HISTORY OF CLASSIC THERMODYNAMICS AND THE FUTURE OF THERMODYNAMICS

ZGODOVINA KLASIČNE TERMODINAMIKE IN PRIHODNOST TERMODINAMIKE

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Keywords: thermodynamics, classic thermomechanics, viscosity, statistical mechanics

Abstract

Whenever they hear the word "thermodynamics", many students of energy engineering, mechanical engineering, chemistry, physics and other natural sciences are filled with apprehension. This science has a reputation because of its abstract nature and the laws of thermodynamics. This review paper deals with the history of thermodynamics and shows how it is likely to evolve in the future.

Povzetek

Mnogim študentom energetike, strojništva, kemije, fizike in drugih naravoslovnih znanosti gredo lasje pokonci in jim obraz potemni, ko slišijo za besedo termodinamika. Tak sloves si je ta veda pridobila zaradi svoje abstraktne narave in zloglasnih termodinamičnih zakonov. Predstavljen pregledni članek obravnava zgodovino nastanka termodinamike in prikazuje, kako bi se naj termodinamika razvijala tudi v prihodnosti.

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1   INTRODUCTION

In a book on thermodynamics, I read the following sentence written by Professor M. L. McGlashan 1965: "I can't recall whom I lent specific books, but I remember well when I burnt one: it was a textbook on laws of thermodynamics". In contrast, Albert Einstein, the greatest physicist of all time, had a very respectful attitude to classical thermodynamics. In 1951, he said at a convention: "A theory is more impressive the greater the simplicity of its premises, the more different are the kinds of things it relates, and the more extended its range of applicability. Therefore, the deep impression which classical thermodynamics made on me. It is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown", *[1-8]*

2   HISTORY OF CLASSIC THERMODYNAMICS

As its name suggests, thermodynamics is the study of heat dynamics and their dynamics and energy transformation. It is one of the newest classical scientific disciplines, which began to develop only at the end of the 19th century. However, the beginnings of thermodynamics go back over two thousand years. Democritus and his mentor Leucippus may be regarded as the first serious researchers in the field of thermodynamics, in the 4th century B.C. They argued that all matter is composed of small indivisible, unchangeable, and indestructible particles – atoms. Only empty space is supposed to exist in addition to them. Even the human mind and gods should be made of such particles. Any changes that take place in the universe were attributed to the motion of atoms rather than to the capriciousness of the gods. Other philosophers at that time did not like the idea of the atomic structure of the universe and followed Socrates and his disciples instead. Therefore, Democritus is considered to be the founder of atomic theory, which is, in fact, the basis of statistical thermodynamics – a revolutionary theory describing nature through the understanding of the motion and interactions between molecules and atoms, *[2-6]*.

In addition to the beginnings of the atomistic view of the universe, the first researchers who studied the behaviour of matter appeared in that period. One of them was Philo, who was born around three hundred years B.C. in Byzantium. He discovered that air expands in response to a temperature increase and that a burning candle in a vessel consumes oxygen from the surrounding air, *[1-11]*.

The Greek inventor Heron (born in 20 AD), known for numerous ingenious solutions, continued Philo's work. His most important invention is that of a hollow sphere fitted with two bent tubes. When the water in the sphere was brought to a boil, the steam escaped through the tubes. As a result of the action-reaction principle, the sphere started to rotate rapidly, which is known as the first method of the transformation of steam energy into motion (steam engine). This invention began to be used for moving doors and statues, *[2-7]*.

Moreover, Heron wrote books on mechanics, air, and mirrors that were far ahead of their times. His book on air, in which he proved that air is matter, is particularly significant. Based on the fact that air is compressible, he also argued that it is composed of individual particles separated by void spaces.

Heron did not have a worthy successor for more than 1600 years. Only Daniel Bernoulli (1700-1782), a member of the renowned Swiss school of mathematicians and physicists, continued his

work. Today, he is famous primarily for his innovations in fluid mechanics. In 1738, he wrote a book entitled "Hydromechanics", in which he derived what became known as Bernoulli's equation. His contribution in the field of thermodynamics is perhaps even more critical. He was the first to attempt to explain the behaviour of gases when pressure and temperature vary. He used the assumption from the times of Heron, namely that gases consist of a large number of tiny particles. As part of further mathematical treatment, he used probability approaches developed by Pascal (1623-1662) and Fermat (1601-1665). Therefore, Bernoulli is considered to be the founder of the kinetic theory of gases.

The true discovery of the laws of thermodynamics began only in the 19th century in the most developed countries in that period: France, England, and Germany. The work of James Prescott Joule (1818-1889), the father of the law on conservation of energy or the first law of thermodynamics, is of immense value for the field of thermodynamics. Today, the first law of thermodynamics is attributed to Joule, Julius Robert Mayer (1814-1878) and Ferdinand Helmholtz (1821-1894), who discovered the law entirely independently of one another. Mayer was the first to publish the law on conservation of energy in 1842, which was as many as five years ahead of Joule, and in his very systematic paper, he also published in the law on conservation of energy, the impact of the tide, heating by meteorites and vital processes. Nevertheless, his paper aroused no interest within the scientific community at that time, *[1,5,8,11-15]*.

Today, the definition of the first law of thermodynamics is twofold: the first part defines that heat is energy, whereas the second part is the law on conservation of energy. The types of energy can be divided into two groups: stored energies and transitional energies. As regards the stored energies, they can be preserved in the given form to the extent desirable. They include potential energy (E_{pot}), kinetic energy (E_{kin}), and internal energy (U). Transitional energies, on the other hand, pass through the borders of the systems in processes and are characterised by their short duration. It is impossible to store them in the given form, and they appear when the stored energy passes from one system to another. They include mechanical work, heat (Q), and the energy of electric current. Heat is energy, whereby a specific name is used to define how energy passes from one body to another. As far as the second energy exchange method is concerned, a body passes mechanical work to another body or receives it from the other body. The first law states that the change in overall energy (kinetic ΔE_{kin}, potential ΔE_{pot} and internal ΔU) of a system is equal to the difference between the heat Q added to the system and the work W done by the system. The mathematical expression of the first law is the following:

$$Q - W = \Delta U + \Delta E_{kin} + \Delta E_{pot} + \sum \Delta W_i$$

(2.1)

The last term covers the changes in other forms of energies of the entire system, e.g. potential energy in an electric or magnetic field, elastic energy, etc. Of course, a number of enthusiasts wanted to challenge the correctness of the first law. The machines they used in order to demonstrate the incorrectness of the first law are called perpetual motion machines of the first kind. Some scientists made much money through fraud based on such machines. J. W. Kelly from Philadelphia [8], for example, tried to prove between 1874 and 1894 that his "hydro-pneumatic-pulsating-vacuum engine" could supposedly push a railroad train 3000 miles on 1 litre of water. Only after his death, the investors who paid 2.5 million dollars discovered that it was a case of fraud because an additional engine was hidden inside the locomotive. The above-mentioned amount of money is a huge sum even today, but at the time it was truly astronomical, *[2,5,8,12]*.

Rudolf Julius Clausius (1822-1888) was the founder of the second law of thermodynamics. He continued his research on the basis of the works by the French inventor Sadi Carnot, while at the same time he monitored the development of the work of William Thomson, the most acknowledged expert on thermodynamics at that time in England. In 1850, when he was a professor in Berlin, he sent to the Berlin Academy of Sciences a report in which he proved that the ratio between heat in a closed system and its absolute temperature only increases and can never decrease. He also introduced the notion of entropy, in connection with which he proved that the entropy of the universe always increases until its final thermal death. Then, all the planets will be in a state of thermal equilibrium; there will not be any changes and consequently no time which is actually measured by the course of such changes. Thanks only to the German mathematician, Constantin Carathéodory (1873-1950), the second law and entropy were explicitly derived by means of Pfaffian differential equations. Using entropy, the second law of thermodynamics can be expressed in a simple mathematical form:

$$dS \geq \frac{dU + dW + \sum y_i dX_i}{T}$$

(2.2)

The record with the equal sign applies to reversible processes, and the record with the not equal sign stands for inequality, determining the direction of natural processes. The last term in equation (2) is essential whenever thermoelectric and chemical processes, processes associated with magnetism, etc., are to be documented. The machines that would violate the second law are called perpetual motion machines of the second kind. Due to its abstract concept, the second law, in particular, makes students apprehensive. Thanks to statistical thermodynamics, we now know that entropy is a measure of the level of disorder of a system.

The third law of thermodynamics was developed in 1906 by Walther Hermann Nernst (1864-1941). The entropy change approaches zero at absolute zero temperature. Hence, it is possible to prove by means of mathematical procedures that absolute zero cannot be reached. The third law has also not been overthrown so far. In 1960, 10^{-6} K was attained using very expensive procedures, such as isentropic nuclear demagnetisation; however, nobody has achieved absolute zero as yet.

Sometime later, the so-called zero-th or empirical law of thermodynamics was developed randomly, also known as the fundamental law of thermodynamics: "If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other. If the notion of temperature is introduced, we can also say that two systems are in thermal equilibrium when having the same temperature", *[2-8]*. This law was first formulated in 1931 by the American scientist R. H. Fowler.

Thermodynamics was also developed more recently with Ilya Prigogine (1917-2003), called the father of nonequilibrium thermodynamics, *[22, 23].* Thermodynamics is under development of Constructal Theory much more comprehensive. Prof. Adrian Bejan developed this modern theory to explain many natural, economic and social processes, *[24].* On the basis of the molecular motion of atoms and molecules in solids, liquids, gases and plasmas, as well as statistical thermodynamics theory, the work of Austrian physicist Ludwig Boltzmann (1844-1906) was published in 1870. In 1896, he also published a book of lectures on gas theory. After this period, many enormous important contributions were made both on theoretical, experimental and numerical parts, from many researchers, including Albert Einstein, Enrico Fermi, Paul Dirac, Stajedra Nath Bose, Keith Gubbins and many others.

On the basis of knowledge from statistical thermodynamics, researchers now are able to calculate thermodynamic functions of state for pure components, mixtures, for single-phase and multi-phase systems. Austrian Physicist Ludwig Boltzmann was also one of the founders of nonequilibrium statistical thermodynamics, this theory was developed from kinetic gas theory. On the basis of the Maxwell-Boltzmann transport equation, it is possible to calculate transport properties like thermal conductivity and viscosity for pure components and mixture. For the calculation of transport properties for polyatomic molecules in principle, a quantum mechanical treatment of processes is necessary to account for the changes of internal state. The quantum mechanical kinetic theory of polyatomic gases is based on the Waldman-Snider equation and summarized by McCourt and co-workers. Wang-Chang and Uhlenbeck (1951), de Boer (WCUB), and Taxman (1958) formulated a semiclassical kinetic theory.

2   APPLICATIONS OF THERMODYNAMICS

Thermodynamics explains that energy is indestructible and how energy can be converted from one form to another. With its help, we can now explain the operation of all power machines. The table below shows when they start using thermodynamics in practice.

Table 1: Some critical moments in history regarding thermodynamics applications

1698, *[25]*	T. Savery	First steam water pump
1712, *[25]*	T. Newcomen	First steam piston engine
1791, *[27]*	J. Barber	First working gas turbine
1801, *[18]*	H. Davy	Development of principle of the fuel cell
1852	W.T. Kelvin	Theory of heat pump
1853, *[9]*	E. Brisanti and F. Matteucci	First patent of internal combustion engine
1855	P.v. Rittinger	First working heat pump
1864, *[9]*	N. Otto	Patent of Laval nozzle
1873	Johannes Diderik van der Waals	VDW equation of state
1882, *[26]*	Edison	First cogeneration system and first coal power plant
1887, *[9]*	G.d. Laval	Invention of Laval nozzle
1893, *[9]*	R. Diesel	First patent of diesel engine
1939, [28]	H. von Oheim	First turbojet engine
1969, *[19]*		Apollo 11 First successful flight to the moon
1995, *[21]*	Adrian Bejan	Constructal theory

3   FUTURE DEVELOPMENT OF THERMODYNAMICS

Thermodynamics is developing today in many areas, as shown in Figure 1. One vital part is the calculation of thermodynamic properties. The calculation of thermodynamic properties of a state is possible using classical or statistical thermodynamics. Classic thermodynamics has no insight into the microstructure, but it allows the calculation of thermodynamic function of state with the assistance of the macroscopic observation of phenomena. Unlike classic thermodynamics, however, the statistical thermodynamics (ST) does enable the computation of the thermodynamic functions of the state by studying the molecular structure of the matter, *[11-15]*.

The basis for molecular motion is the motion of atoms in molecules and performance of diverse, attractive and repulsion forces are intramolecular and intermolecular interactions between electrons and nuclei in a molecular system. The energy inherent in such a molecule system consists of *[11-17]*:

- kinetic energy of molecules and atoms (translation (trans), rotation (rot), internal rotation (ir), vibration (vib)).
- potential intermolecular energy (pot). Utilized as an intermolecular potential was the Lennard - Jones potential, *[5]*.
- energy of electrons as to the energy level they belong to (el).
- energy of nuclei as to the energy level they belong to (nuc).

$$E = E_0 + E_{trans} + E_{rot} + E_{vib} + E_{el} + E_{nuc} + E_{ir} + E_{konf} \tag{3.1}$$

To calculate the thermodynamic functions of state, the canonical partition function [12-14] is applied:

$$Z = \sum_i \exp\left(-\frac{E_i}{kT}\right) \tag{3.2}$$

In equation (3.2), the sum runs over all feasible quantum states, EI is the energy of the I- quantum states.

Utilizing the semi-classical formulation for the canonical ensemble for the N indistinguishable molecules can be expressed as follows)[12-14]

$$Z = \frac{1}{h^{3N}} \int ... \int \exp\left(-\frac{E_{trans} + E_{rot} + E_{ir} + E_{vib} + E_{el} + E_{nuc}}{kT}\right) d\vec{p}_1 \cdot d\vec{p}_2 .... d\vec{p}_N \cdot$$
$$\cdot \int ... \int \exp\left(-\frac{E_{pot}}{kT}\right) d\vec{r}_1 \cdot d\vec{r}_2 ... d\vec{r}_N \tag{3.3}$$

The second part of equation (3.3) on the right side we call the configurational integral. Using the canonical ensemble for the system of N, molecules can be like this:

$$Z = Z_0 Z_{trans} Z_{vib} Z_{rot} Z_{ir} Z_{el} Z_{nuc} Z_{conf} \tag{3.4}$$

Thus, the partition function Z is a product of terms of the ground state (0), the translation (trans), the vibration (vib), the rotation (rot), the internal rotation (ir),the influence of electrons excitation

(el), the influence of nuclei excitation (nuc) and the influence of the potential intermolecular energy (conf).

Utilizing the canonical theory for computing the thermodynamic functions of the state can be put as follows:

$$p = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T, \quad U = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V, \quad H = kT\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_V + V\left(\frac{\partial \ln Z}{\partial V}\right)_T\right].$$

(3.5)

Equilibrium statistical thermodynamics could be further divided to classic, Fermi-Dirac, and Bose-Einstein. For the calculation of the thermodynamic functions of state with the help of classical thermodynamics, we used the following equations of state:

Van der Waals TES (VDW) equation of state (EOS)

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

(3.6)

Peng- Robinson TES (PR) EOS

$$p = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2}$$

(3.7)

3) Bennedict-Webb-Rubin (BWR) EOS

$$p = \frac{RT}{v} + \frac{B_0 RT - A_0 - C_0/T^2}{v^2} + \frac{bRT - a}{v^3} + \frac{a\alpha}{v^6} + \frac{c}{v^3 T^2}\left(1 + \frac{\gamma}{v^2}\right) \cdot \exp\left(-\frac{\gamma}{v^2}\right)$$

(3.8)

Figure 2 shows the deviation of the speed of sound for carbon dioxide between the analytical computation with the help of statistical thermodynamics (ST), classical thermodynamics (VDW-Ven der Waals equation of state, RK- Reedlich Kwong equation of state, PR- Peng-Robinson equation of state) and experimental data (exp.).
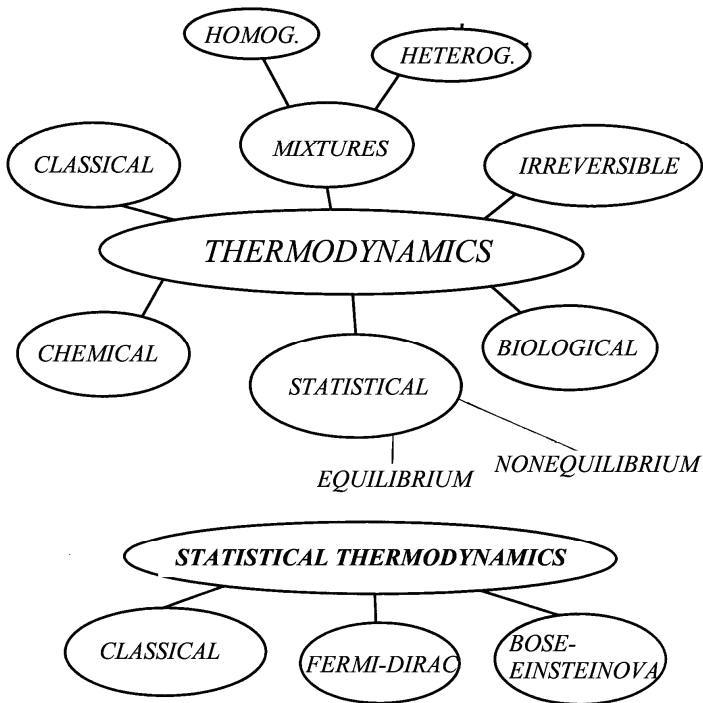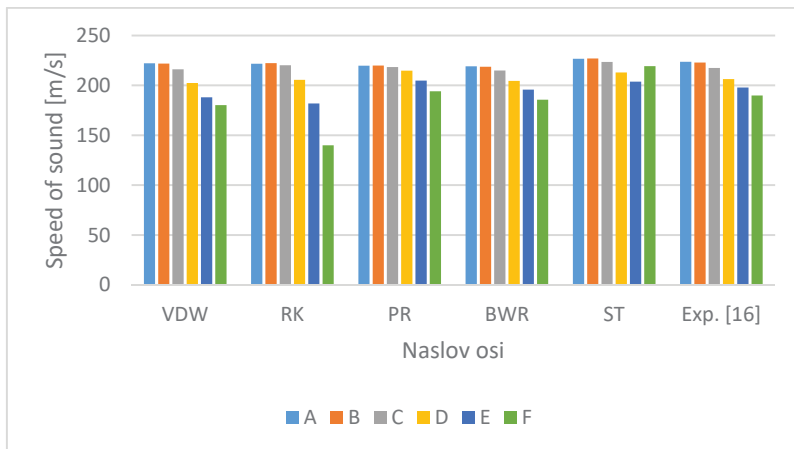
Figure 1: Scientific disciplines in thermodynamics

A (T=223 K) , B (T=243 K), C (T=263 K), D(T=283 K), E (T=293 K), F (T=301 K)

Figure 2: The speed of sound c_0 for CO_2 (R-744) (saturated vapour) with various thermodynamic models

In all scientific areas of thermodynamics, the development in the coming years will be extremely exciting. Some of the most interesting topics for the future include:

- further development of the constructal thermodynamics theory (classical thermodynamics)
- calculation and measurement of thermodynamic properties for unknown substances (classical thermodynamics, statistical thermodynamics, experimental thermodynamics and thermal calorimetry)
- development of thermodynamic models for ionic liquids
- the application of new materials in fuel cells, nuclear engines, and similar technologies.
- the development of new thermal devices with better energy and exergy efficiency

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