Thermodynamics - Past, Present and Future

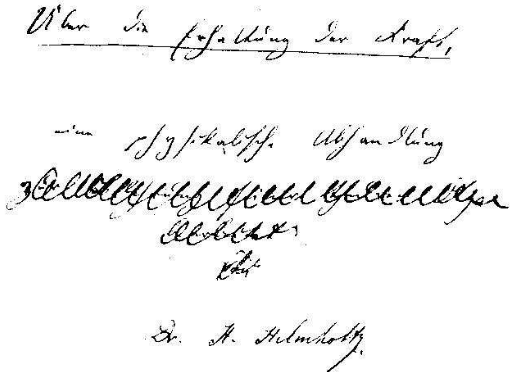
Werner Ebeling

Institute of Physics, Humboldt–University Berlin, Newtonstr. 15,
D–12489 Berlin, Germany

Abstract. We begin with historical remarks on the basic contributions to thermodynamics and statistics with some bias to scientists working in Berlin as Helmholtz, Clausius, Nernst and Einstein. We underline the key role of thermodynamic ideas in the scientific revolutions in the 20th century. Further we discuss several recent applications to natural, evolutionary and informational systems, exotic applications as well as perspectives and open problems.

1 Foundation of the three fundamental laws

Thermodynamics as a branch of science was established in the 19th century by Sadi Carnot (1796-1832), Robert Mayer (1814-1878), Hermann Helmholtz (1821-1894), William Thomson (1824-1907) and Rudolf Clausius (1822-1888). Evidently Mayer was the first who formulated the law of energy conservation. His paper *"Bemerkungen über die Kräfte der unbelebten Natur"* published 1842 in Liebig's Annalen is expressing the equivalence of work and heat. Joule's conclusions on this matter were based on direct measurements of the conversion of work into heat. A great role in the foundation of thermodynamics played physicists working in the middle of the 19th century in Berlin. We will discuss their contribution here in some more detail, just to illustrate the *genius loci.* In particular it was Hermann Helmholtz who determined the direction of thermodynamic research [1,2]. At 27 years of age Helmholtz - at that time still working as a military surgeon in Potsdam - reported 1847 to the *"Berliner Physikalische Gesellschaft"* about a new principle of conservation of energy. The underlying experimental research which he carried out in the laboratory of his adviser Professor Magnus was primarily devoted to the conversion of matter and heat in such biological processes as rotting, fermentation and muscular activity. From experiments and brilliant generalization emerged the principle of conservation of energy or what is now called the first law of thermodynamics. Neither Mayer nor Joule recognized its fundamental and universal character as clearly as Helmholtz. The work of Mayer and Joule was unknown to Helmholtz at that time. Helmholtz had to fight hard for the recognition of his work - Professor Poggendorf, the editor of the *"Annalen der Physik und Chemie"*, rejected the paper which seemed to him too speculative. Professor Magnus also did not like the work, but at least he recommended to print it as a brochure, as was quickly managed with the help



Über die Erhaltung der Kraft,

eine physikalische Abhandlung

von

Dr. H. Helmholtz.

Fig. 1. Title page of the manuscript of Helmholtz's work "Über die Erhaltung der Kraft - eine physikalische Abhandlung".

of Professor Jacobi.

Rudolf Clausius (1822-1888) one of the young colleagues of Helmholtz played an essential role in the further elaboration of the new law [3]. After studying in Berlin, he taught for some years at the Friedrich-Werdersches Gymnasium in Berlin and was a member of the seminar of Professor Magnus at the Berlin University. A report on Helmholtz's work, given to Magnus' colloquium, was the beginning of Clausius' involvement in this matter. Building on the work of Helmholtz and Carnot he published 1850 in Poggendorff's Annalen a first formulation of the second law of thermodynamics. Clausius was fully aware of the impact of his discovery. The title of his paper explicitly mentions *"laws"*. Clausius stated that heat cannot pass spontaneously from a cooler to a hotter body. Unlike Carnot, and following Joule, Clausius interpreted the passage of heat as the transformation of different kinds of energy, in which the total energy is conserved. To generate work, heat must be transferred from a reservoir at a high temperature to one at a lower temperature, and Clausius here introduced the concept of an ideal cycle of a reversible heat engine. In 1851 Thomson formulated independently of Clausius another version of the second law. Thomson stated that it is impossible to create work by cooling down a thermal reservoir. The central idea in the papers of Clausius and Thomson was an exclusion principle: *"Not all processes which are possible according to the law of the conservation of energy can be realized in nature"*. This means, the second law of thermodynamics is a selection principle of nature. Although it took some time before Clausius' and Thomson's work was fully acknowledged, it was fundamental not only for the further development of physics, but also for science in general. In later works Clausius arrived at more general formulations of the second law, in particular he introduced the quotient of the quantity of heat absorbed by a body and the temperature of the body $d'Q/T$ as the change of entropy. In a next step Clausius was thinking about an atomistic foundation of thermodynamics and published two papers *"Über die Art der Bewegung, die wir Wärme nennen"*, which appeared 1857/1858 in the *Annalen der Physik.* This work is the first comprehensive treatment of the kinetic theory of gases. Clausius developed new terms like the mean free path, cross section etc. and introduced in 1865 the new quantity entropy. Further he derived in 1870 a virial theorem for gases. Parallel to Clausius's work the statistical theory was developed by Maxwell, who derived in 1860-66 the probability distribution for the velocities of molecules in a gas and formulated a first version of a transport theory. In 1867 Maxwell discussed first the statistical nature of the second law of thermodynamics and considered the connection between entropy and information. His *"Gedankenexperiment"* about a demon observing molecules we may consider as the first fundamental contribution to the development of an information theory. In 1878 Maxwell proposed the new term *"statistical mechanics"*.

Ludwig Boltzmann (1844-1906) studied physics at the University of Vienna. He was deeply influenced by Josef Stefan (1835-1903) and Johann Loschmidt (1821-1895). Boltzmann started to work on the kinetic theory of gases. In 1866, he found the energy distribution for gases. In 1871 he formulated the ergodic hypothesis, which is fundamental for the modern version of statistical physics and for the connection to nonlinear dynamics and his work culminated in 1872 with the formulation of a kinetic equation and the H-theorem, which established a connection to the second law. In the year 1872, which was so central for his work, Boltzmann visited Helmholtz in Berlin. In the mean time, after professorships in anatomy and physiology at several German universities, Helmholtz had returned to Berlin to succeed Magnus as director of the physical institute of the university. Then began a very productive period in the history of physical research in Berlin. No burning questions of contemporary physics remained untouched by Helmholtz or his fellow workers, but thermodynamical problems remained central. During Helmholtz's second period in Berlin his work revolved around pure and applied problems of thermodynamics. He developed the concept of free energy and investigated the relationship between the heat of reaction and the electromotive force of a galvanic cell. As president of the Physikalische-Technische Reichsanstalt Helmholtz stimulated studies of the properties and applications of light. The investigations in particular by Wilhelm Wien led later to the development of a thermodynamical theory of heat radiation by Max Planck. In 1889 Max Planck (1858 - 1947) succeeded Kirchhoff at the Berlin Chair of Theoretical Physics. He was a pioneer in understanding the fundamental role of entropy and its connection with the probability of microscopic states. Later he improved Helmholtz's chemical thermodynamics and his theory of double layers. He was the first who wrote down explicitely the famous formula

$$S = k \log W. \tag{1}$$

An independent and more general approach to statistical thermodynamics and the role of entropy was developed by the American physicist Josiah

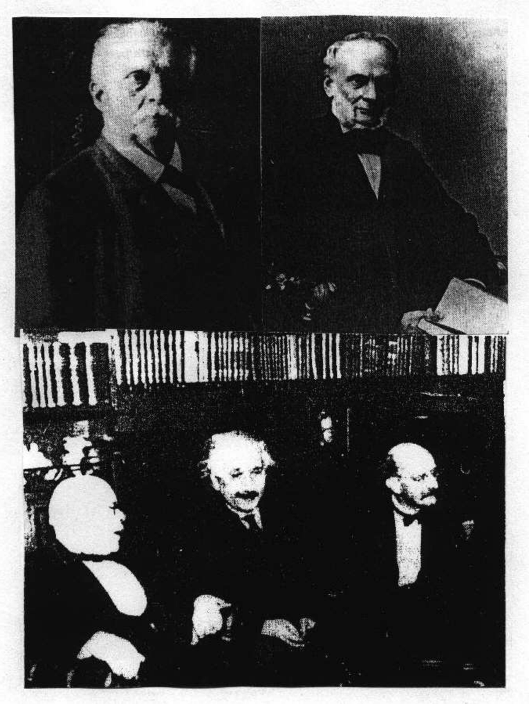


Fig. 2. Leading scientists in Berlin: Helmholtz (1821-1894), Clausius (1822-1888), Nernst (1864-1941) Einstein (1879-1955) und Planck (1858-1947).

Willard Gibbs (1839 - 1903). Gibbs developed the ensemble approach, the entropy functional and was the first to understood the role of the maximum entropy method which was later further developed by Jaynes.
The next important contribution to thermodynamics is connected with the work of Walther Nernst (1864-1941) who accepted in 1905 a call on a chair at the Berlin university. In 1905 Nernst detected the "missing stone in thermodynamics", the third law of thermodynamics. Nernst's seminal idea arose from the critical analysis of experimental data on chemical and electrochemical reactions at low temperatures, where there appeared good correspondence between the free energy and the internal energy. Nernst found that the agreement improved at lower temperatures. This led him to the 3rd law. Some years later Planck gave Nernst's new principle the following general and widely known formulation: *"The entropy of all bodies which are in internal equilibrium vanishes at the zero point of temperature"*. After postulating his new theorem Nernst and his collaborators took great efforts to prove this new law of nature. The specific heat, being of special importance, was determined for several substances at low temperatures. This was a very difficult scientific problem which called for the construction of equipment and instruments from

scratch and finally led to a new and very fruitful branch of investigations - low temperature physics and technology.

Let us devote the final part of this section to the question *How to present the three fundamental laws today?*. The experience in teaching of physics shows that the three basic laws of physics are difficult to understand. Students reproduce quite often just several formulae without reaching a deeper understanding. Therefore we want to discuss here the problem: How to present the 3 laws today in a most clear version ?

Zeroth law: Thermodynamic systems possess a special state - thermodynamic equlibrium. A system in this particular state shows no changes after isolation. Systems in thermodynamic equilibrium are characterized by a scalar, transitive variable T, the temperature.

First law: Thermodynamical and other macroscopic real systems are characterized by an extensive quantity energy E. Energy can neither be created nor destroyed. Energy can be exchanged with other systems and appears in such processes in different forms, as e.g. heat, work, chemical energy. Energy can be converted from one form to other forms and moved to other systems:

$$dE = d_i E + d_e E, \quad d_i E = 0, \quad d_e E = d'Q + d'A + \sum \mu_k dN_k \tag{2}$$

In isolated systems we find $dE = 0$ and consequently, energy is conserved. A precise definition of energy is not known. The question:*"What is energy?"* is commented by Poincare in the following way: *"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)"*.

The second law: Thermodynamical and other macroscopic real systems are characterized by an extensive quantity entropy S. Entropy can be created but never by destroyed. Entropy can be exchanged with other systems and in particular by exchange of heat.

$$dS = d_i S + d_e S, \qquad d_i S \geq 0, \qquad d_e S = \frac{d'Q}{T} + ... \tag{3}$$

In isolated systems we find $dS \geq 0$, i.e. that the entropy will always increse or remain constant (in thermodynamic equilibrium). The expression for the exchanged entropy is not unique, since several definitions of heat exist.

Gibbs - Helmholtz fundamental relation: In thermodynamic equilibrium, energy, entropy, the extensive volume-type variables L_k and the particle numbers N_k are depending on each other. This is expressed by the differential relation (Pfaffian form):

$$dE = TdS + \sum l_j dL_j + \sum \mu_k dN_k \tag{4}$$

The third law: Energy and entropy are finite for finite sytems and bounded from below $E > 0$, $S > 0$. In the limit $T \to 0$, the entropy as well as its derivatives with respect to extensive variables disappear asymptotically:

$$S \to 0, \qquad \frac{dS}{dL_k} \to 0 \tag{5}$$

The first and the second fundamental laws are valid for any macroscopic process in nature and society. May be, these are the only laws which have a universal range of validity? Quantum theory and general relativity theory modified our understanding of the energy and entropy concepts, however their fundamental role for all macroscopic processes remained untouched. The third law is less fundamental, it is a law of thermal systems only. However it has deep implications for physical systems. Low temperature physics is of increasing importance.

2 The key role of thermodynamics in the 20th century

The three fundamental laws of thermodynamics had a deep influence on the physics of the development of physics in the 20th century. In particular we mention applications to:
QUANTUM THEORY,
LOW TEMPERATURE PHYSICS,
LARGE SCALE PHYSICS (the universe, stellar objects, black holes),
SMALL SCALE PHYSICS (nuclei, elementary particles),
BIOLOGICAL, ECOLOGICAL and SOCIAL SYSTEMS,
INFORMATIONAL SYSTEMS.
The pioneers of the first revolutionary applications to physical problems were Planck, Nernst and Einstein. Planck applied thermodynamic methods to radiative processes aand searched for relations between energy and entropy. In order to get agreement with experimental fiondings, he could not avoid the introduction of a new elementary quantum of action h. This was the first revolution in physics raised by thermodynamics. The second one is connected to the work of Nernst who worked since 1905/06 with a group of talented physicists on the experimental verification of his heat theorem. This led to the development of low temperature physics and stimulated the work of Einstein. Einstein started his work on statistical physics in 1902/03 with two very interesting papers on *"The kinetic theory of thermal equilibrium and the second law of thermodynamics"*, published in the *"Annalen der Physik"*. Here independently of Gibbs, Einstein developed the basic ideas of ensemble theory and the statistics of interacting systems. In his dissertation, presented in 1905 to the Zürich University, he developed a first correct theoretical interpretation of Brownian motion. This work was published in volume 17 of the *"Annalen der Physik"*. Einstein was at that time only 26 years old. As well known, he published in the same volume of the "Annalen", also two other fundamental papers devoted to the theory of relativity and the theory of the photo effect.

In 1907, Einstein turned to problems of low temperatures connected with the third law. He proposed that quantum effects lead to the vanishing of the specific heat at zero temperature. His theory led to a deeper understanding of the low temperature thermodynamics and may be considered as the origin of quantum statistics. Einstein's work attracted the attention of Nernst and his collaborators and by 1910 they succeeded in confirming this prediction. In this way the third law of thermodynamics as well as the young and still controversial quantum theory found one of its first experimental verifications. In 1913, Nernst together with Planck, was able to bring the *"new Copernicus"* Einstein to Berlin, they could offer the unconventional genius excellent working and living conditions. As a *"paid genius"* in Berlin, Einstein could complete his general theory of relativity, and make further important contributions to thermodynamics and statistical physics. In 1924, he generalized the Bose theory of photon gases, developed a new quantum statistics, the so-called Bose-Einstein statistics. In addition to the Bose-Einstein condensation his ideas about the interaction between radiation and matter should be emphasized. In 1916 his discussion of spontaneous emission of light and induced emission and adsorption forms the theoretical basis of the nonlinear dynamics and stochastic theory of the modern lasers. Concerning the many other fundamental contributions to thermodynamics and statistical physics in the last century we must restrict ourselves to brief remarks. The German-Greek mathematician Constantin Caratheodory formulated thermodynamics on an axiomatic basis. His analyses of such fundamental concepts as temperature and entropy in terms of the mathematical theory of Pfaffian differential forms were not appreciated by most of his contemporaries, although Planck was an early supporter of what has become one of the important branches of modern thermodynamics. Walter Schottky (1886-1976) developed industrial applications of thermodynamics and wrote a famous textbook "Thermodynamik" (1929).

3 Thermodynamics of selforganization and evolution processes

First applications of thermodynamics to the evolution of the UNIVERSE go back to Helmholtz, Clausius and Boltzmann and are connected with the idea of the *"Wärmetod"*. A completely new approach was based on a cosmological model presented 1922 by the mathematician Alexander Friedmann in Petersburg based on Einstein's general relativity. Friedmann derived the model of an expanding matter-filled UNIVERSE from Einstein's field equations. The first who applied thermodynamics to this model was George Gamov, a former student of Friedmann. Together with Alpher, Bethe and Hermann he developed in the 40th the thermodynamic model of the BIG BANG. The BIG BANG theory of the history of the UNIVERSE is essentially a thermodynamical theory based on thermodynamical relations applied to the very exotic early stages of the expansion. The assumption of adiabatic expansion leads to the following law of temperature decay in time:

$$T \simeq \frac{const}{\sqrt{t}} \tag{6}$$

In the last stages of evolution, matter is self-structuring. It forms stars and planets and the temperature gradient between sun and earth - the photon mill - gives rise to selforganizaion on earth [4]. The earth is an open system which exports entropy in the amount of about $1W/m^2K$. This is the driving force of evolution on earth. Essential contributions to our understanding of the thermodynamic basis of life were given by Mayer, Boltzmann, Schrödinger and Prigogine. The main idea of these pioneers is that the exchange with surrounding is relevant. In open systems with entropy export - the formation of structures does not contradict the 2nd law.

This research lead to the development of a thermodynamics of open systems and a theory of selforganization [4]. Well-known examples of selforganization in nature are the Belousov-Zhabotinsky -waves, the Liesegang-rings and Benard's hydrodynamic cells.

Another closely related line of the developement of thermodynamics is the foundation of irreversible thermodynamics. We mention only the early work of Thomson, Rayleigh, Duhem, Natanson, Jaumann and Lohr. The final formulation of the basic relations of irreversible thermodynamics we owe to the work of Onsager (1931), Eckart (1940), Meixner (1941), Casimir (1945), Prigogine (1947) and De Groot (1951). Irreversible thermodynamics is essentially a nonlinear science, which needs for its development the mathematics of nonlinear processes, the so-called nonlinear dynamics.

Let us discuss now in brief the important question of evolution principles: The most general evolution principle results from the second law which leads to the following requirement for the entropy production:

$$P = \frac{d_i S}{dt} \geq 0 \tag{7}$$

For irreversible processes the entropy production is positive, the inverse process would destroy entropy, what is forbidden by the 2nd law.

An independent principle was found by Prigogine:

$$\frac{dP}{dt} \leq 0 \tag{8}$$

Entropy production decreases in the realm of linear processes. A more general principle formulated by Glansdorff and Prigogine states that the change of the force-determined part $d_x P$ is non-positive for all processes. Landauer and several other workers have shown that this statement is not correct for all processes and is not a general evolution citerion.

There exist several more special evolution criteria. For example for all Markov processes with the time-dependent probability $P(x,t)$ there exists a functional (Kullback-Leibler entropy):

$$K = \int dx P(x,t) \log[P(x,t)/P_0(x)] \tag{9}$$

($P_0(x)$ - stationary distribution) which is positive and never increasing (Bergmann - Lebowitz - van Kampen - Schlögl et al.)

$$K \geq 0, \qquad \frac{dK}{dt} \leq 0 \tag{10}$$

This very general and interesting statement contains the second law and other evolution criteria. We mention that there exist several other statements [2] as e.g. the Jarzynski theorem which states that equilibrium information (on free energy) can be extracted from an ensemble of nonequilibrium measurements.

4 Thermodynamics, nonlinear dynamics, information processing and life

The pioneers of this direction of thermodynamics were Mayer, Maxwell, Boltzmann, von Neumann, Szilard, Schrödinger, Brillouin and Wolkenstein. In the 19th century a close relation between statistical thermodynamics and nonlinear science was not known. Henri Poincare, the father of nonlinear science, was the strongest opponent of Ludwig Boltzmann. In recent times it became clear that Poincare's work contains the keys for the foundation of Boltzmann's theory. In particular this refers to the concept of instability of trajectories developed by Poincare. Today nonlinear science and thermodynamics are closely connected, e.g. the thermodynamic formalism plays an important role in nonlinear dynamics as well as the Kolmogorov-Sinai entropy.

A significant progress was made through the investigations of G. Birkhoff and J. von Neumann. The Hungarian Johann von Neumann (1903-1957) came in the 1920s to Berlin attracted by the sphere of action of Planck and Einstein in physics and von Mises in mathematics. Von Neumann made important contributions to the statistical and quantum-theoretical foundations of thermodynamics. Von Neumann belonged to the group of "surprisingly intelligent Hungarians" (D. Gabor, L. Szilard, E. Wigner), who studied and worked in Berlin around this time. Von Neumann formulated a general quantum-statistical theory of the measurement process, including the interaction between observer, measuring apparatus and the object of observation. This brings us back to Maxwell. In fact information-theoretical considerations in statistical physics start with Maxwells speculations about a demon observing the molecules in a gas. Maxwell was interested in the flow of information between the observer, the measuring apparatus and the gas. In fact this was the first investigation about the relation between observer and object, information and entropy. This line of investigation was continued by Leo Szilard, prominent assistant and lecturer at the University of Berlin and a personal friend of von Neumann. His thesis (1927) *"Über die Entropieverminderung in einem thermodynamischen System bei Eingriffen intelligenter Wesen"* investigated the connection between entropy and information. This now classic work is probably the first comprehensive thermodynamical approach to a theory of information processes. The first consequent approach to connect the foundations of statistical physics with information theory is due to Jaynes in the years (1957-1975). The information-theoretical method is based on the maximum entropy principle. In highest generality this approach was developed by Rouslan Stratonovich.

We have to mention also of the important contribution of Erwin Schrödinger to the foundation of statistical and biological thermodynamics. In 1927, Schrödinger succeeded Planck in the chair of theoretical physics. In the fall of 1933 he resigned from this post and after some years of travelling he found his final refuge in Dublin. Here in 1944 he published two little but very influential books *"Statistical Thermodynamics"* and *"What is Life?"*, which considerably influenced the development of science and especially statistical thermodynamics and its applications to life sciences.

We consider life is a high (the highest?) form of selforganization, it is connected with export of entropy to the surrounding, and information processing. Information processing is a "conditio sine qua non" for life. Living systems are "by definition" information processing systems originated from natural evolution (they not based on design and this takes time!). Thermodynamic models are important for the understanding of living systems (studies of the balance of matter, energy, entropyexport and production) [4]. Thermodynamics also plays a key role for modelling ecosystems.

5 Exotic applications

We consider here a new application of thermodynamics to hydrogen and deuterium plasmas at Mbar pressures [5,6]. This is a problem of much interest for astrophysical applications since hydrogen is the most abundant element in the universe. Recently several new experimental devices reach Mbar pressures as gas guns, explosive shocks, wire explosions, laser shocks. Already Wigner and Abrikossov suggested for $T = 0$ the existence of a phase transition to a highly conducting state in the Mbar region. New theories of dense plasma desribe this second phase transition in the whole temperature [7]. At low temperatures and pressures, hydrogen is a molecular solid or fluid. At high pressures above $100GPa$, hydrogen is supposed to undergo a transition to a highly conducting state which has been verified experimentally for the first time in the shock-compressed fluid around $140GPa$ and $3000K$ [8]. Similar conductivity data have been reported recently for that high-pressure fluid domain [9]. The physical nature of this transition at extreme conditions is not fully explored. The interesting question, whether or not this transition is accompanied by a first-order phase transition with a corresponding instability region, a coexistence line, and a critical point has been treated in our work within advanced many-particle methods adopting a chemical picture. There, the different components in a dense, partially ionized plasma such as molecules H_2, atoms H, molecular ions H_2^+ or H^-, electrons e and protons p interact via effective pair potentials [5,6]. Several results for hydrogen plasmas are demonstrated in Figs. 3-4. Several estimates for the critical point of the phase transition which is first-order phase transition have also been obtained [7] which are around

$$T_{cr} \simeq 16000K. \tag{11}$$

These problems attract in recent times much experimental and theortical interest, however many problems still remain unsolved, on the experimental as well on the theoretical side.

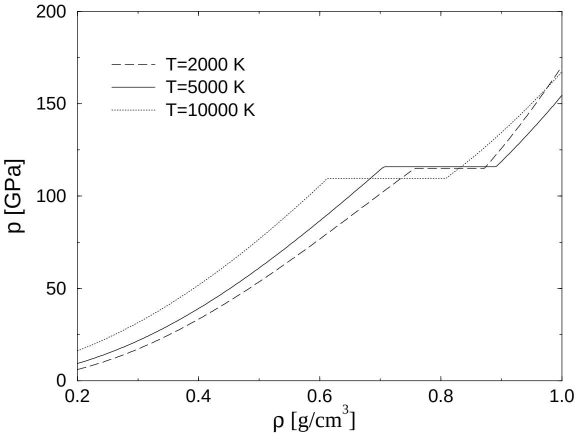


Fig. 3. Pressure as function of the density for various temperatures. A Maxwell construction was performed in the instability region leading to constant pressure in the coexistence region.

6 Open problems - 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 selforganisation and evolution, and also for many exotic processes. The great open problems are connected with the theory of far from equilibrium processes

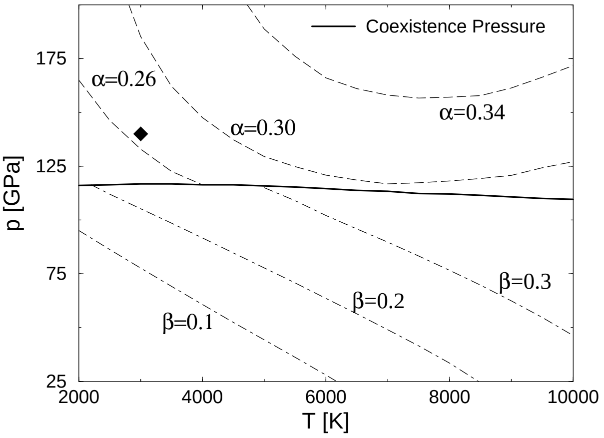


Fig. 4. Coexistence pressure and lines of constant degree of dissociation β and ionization α, respectively, as function of the temperature. The conditions where Weir *et al.* [8] observed metallic conductivity is indicated by a diamond.

and information-processing. Here In this field most questions are still open. Open problems are in particular connected with evolutionary principles and the the evolution of information- processing in nature.

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