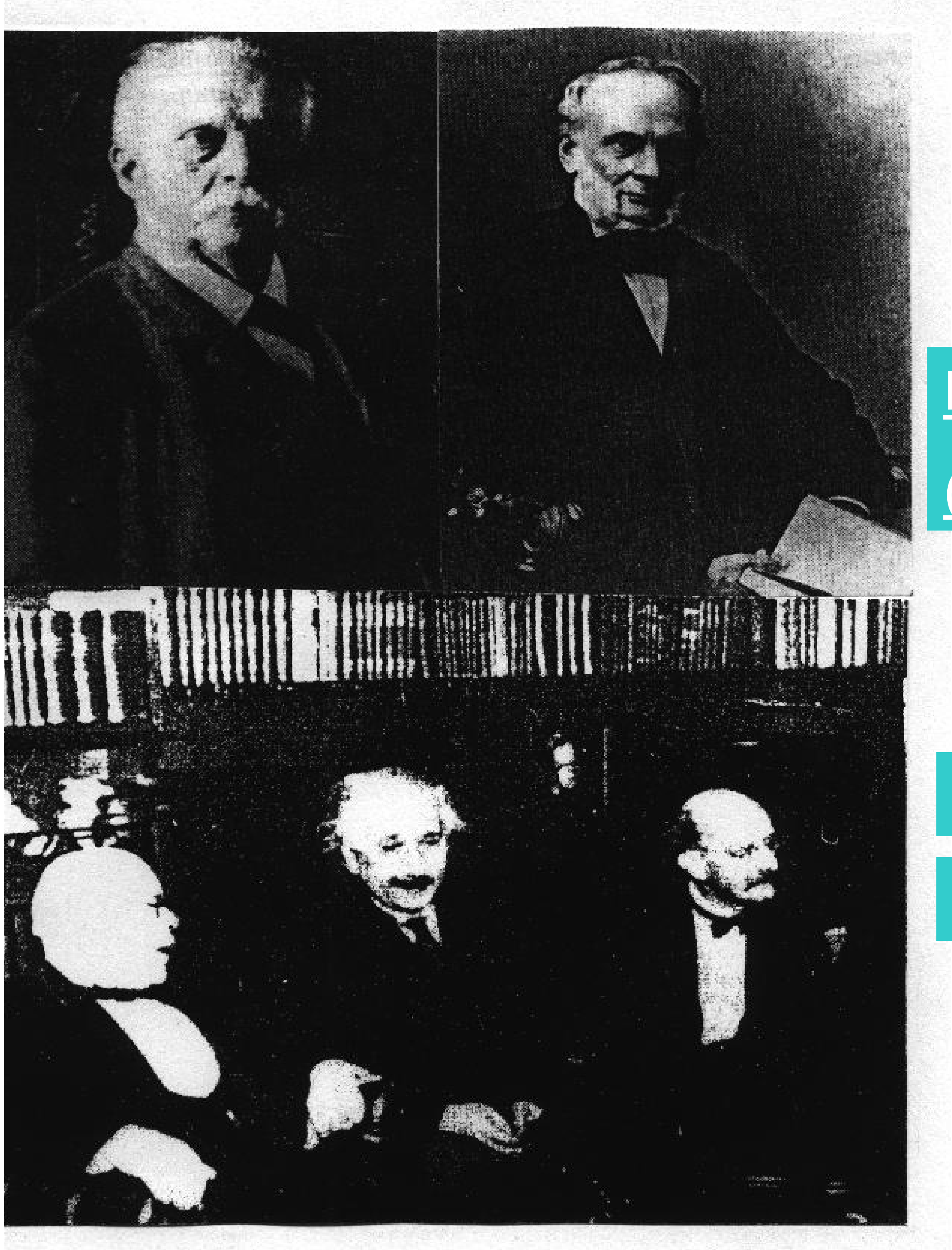
- Since 1871 Professor of physics, director of institute near Reichstag, calls to Kirchhoff, Planck.
- Very influential: Reichskanzler für Physik
- formed a big school: Wien, Kurlbaum, Blasius, Lummer, Paschen, Rubens, Börnstein

Foundation of the 2nd law:

- Rudolf Clausius (1922-1888) studied physics in Berlin (Dove,Magnus), as a member of Magnus seminar, reported 1848 on Helmholtz' and Carnots work.
- Clausius (1850): "Über die bewegende Kraft der Wärme und die Gesetze, die sich daraus ... ableiten lassen". Heat transfer from hot to cold bodies = transformation of energy!
- 1857/58 atomistic theory of heat,
- More general formulations 1865 $dS = d'Q/T$

Rudolf Clausius, the founder of the second fundamental law

- *1822 in Köslin (now Poland) sun of a teacher, gymnasium math Grassmann
- 1840 Berlin: physics and mathe Dove, Magnus, Steiner, Dirichlet.
- 1844 FW gymnasium, exp in Magnus lab (light diffraction)
- 1848 PhD Halle, 1850 habil 1855 Prof. ETH, + 1888



Helmholtz, Clausius

(and Kirchhoff)

The next generation:

Nernst, Einstein & Planck

Foundation of the third law

- In 1889 Planck was called to succeed Kirchhoff and to develope TD in Berlin,
- in 1905 Nernst accepted a call on a chair, soon after it he found the “missing stone”:
- The difference between internal energy and free energy $F = E - T S$ vanishes for $T \rightarrow 0$.
- Planck: “The entropy of TDS in equilibrium vanishes at the zero point of temperature:”

How to teach the 3 laws today ?

- **Zeroth law:** TDS have a special state, TD equilibrium. No changes after isolation! Exists a scalar, transitive variable TEMPERATURE **T,** two bodies in contact ---> T_1 = T_2.
- **First law:** TDS are charact by an extensive quantity ENERGY, which can neither be created nor destroyed, only exchanged. ENERGY can be converted to other forms (mechanical, chemical, electrical E, ...) or moved to other systems.

First law balance:
no production, exchange in different forms

$$dE = d_e E + d_i E, \qquad d_i E = 0,$$

$$d_e E = d'Q + d'A + \sum \mu_i dN_i;$$

in isolated systems: d E = 0, energy is conserved

What is energy ???

- **Poincare:** In every instance it is clear what energy is, and we can give at least a provisional definition of it; it is impossible however, to give a general definition ....
  One sees it dissolve before one's eyes, leaving only the words: There is something, that remains constant (in isolated systems).
- Note: A similar difficulty is with the definition of force in Newton's law !!!

The second law:

- TDS are characterized by another extensive quantity ENTROPY.
- ENTROPY can be created but never be destroyed !
- In irreversible processes, ENTROPY is gene-rated, in reversible proc it remains const.
- In isolated systems, ENTROPY is never decreasing!

The second law balance: destruction of S is impossible!

$$dS = d_e S + d_i S \ , \qquad d_i S \geq 0$$

$$d_e S = \frac{d'Q}{T} + \ldots$$

<u>The definition of d'Q is not unique !</u>

Gibbs - Helmholtz fundamental relation:

$$dE = TdS + \sum_k l_k dL_k + \sum_j \mu_j dN_j$$

The extensive variables energy, entropy, particle numbers & volume-type variables are not independent (Pfaffian form)

What is entropy ???

- **Modified Poincare:** In every instance it is clear what entropy is and we can give at least a provisional definition of it; it is impossible however, to give a general definition .... One sees it dissolve before one’s eyes, leaving only the words: There is something, that increases (in irreversible processes).
- Sometimes the entropy definition is quite unconventional e.g. S ~ A for black holes

PHYSICS of GRAVITATION

- Application of thermodynamical relations to stellar objects, black holes (S = A/4)
- phase transitions: disks/black holes
  (G. Neugebauer, Angular momentum in general relativity, GR 8.1)

$$TdS = dE - \Omega dJ - \mu dM$$

The third law:

- *Energy and entropy are finite for finite systems and bounded from below E>0, S>0.*
- *In the limit T ---> 0, the entropy as well as its derivatives with respect to extensive variables disappear asymptotically:*
- S --> 0, d S / d L_k ---> 0
- In the limit T ---> 0, internal energy E and free energy F coincide, specific heat etc. disappear!

UNIVERSALITY:

- The first and the second fundamental laws are valid for any macroscopic process in nature and society. May be, these are the only known laws which have a universal range of validity ?
- The third law is less fundamental, it is a law of thermal systems only (needs T). However it has deep implications for physical systems. Low temperature physics is of increasing importance !!!

The key role of TD in the 20th century physics

- QUANTUM THEORY,
- LOW TEMPERATURE PHYSICS,
- LARGE SCALE PHYSICS (the universe, stellar objects, black holes),
- SMALL SCALE PHYSICS (nuclei, elementary particles),
- BIOLOGICAL, ECOLOGICAL, SOCIAL SYSTEMS,
- INFORMATIONAL SYSTEMS.

First discoveries influenced by thermodynamics:

- QUANTUM THEORY:
  Planck’s first quantum hypothesis is essentially based on thermodynamic reasoning
- LOW TEMPERATURE PHYSICS: TD gives the whole direction of measurements and development of devices by Nernst, Lindemann, Kamerling-Onnes,.. and theoretical foundation by Einstein, Bose,...

“Das Berliner Kolloquium,

- wie dieses (von Magnus gegründete) wöchentliche Treffen genannt wurde, war kein Ort für müßiges Gerede und höfliche Umschreibungen ... Neben Nernst waren da Einstein, Planck, von Laue, Schrödinger, Hertz, Hahn und Meitner

- Das einzige, was für sie zählte war Physik, und es ging dabei hart her bei dieser Diskussion um Physik.

- Zitat nach Kurt Mendelssohn

List of big names in TD

- Planck, Nernst,
- Einstein, von Laue
- Kundt, Warburg, Drude
- Lindemann, Haber
- Caratheodory, Schottky
- Saha, Bose,
- Schrödinger,
- Szilard, v. Neumann
- Gamov,
- Delbrück,
- Eckardt, Meixner
- Prigogine, De Groot, Mazur

HIGH ENERGY PHYSICS:

- **Collisions of fast nuclei:** thermodynamic description using energy, temperature, entropy (HK 18 Physik mit schweren Ionen)

- **Elementary particle physics:** again thermodynynamic descriptions work (QCD phase diagram HK 15.3)

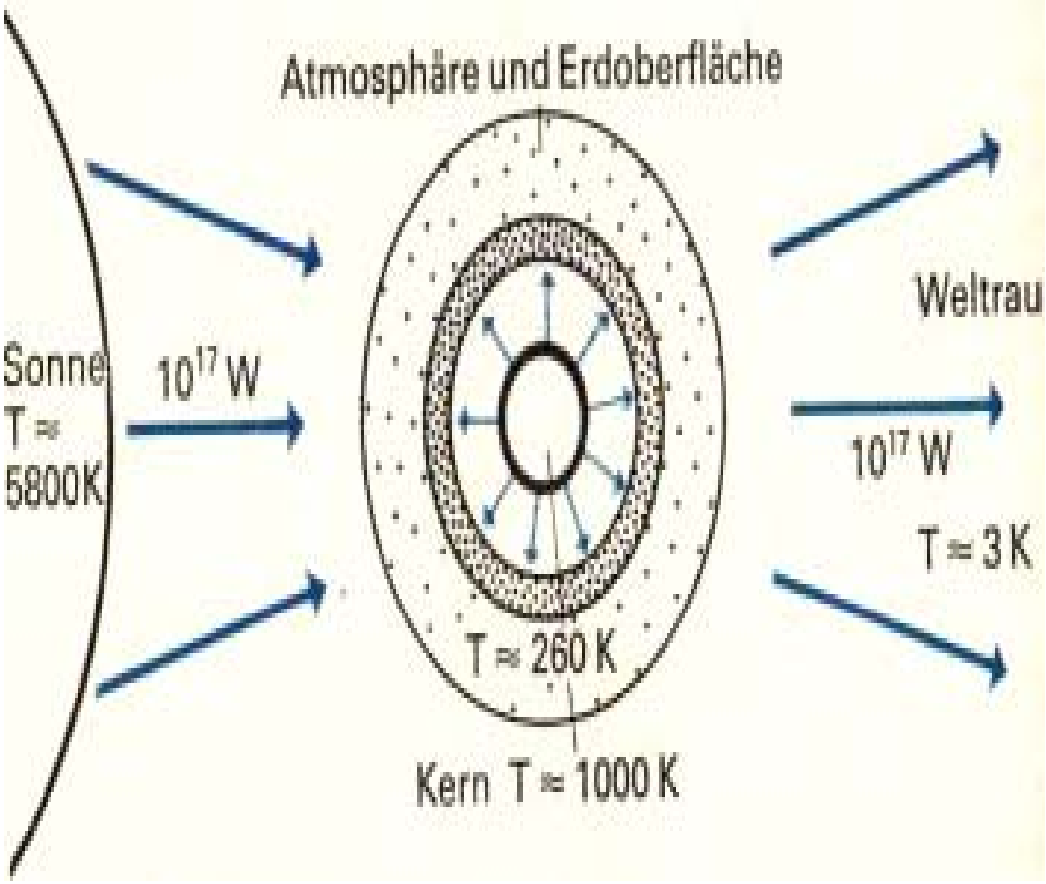
Physical theory of Self-organiz./evolution of the Universe

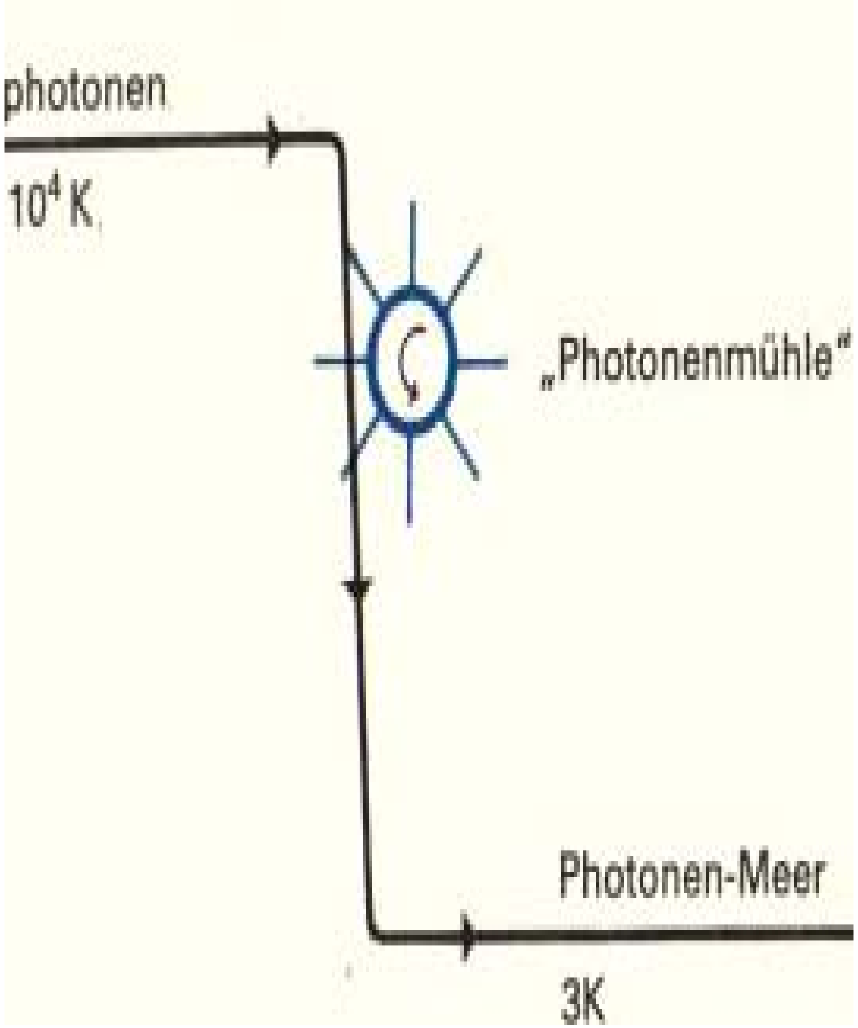
- Based on Einsteins General relativity theory and Friedmans model of an expanding Universe Alpher, Bethe, Gamow, Zeldovich invented the “BIG BANG”.
- The BIG BANG theory of the history of the UNIVERSE is essentially a thermo-dynamical theory based on thermo-dynamical relations applied to extreme cond at very exotic early stages of the expansion.

12 epochs of the Universe

- T ~ 1 / sqrt (t)
- 1. - 6. Story of the elementary particles: Physical vacuum (-43) leaving vacuum (-33) quark photon gas (-11) quark annihilation (-6) formation of electrons and nuclei,
- 6. decoupl of neutrinos
- 8. Story of He (synthesis of nuclei) x p+n =He
- 9. Story of atom formation H-atoms, He-atoms form a neutral gas, decoupling of the photons, independent evolution of 2 subsys- tems: matter -radiation, now 2.7 K Penzias/Wilson,
- 10. Matter self-structuring

11-12 Photon mill: Sun-Earth, EVO on earth, Selforganization

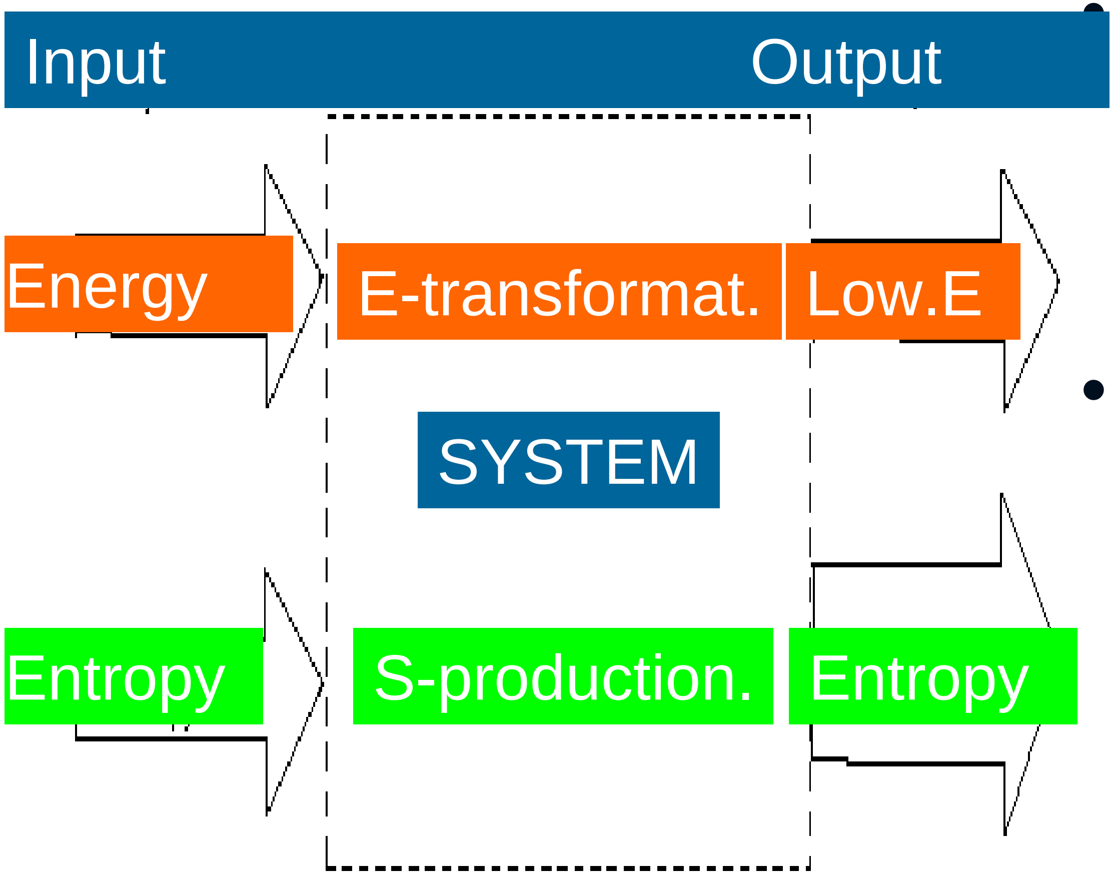




Thermodynamics of open systems Selforganization

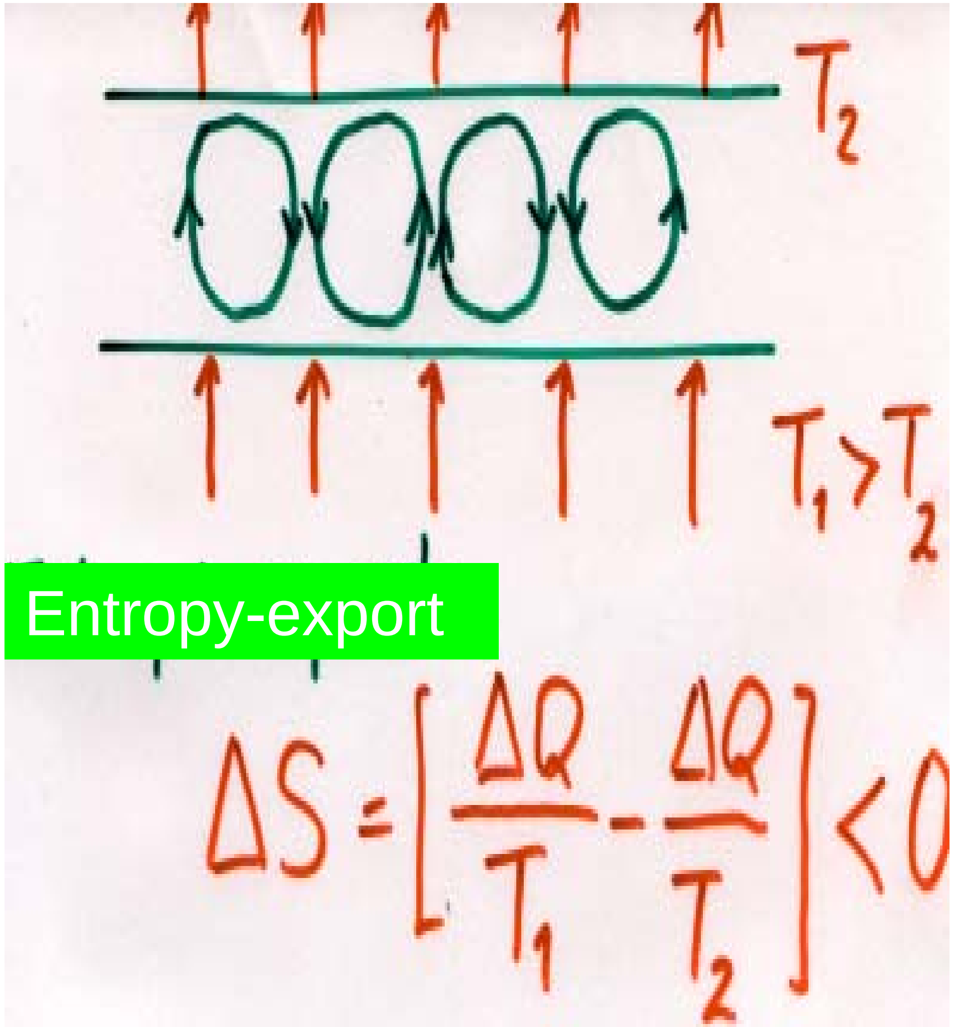
- Pioneers:Mayer/Boltzmann/Schrödinger
- Idea due to Schrödinger/Prigogine: Exchange with surrounding is relevant !
- In open systems with entropy export - formation of structures does not contradict the 2nd law
- $dS < 0$ requires $d_e S < 0$ export and $|d_e S| > d_i S$

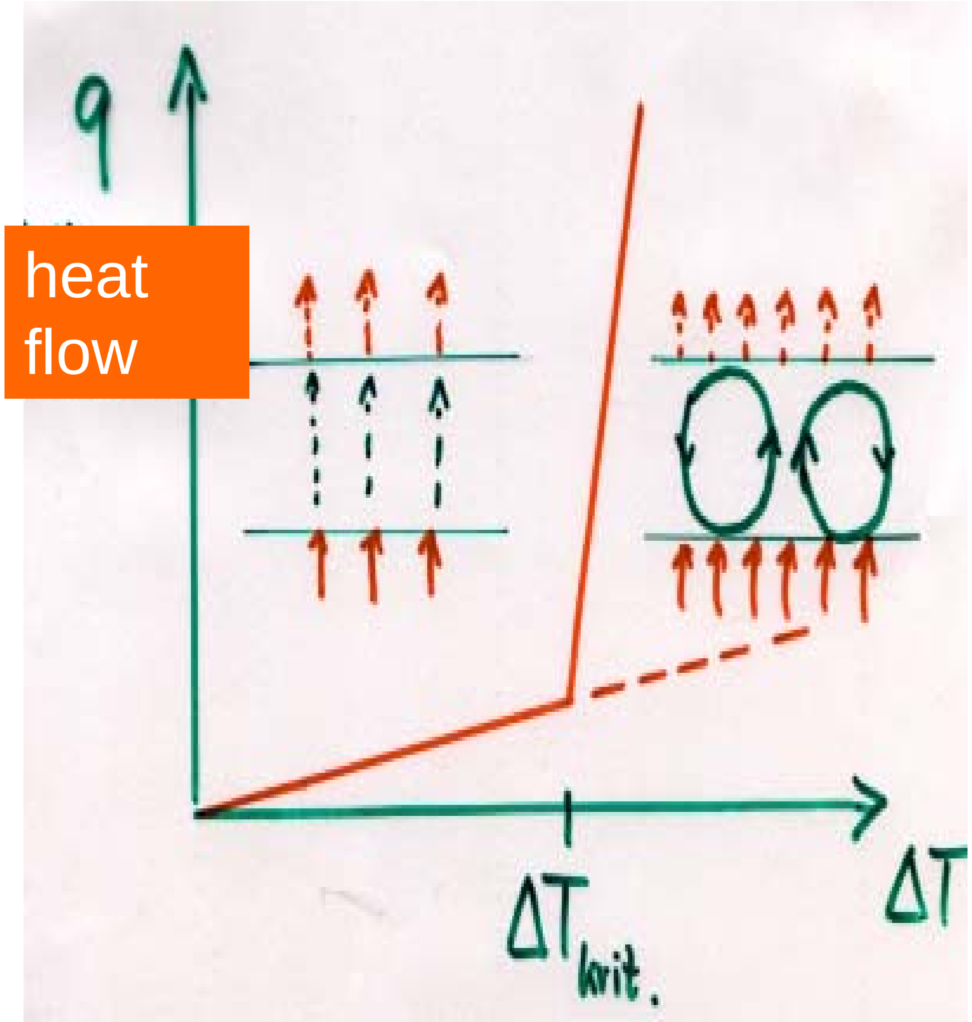
Open systems: energy-transform. entropy export



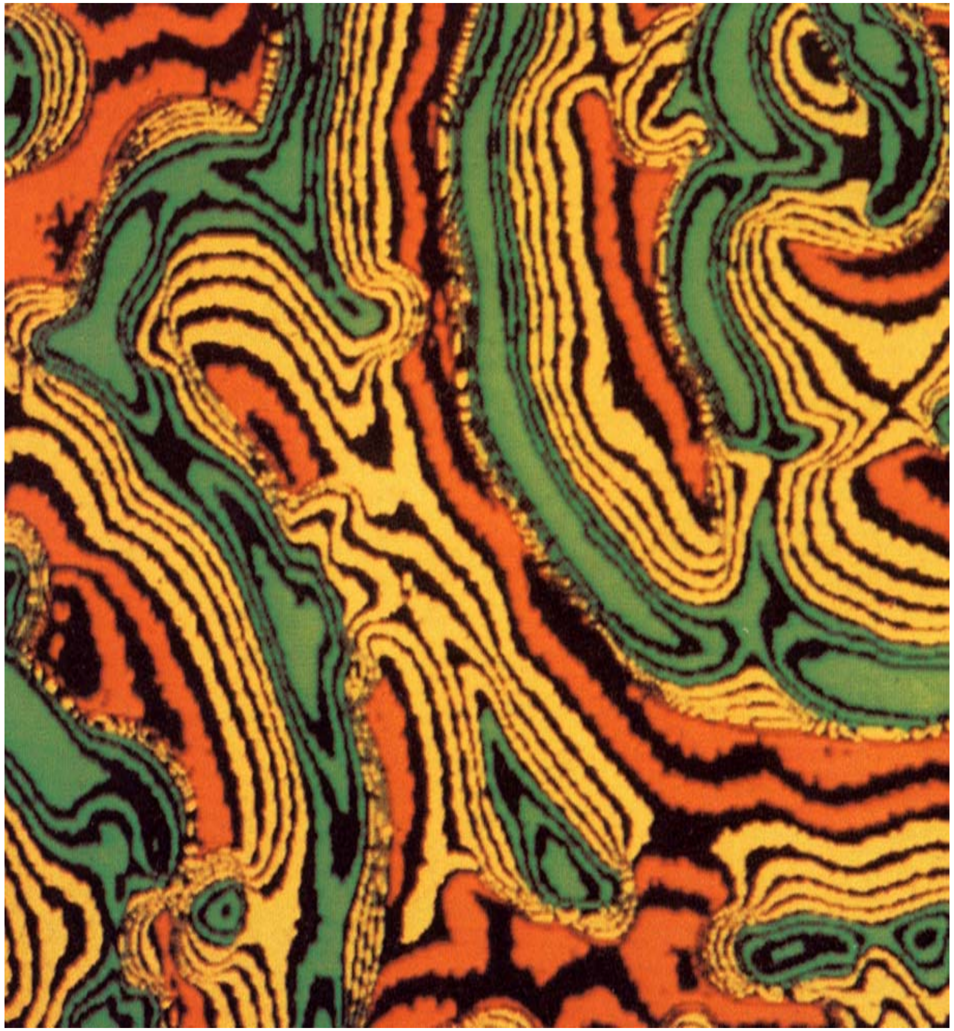
- import high-valued energy and export low-valued energy = conditio sine qua non.
- In other terms: entropy export, compensating the unavoidable entropy production in the system !!!

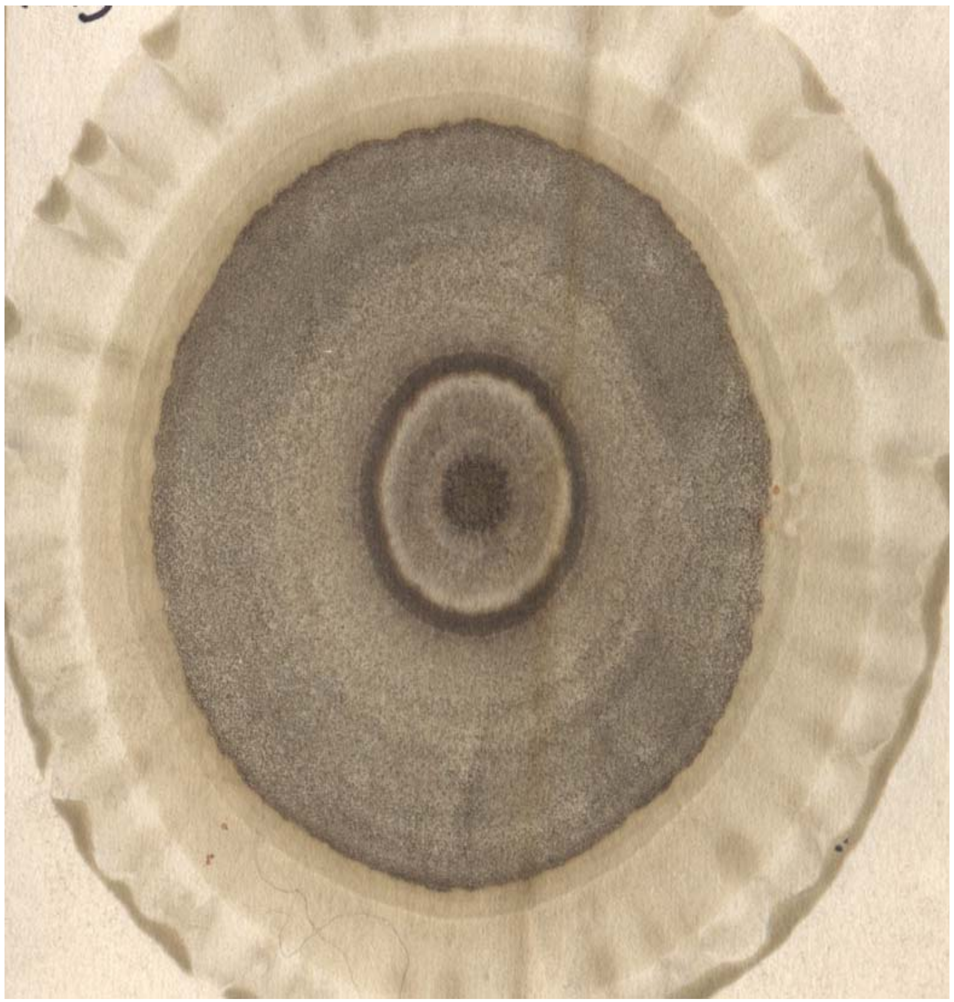
Benard-hydrodynamic cells





Examples of SO in Nature
BZ-waves Liesegang-rings





Ilya Prigogine - pioneer of the modern therm.theory of SO

- * 25.1. 1917 Moskau
- since 1951 Prof. of physikal. Chemistry University Brüssel
- since 1977 Center Statist. Physics Austin
- 1977 Nobel price in chemistry
- + 28.5.03 Brussels

Our contribution to this field: Physik der

Akademie-Verlag, Berlin 1982

Physik der Evolutionsprozesse, AV, Berlin 1990

Evolution principles I:

Second law: Entropy production is zero or positive for all processes in nature or society

$$d_i S \geq 0, \quad P = \frac{d_i S}{dt} \geq 0$$

It is impossible to destroy entropy. This determines the direction of all real processes. Is true at least for our expanding UNIVERSE

Evolution principles II:

- Prigogine principle: Entropy production decreases in the realm of linear processes

$$P \geq 0, \qquad \frac{d\ P}{d\ t} \leq 0$$

- Glansdorff-Prigogine principle: The force-determined part d_x P is non-positive for all processes (Landauer: This is not correct !)

Evolution principles III: StochProc

- Evolution principle for Kullback entropy:

$$K \geq 0, \qquad \frac{dK}{dt} \leq 0$$

- Jarzynski theorem: Equilibrium information (on free energy) can be extracted from an ensemble of nonequilibrium measurements.

Thermodynamics of information processing and life

- Pioneers: Mayer/Boltzmann/Szilard/ Schrödinger/Brillouin/Wolkenstein,
- Life is a high (the highest?) form of SO, is connected with entropy exchange,
- Information processing is a high form of SO,
- Information processing is a „conditio sine qua non“ for life,
- living systems are „by definition“ information processing systems based on natural evolution (not based on design, takes time!)

Living systems: General thermodynamic models

- study the balance of matter, energy, entropy,
- consider export/import and production ,of entropy
- search for general evolutionary principles. The first Prigogine principle (minimization of entropy production) does not hold: In the early ontogenis and in wound healing P increases first

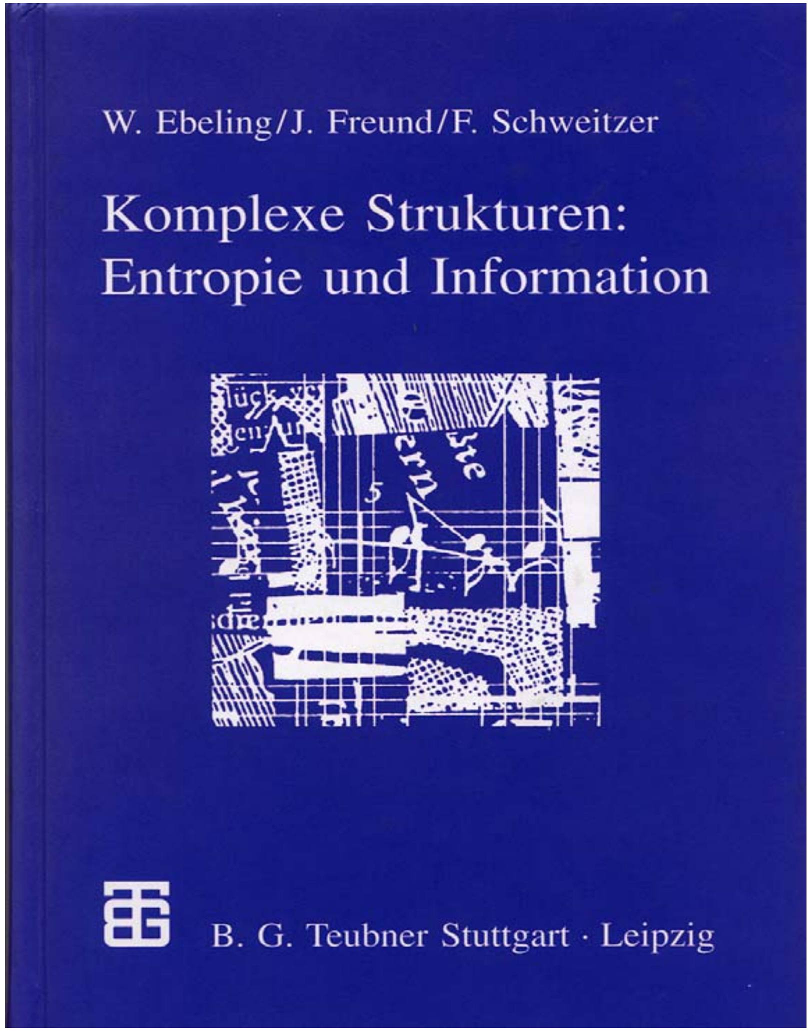
Thermodynamics plays a key role for modelling ecosystems

Entropy:basic quantity of information theory (Shannon)

- Information theory is in some sense more general (Stratonovich, 1930-1997)
- we come back to classical thermodynamics if and only if the theory is applied to systems with a physical phase space having an energy and consequently $T = d E / d S$
- Thermodynamics is a special case of a more general systems theory: TD = theory of systems with energy, entropy +temperature

Entropy and information

- Information is a binary relation between 2 systems !!!
- Information transfer is always connected with exchange of entropy (min 1 bit)
- Equality of Shannon and Boltzmann-Gibbs entropy holds only is Shannon is applied to physical space!!!

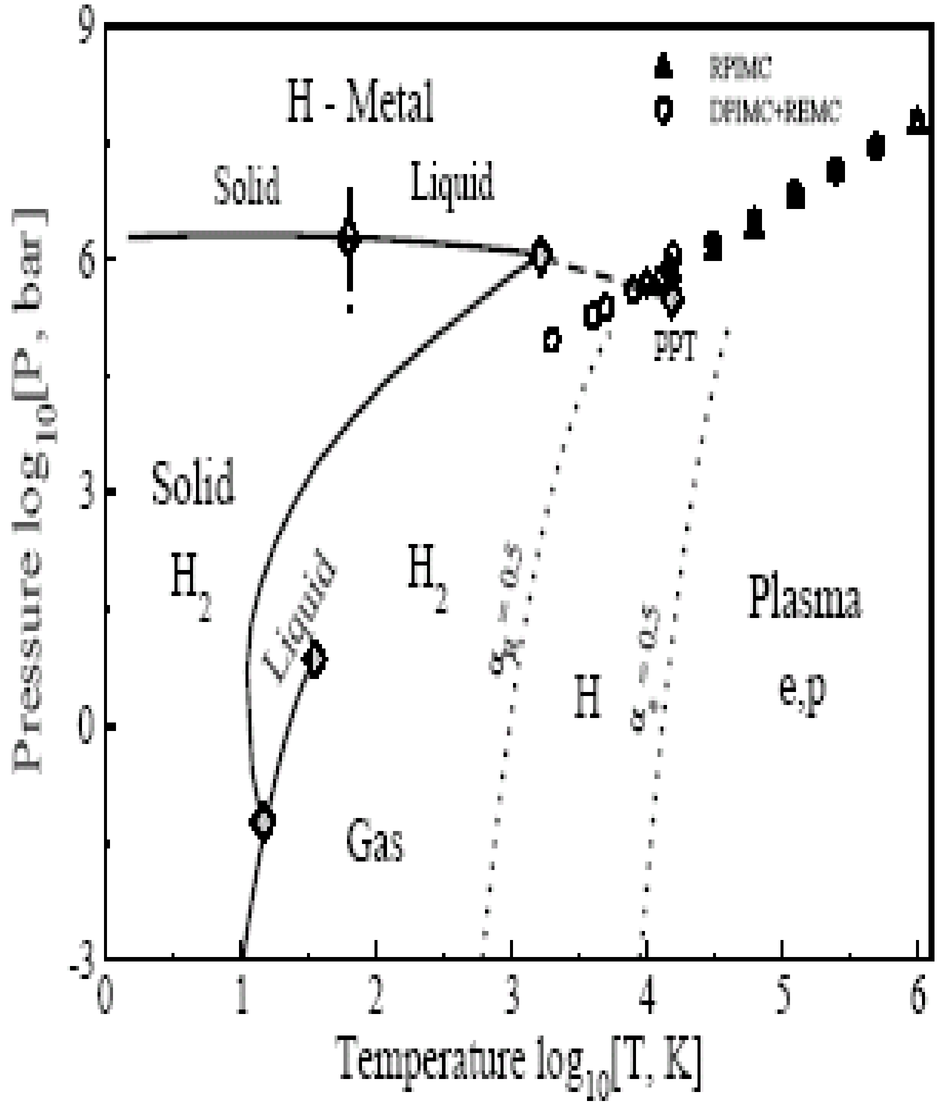


Open problems: evolutionary principles, evo of info-process.

- EVO is connected with optimum-seeking search (thermodynamic functions, fitness, ...)
- Question about general principles: Exists a general GOAL ???
- Our point of view: Probably beside the second law no other general EVO principles exist. Exist special principles!
- Far from equilibrium theory ? EVO of inf?

Exotic applications:
Hydrogen/Deuter at Mbar pressures

- New exp devices reach Mbar pressures: gas guns, explosive shocks, wire explosions, laser shocks.
- The theory predicts for H a second phase transitions
- T_cr ~ 16000 K below 1 Mbar



Plasma phase transition
T_cr ~ 16000 K

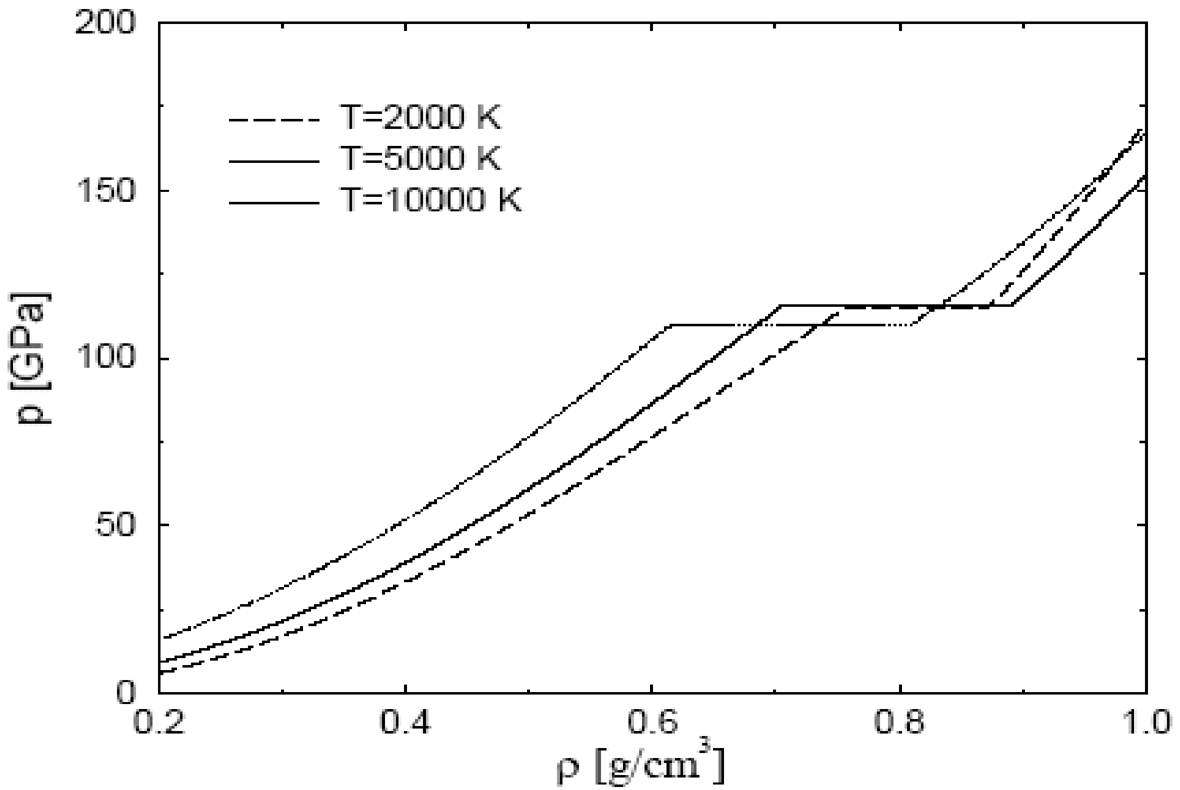


Figure 1: Pressure as function of the density for various temperatures. A Maxwell construction was performed in the instability region leading to constant pressure in the coexistence region.

Coexistence line in the Mbar region

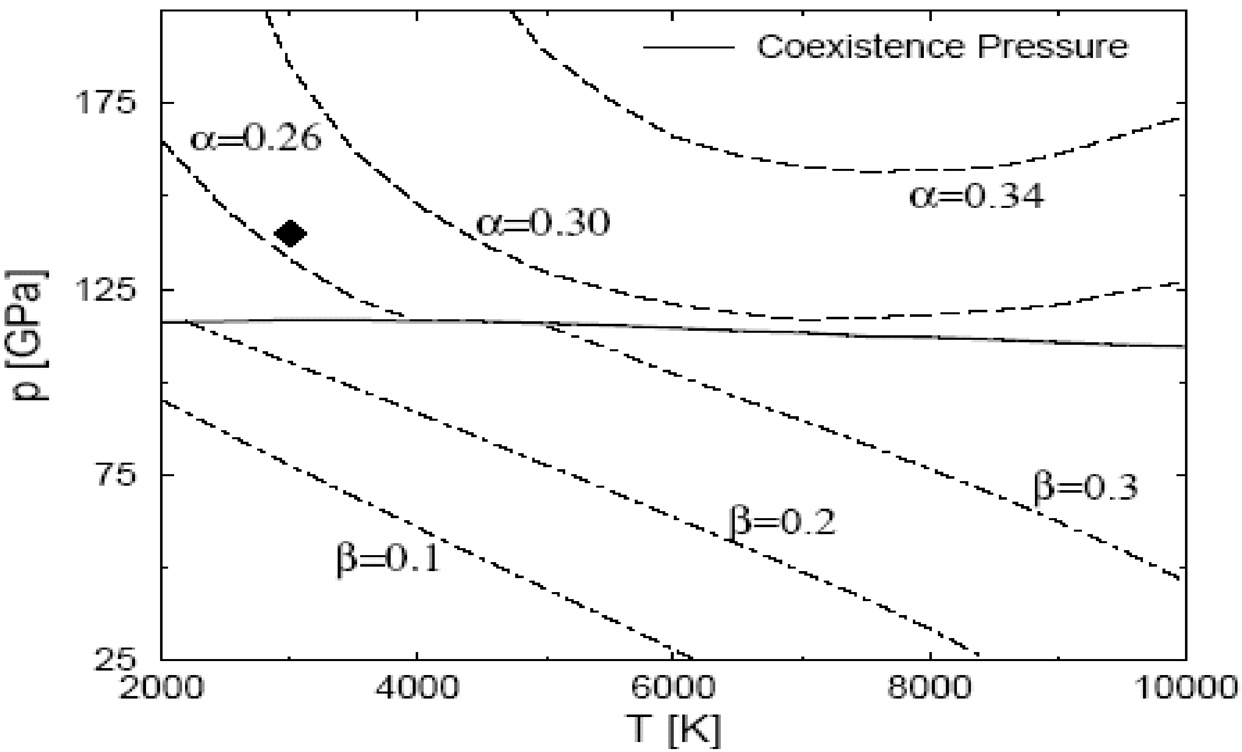


Figure 2: Coexistence pressure and lines of constant degree of dissociation β and ionization α, respectively, as function of the temperature. The conditions where Weir *et al.* [?] observed metallic conductivity is indicated by a diamond.

Isentropes

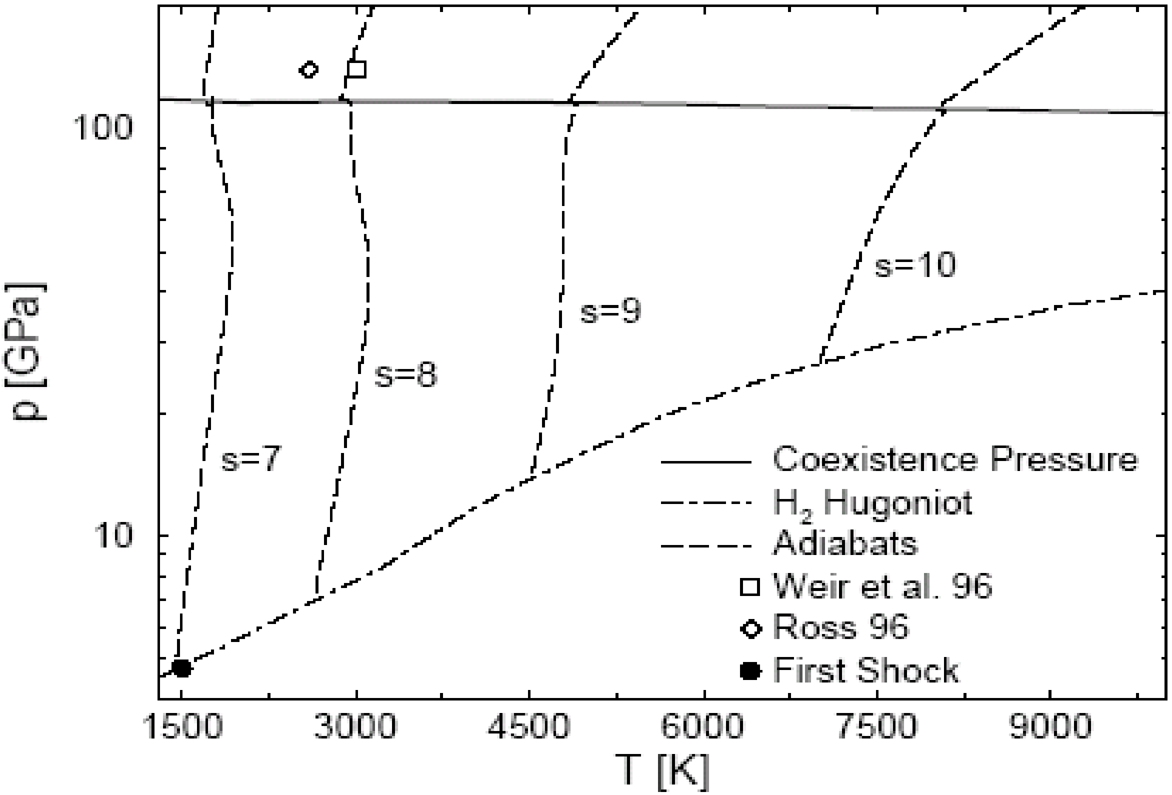
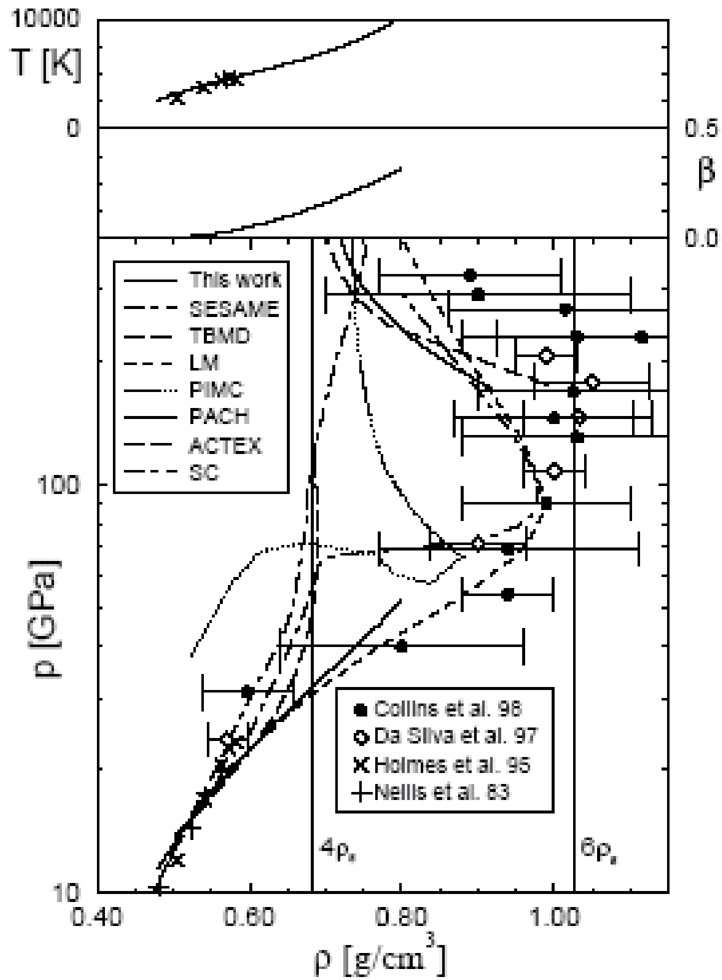


Figure 4: Isentropes for different values of the specific entropy s together with the single-shock Hugoniot (initial state see text) and the coexistence line for hydrogen. Square (): Location of the insulator-to-metal transition

Hugoniots: theory and experiment

- + and x: gas gun exp.
- Fat points and rhombs: from Nova laser exp
- thick line: present theoretical results (with Beule, Förster, Redmer, Juranek, Röpke, Phys.Rev. B 2000)



Conclusions

- Thermodynamics contributed to the big discoveries of the 20th century and to the theoretical understanding of our world (Weltbild) and **survived**.
- We have now good models for many special processes/mechanisms of SO and EVO, and for many exotic processes.
- The great open problems are connected with far from equil. processes and info-processing. Here most questions are still open !!!