Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 681–686

AN ATTEMPT AT QUANTUM THERMAL PHYSICS

J. J. Mareš and J. Šesták*

Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-162 53 Praha 6, Czech Republic

This paper outlines an alternative exposition of the structure of quantum thermodynamics which is essentially based on Carnot's theory where fluxes of caloric are identified with negative information fluxes. It is further assumed that the thermal energy evolved by thermal processes is identical with the electromagnetic zero-point background energy evolved by the destruction of information inscribed in a structural unit (qubit). Theoretical arguments on an elementary level are accompanied by illustrative examples.

Keywords: *caloric, entropy, information, quantum thermodynamics, zero-point radiation*

Introduction

Motivation for this work were mainly informal discussions at two conferences [1] concerning the validity of the Second law of thermodynamics in case where the quantum nature of the system must be taken into account. As we were in the past engaged in research into practical problems requiring application of thermodynamics to quantum systems [2–6], we feel ourselves in the position to express our meaning also to the fundamental questions involved. Therefore, the main purpose of this work is to express our opinion on these questions and to present a sketch of an alternative conceptual structure of quantum thermal physics rather than to investigate a particular problem in detail. Our subject should be, of course, distinguished from that of quantum thermodynamics based on the consequent implementation of quantum-mechanical concepts into classical thermodynamics as is known from standard literature (e.g. [1, 7]).

Besides analytical mechanics and theory of electromagnetic field, it is thermodynamics that is considered to be a well-established, logically closed theory. There are even various axiomatic forms of the thermodynamics, which seem to guarantee absolute clearness of concepts involved. In spite of that we have serious difficulty in finding any book where the subject is treated in a way really clear to an ordinary student. As we are convinced, the very origin of the difficult understanding of thermodynamics is connected just with an inconvenient choice of conceptual basis more than 150 years ago. Traditionally the most obscure is an artificial concept of entropy and rather exceptional form of the 'Second law' of thermodynamics. Whereas the universal laws have mostly the form of conservation laws, the logical structure of the Second law is quite different. Ultimately formulated, it is a law of irreparable waste of 'something' in every real physical process. This imperative negativistic and pessimistic nature of the Second law is very likely, for philosophers but also for many active researches in the field, the permanent source of dissatisfaction. That is why the criticism aimed at the Second law has the history as long as the Second law itself. Moreover, in recent decade an unprecedented number of challenges have been raised against the Second law from the position of quantum mechanics [1]. These arguments, however, are as a rule, enormously complicated with numerous approximations and neglects and consequently rather questionable.

It is a very old empirical fact that the thermal processes in the nature are submitted to certain restrictions strongly limiting the class of possible processes. The exact and sufficiently general formulation of these restrictions is extremely difficult and sometimes incorrect (cf. e.g. the principle of antiperistasis [8], Braun-le Chatelier's principle [9] and Second law) but in spite of it very useful. That is why the authors of this paper believe that the Second law (or another law which puts analogous limitations on thermal processes) does reflect experimental facts with an appreciable accuracy and thus it should be incorporated into the formalism of thermodynamics. On the other side, being aware of the fact that the contemporary structure of thermodynamics with its rigid conceptual basis may have intrinsic flaws, we claim that the absolute status of the Second law should not be criticized or denied from the point of view of another physical theory (e.g. quantum mechanics) prior the correction of these imperfections has been made.

---

* Author for correspondence: semicon@fzu.cz

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Reformulation of fundamental laws of thermodynamics

A serious flaw in the conceptual basis of classical thermodynamics concerns even the so-called First law of thermodynamics. The first step toward this law was made by Benjamin Count of Rumford by the generalisation of his observations made at an arsenal in Munich (1789) [10]. Accordingly, practically unlimited quantity of heat was possible to produce only by mechanical action i.e. by boring of cannon barrels by a blunt tool and this experimental fact was by Rumford analysed as follows: 'It is hardly necessary to add, that any thing which any insulated body, or system of bodies, can continue to furnish without limitations, cannot possibly be a material substance: and it appears to me extremely difficult, if not quite impossible, to form any distinct idea of anything, capable of being excited and communicated, in the manner the heat was excited and communicated in these experiments, except it be motion'. The same idea that heat absorbed by a body, which is particularly responsible e. g. for the increase of its temperature, is identical with the kinetic energy of its invisible components was further apparently supported by arguments due to J. P. Joule [11]. Results of his ingenious and marvellously accurate experiments have been summarized into two points: The quantity of heat produced by the friction of bodies, whether solid or liquid is always proportional to the quantity of force expended. The quantity of heat capable of increasing the temperature of a pound of water by 1° Fahrenheit requires for its evolution expenditure of a mechanical force represented by the fall of 772 lbs. through the space of one foot (here the term 'force' has evidently meaning of energy). In spite of clearness of these correct statements, Joule did not stressed out explicitly the fact that in his experiment we have to do only with one-way transformation of work into the heat. Instead he tacitly treated throughout the paper the heat as it were a physical entity fully equivalent or identical with mechanical energy. It was probably due either to influence of Rumford or to the reasoning that in the experiment heat appears just when mechanical work disappears and ipso facto these two entities must be identical. Such an extremely suggestive but incorrect idea was later canonized by Clausius [12] who proclaims an object of thermodynamics to be 'die Art der Bewegung, die wir Wärme nennen' i.e. the kind of motion we call heat.

In the history of thermodynamics objections appeared against such an energetic interpretation of the heat. Unfortunately, these objections were only rare and with no adequate response. One of them is due e.g. to Mach [13]. Accordingly, it is quite easy to realize device of Joule's type where a given amount of energy W is completely dissipated and simultaneously the heat in amount $Q=JW$ is evolved, where J is universal Joule's proportionality factor. On the other side, as far as it is known, there is no single real case where the same amount of heat Q is transformed back into mechanical work $W=Q/J$ only by reversion the original process. Taking into account this circumstance together with the very generic property of the energy, which can be principally converted into another form of energy without any limitation, we must exclude the logical possibility that the heat is energy at all. Of course, postulating the equivalence of energy and heat a meaningful mathematical theory of thermal processes can be and actually has been established. The price paid for the equivalence principle is, however, rather high. In order to make the theory consistent it was necessary to create somewhat artificial and highly abstract quantities like entropy, enthalpy, free energy, and various thermodynamic potentials the meaning of which is more formal than physical. The mathematical manipulations with their ~720 derivatives and differentials (which are sometimes total) [14] actually do provide results the interpretation of which is, however, rather matter of art than of science.

Heat as an Entropy–Caloric

Astonishingly an elegant way leading out from these problems was very likely for the first time suggested by Callendar [15] and later in more sophisticated form worked out by Job in his impressive book [16]. The main idea is that the heat in common sense (e.g. as a cause of elevation of temperature of bodies exposed to the heating) should not be identified with a kind of energy but with the entropy, which is known from classical thermodynamics. It was shown by Larmor [17] and especially by Lynn [18] in a very pregnant way that the heat could be measured in energy and entropy units as well. In the latter case the heat–entropy concept attains the content identical with the concept of Carnot's 'caloric' ς [19], whereas the empirical temperature θ, i.e. 'hotness' [13], automatically starts to play the role of its potential. (We are using for caloric Greek final letter ς as this letter involves both, usual S for entropy and C for caloric.) For the increase of potential energy $d\varepsilon$ of the amount of caloric ς due to the increase of temperature by $d\theta$ we may, namely, write:

$$d\varepsilon = \varsigma F'(\theta) d\theta \tag{1}$$

where $F'(\theta)$ is so-called Carnot's function. It is an experimental fact that this function can be reduced to the universal constant = 1 using instead of arbitrary empirical temperature scale θ the ideal gas temperature scale T equivalent to the absolute Kelvin scale [20, 21]. (Notice that Carnot's function in (1) corresponds to the situation where the heat is measured in entropy and not in energy units [22]). In this case for the potential energy ε corresponding to the given amount of caloric ς kept at the temperature T we can write:

$$\varepsilon = \varsigma T \tag{2}$$

The perfect analogy with other potentials known from physics, such as gravitational and electrostatic potentials, is then evident. After the terminological substitution of heat-energy by heat-entropy it is only a technical problem to reformulate two fundamental laws in a manner which is common in classical axiomatic thermodynamics [23], namely:

I.) Energy is conserved in any real thermal process

II.) Caloric (heat) cannot be annihilated in any real thermal process

Notice that the first and second law, formulated in such a way are conceptually disjunctive because caloric has nothing to do with energy. The possible link between these laws and quantities, however, provides formula (2). We shall not discuss here application of theorem *II)* to particular cases known from empirical observations of real processes (it is already done e.g. in [16]) but, instead, we proceed further making use of an important relation existing between entropy and information. It was recognized by Szilárd in his pioneering work [24] that in a certain thermal process the exchange of information must play an essential role. Afterwards, the establishment of fundamentals of information theory [25] enabled Brillouin to reformulate this idea with an appreciable mathematical rigor [26]. (For more recent review on the information-entropy relation, see e.g. [27].) Accordingly, the information Υ has a character of negative entropy (i.e. we are allowed to write $\Upsilon = -\varsigma$) and therefore, in our old-new provisional terminology, we can identify the production of caloric with the destruction of information and the flux of caloric with the information flux in an opposite direction. Theorem *II*) can thus be reformulated in terms of information as:

II*) Information (Υ) is destroyed in any real thermal process

Veracity of this theorem seems to be very obvious at first glance. Indeed, almost everybody has experience that by combustion of newspapers in a stove or petrol in a car engine these materials are lost forever, together with the information involved. On the other hand, it is little convincing that such a 'tiny thing' as the information is, can really be able to control natural thermal processes. Isn't it more likely that statement *II**) concerns only side effects taking place in certain cases? We do not think so and we assume that the validity of postulate *II**) is quite general and apt for substitution of the Second law of thermodynamics. Moreover, besides the properties of the caloric already discussed, just the existence of the direct link between caloric (i.e. heat) and information is the very reason for which we prefer to use for the quantum description of thermal processes rather the conceptual basis of caloric theory than that of classical thermodynamics. In conclusion of this paragraph and as illustration of such an approach, let us paraphrase Rumford's original analysis of his experiments cited above by simply writing there instead of the word 'motion' the phrase 'perished information'.

Quantum nature of information bound to caloric

In order to involve the information into the physical reasoning it is convenient to convert information coded, as usual, in binary units Υ_2 (bits) into the information Υ_p expressed in physical units. This relation obviously reads:

$$\Upsilon_p = (k\ln 2)\Upsilon_2 \tag{3}$$

where k is Boltzmann's constant ($k = 1.38 \cdot 10^{-23}$ J K^{-1}). It should be stressed here that by choosing Boltzmann's constant as a conversion factor simultaneously the absolute Kelvin scale was chosen for temperature measurements.

We assume now that there is no information 'an sich' or in other words information needs in all cases a material carrier. From the point of view of macroscopic thermal physics there is, however, fundamental difference between e.g. genetic information inscribed in the DNA and information provided by a gravestone inscribed with personal data. Whereas in the former case for coding of information structural units on molecular level are used, which should be described by microscopic many-body formalism, to the later case rather a macroscopic description in terms of boundary–value problem is adequate. To distinguish without ambiguity between these two extreme cases we need, however, a criterion which, having a sign of universality specifies what the 'molecular level is'. As far as we know, a good candidate for such a criterion is modified Sommerfeld's condition distinguishing between classical and quantum effects [28, 29]. It reads:

$$\Omega \leq 2\pi\hbar \tag{4}$$

where Ω is phase space occupied by a structural unit ('qubit') where minimally 1 bit information is stored and $\hbar$ is the Planck's universal constant ($\hbar = 1.05 \cdot 10^{-34}$ Js). Direct computation of the action Ω corresponding to one atom built in an ordinary crystal, liquid or gas confirms the validity of condition (4) in these cases. It proves the fact that every atom together with its nearest neighbourhood should be treated as a quantum structural unit responsible for information storage on a 'molecular level'. Generalizing this result, we can conclude that the very nature of Carnot's caloric is the destructed information originally coded in occupied quantum states of structural units of which the macroscopic system under investigation consists.

Inexhaustible source of energy for thermal processes

The mechanism of information transfer through the macroscopic system is assumed to be due to erasing information in one particular structural unit which is influenced by the neighbouring one in the field of long range forces defined by macroscopic system as a whole. There are, however, limitations of such a process. First, as the information storage in both neighbouring structural units is submitted to the same condition (4) it is impossible to exchange more information from one unit to another than ~1 bit per $2\pi\hbar$ of the occupied phase space. Second, the exchange of information must be in agreement with boundary conditions put on the macroscopic system as a whole, which are locally realized e.g. by long range forces. It may thus happen that the transfer of some information from one unit to the neighbouring unit is incompatible with these external conditions and information is lost. The loss of information physically means that some characteristic pattern of structural unit has disappeared and a wider class of quantum states becomes accessible. In the frame of the presented model any loss of information should be accompanied with the development of energy. How to explain where the energy comes from?

We are inclined to interpret the stability of quantum objects as a result of existence of zero-point electromagnetic vacuum fluctuations exactly compensating energy loses due to the recoil radiation from this object. Such an approach well known from stochastic and quantum electrodynamics [30, 31], confines our considerations to the systems controlled only by electromagnetic interactions, namely, low temperature plasma, gases, condensed matter and chemical reactions in these systems. Accordingly, the cohesion energy of any such a system is nothing but the energy of electromagnetic modes of the background zero-point radiation accommodated in such a way that they fit the geometry of the system. Characterizing the dimensions of the quantum electromagnetic system (for which the universal constants $\hbar$ and c must be taken into consideration) by a single length parameter a, we immediately obtain for cohesion energy a formula of Casimir's type by applying dimensional analysis [32]:

$$\varepsilon \approx \gamma(\hbar c / a) \qquad (5)$$

where the dimensionless parameter γ should be determined from a particular geometry of the system (usually γ ranges from 0.1–0.001 [30]). The change of dimension a or complete destruction of a structural unit with energy (5) during thermal process has a consequence that just this amount of energy is developed at the place. As this energy is in fact a modified energy of all-pervasive universal zero-point background, we have to do with an energy supply from practically inexhaustible non-local source of energy. Therefore, within the frame of stochastic electrodynamics every thermodynamic quantum system should be interpreted as an open system even in the case where it is finite.

Examples

In order to make the presented system of quantum thermodynamics more intelligible we have given three examples illustrating how should be some common observations within the frame of this system interpreted.

1) How does the heat engine work? Heat engine in the sense of original Carnot's theory is nothing but a kind of mill driven by caloric ς falling from a higher potential T_1 (boiler) to a lower potential T_2 (cooler). Information thus flows from the cooler with condensed water (better ordered than steam) to the cylinder of engine where the information is destroyed (by weakening of correlations among molecules during the expansion) giving rise to useful work originating in zero-point background. Then the residual information continues to flow to the heater where it is dissolved during ordering of configuration of the steam. Notice that the flow of information and the flow of water are just opposite in this case and that the question how the boiler is heated is put aside. In a typical combustion engine at low temperature the fuel with high information content flows into the cylinder of engine. During the combustion of fuel the information which is coded in its structure is destroyed and the useful work from the zero-point quantum electromagnetic energy is produced there. The information, however, flows inside the combustion space for this type of engine also through the exhaust-pipe so that special attention must be paid to this part.

2) There is an interesting device called Bunsen's ice calorimeter. As this apparatus works at a well defined temperature T_M (i.e. melting temperature of ice =273 K) it, in fact, according to equation (2), measures directly inputted caloric and may thus serve as 'entropymeter'. Indeed, the information destroyed and the latent energy of melting is connected here in an especially obvious way. An estimate of the latent energy ε_M per one mol of ice can be obtained as follows. We make a use of an important fact that the H_2O

molecules retain their integrity in both water and ice, simultaneously neglecting the effect of clustering of molecules at temperatures well above the melting point which is responsible for non-trivial macroscopic behaviour of water [33, 34]. Within the frame of such a simplified model it would be then necessary for the melting of ice to break down 4 well-oriented bonds per every water molecule and substitute them by quasi-continuum of states. Such a transformation corresponds approximately to the destruction of $\Upsilon_2=4$ bits of information per molecule [27]. Taking into account equations (2) and (3) we can thus write:

$$\varepsilon_M = (Nk \ln 2) T_M \Upsilon_2 \qquad (6)$$

where N is Avogadro's constant ($N=6.02\cdot10^{23}$ mol^{-1}). The estimate of ε_M then reads ≈6288 J mol^{-1} in an excellent agreement with the experimental value =6007 J mol^{-1}.

3) There are different microscopic parameters characterizing the configuration of a structural unit where the information is stored which can be in principle constructed from quantum numbers describing this system. The relation connecting these microscopic parameters and macroscopic boundary conditions is evidently very complicated. If we, however, as above, confine ourselves only to a single parameter a – characteristic dimension of the structural unit, this relation can be found in an explicit form and compared directly with experimental data. Combining formulae (2) and (3) the temperature change of the potential energy of a structural unit which is due to the erasing of information Υ_2 from it is given by:

$$\mathrm{d}\varepsilon / \mathrm{d}T \approx -(k \ln 2)\Upsilon_2 \qquad (7)$$

Substituting for ε the Casimir's quantum cohesion energy (5) we immediately obtain an estimate for the corresponding relative expansion of the unit:

$$\mathrm{d} \ln a / \mathrm{d}T \approx a(k \ln 2 / \gamma \hbar c)\Upsilon_2 \qquad (8)$$

Assuming that the thermal process is homogeneous and isotropic, this coefficient must be within the order of magnitude identical with the expansion coefficient macroscopically observed. For typical condensed matter where bond length $a \approx 4\cdot10^{-10}$ m and $\Upsilon_2=1$ we obtain from (8) for coefficient of relative thermal expansion a value of $1.2\cdot10^{-7}/\gamma$ which is near to the values experimentally observed (typically $\approx10^{-5}$), provided that $\gamma\approx0.01$.

Conclusions

In conclusion, using elementary arguments without mathematical rigor, changes in the conceptual basis and in the structure of quantum thermodynamics have been suggested. The resulting theory is based essentially on the following points:

- Modified form of Carnot's theory where caloric is identified with the entropy.
- Equivalence of information and negative entropy.
- Interpretation of stability of quantum objects as the consequence of the existence of electromagnetic zero-point vacuum radiation.

The authors are aware that the structure of quantum thermodynamics as sketched out in this paper is far from to be mature, however, they are simultaneously convinced that it is potentially apt to reflect the empirical facts in a more intelligible way than the present theories.

Acknowledgements

This work has been supported by the Grant Agencies of the Czech Republic and of the Academy of Sciences (Projects Nos 202/03/0410 and 522/04/0384).

References

1 1st IC on Quantum limits to the Second law, San Diego '02, Ed. D. P. Sheehan, AIP Proceedings, 643 (AIP, Melville, 2002), see also Proc. of 2nd IC on Frontiers of Mesoscopic and Quantum Thermodynamics, Prague 2004, Ed. V. Špička.
2 J. Šesták, J. Therm. Anal. Cal., 69 (2002) 1113.
3 Z. Kalva and J. Šesták, J. Therm. Anal. Cal., 76 (2004) 67.
4 B. Hlaváček, J. Šesták and J. J. Mareš, J. Therm. Anal. Cal., 67 (2002) 239.
5 J. Strnad, J. Protivínský, Z. Strnad, A. Helebrant and J. Šesták, J. Therm. Anal. Cal., 76 (2004) 17.
6 J. J. Mareš, J. Stávek and J. Šesták, J. Chem. Phys., 121 (2004) 1499.
7 T. Feldmann and R. Kosloff, Phys. Rev., E 68 (2003) 016101.
8 K. Meyer-Bjerrum, Die Entwicklung des Temperaturbegriffs im Laufe der Zeiten (Vieweg u. Sohn, Braunschweig, 1913).
9 P. Ehrenfest, Journ. D. Russ. Phys. Ges., 41 (1909) 347 (in Russian).
10 Count Rumford, Phil. Trans., 88 (1789) 80.
11 J. P. Joule, Phil. Trans., 140 (1850) 61.
12 R. Clausius, Mechanische Wärmetheorie, (Vieweg u. Sohn, Braunschweig, 1876).
13 E. Mach, Die Principien der Wärmelehre (Verlag von J. A. Barth, Leipzig, 1896)
14 P. W. Bridgman, The Nature of Thermodynamics (Harvard University Press, Cambridge, 1941).
15 H. L. Callendar, Proc. Phys. Soc. of London, 23 (1911) 153.
16 G. Job, Neudarstellung der Wärmelehre – Die Entropie als Wärme, (Akad. Verlagsges., Frankfurt am Main, 1972).
17 J. Larmor, Proc. Royal Soc. London, A 194 (1918) 326.
18 A. C. Lynn, Phys. Rev., 14 (1919) 1.
19 S. Carnot, Réflexions sur la puissance motrice du feu, (Bachelier, Paris, 1824).

20 J. J. Mareš, J. Therm. Anal. Cal., 60 (2000) 1081.
21 W. Thompson (Lord Kelvin),Trans. Royal Soc. Edinburgh, 16 (1849) 541.
22 H. T. Wensel, J. Appl. Phys. 11 (1940) 373.
23 C. Truesdell, Rational Thermodynamics (McGraw-Hill, New York, 1969)
24 L. Szilárd, Z. F. Physik, 53 (1929) 840.
25 C. E. Shannon, Bell Syst. Techn. J., 27 (1948) 379, 623.
26 L. Brillouin, J. Appl. Phys., 24 (1953) 1152.
27 A. Wehrl, Rev. Mod. Phys., 50 (1978) 221.
28 A. Sommerfeld, Phys. Z., 24 (1911) 1062.
29 J.-M. Lévy-Leblond and F. Balibar, Quantics, Rudiments of Quantum Physics (North-Holland, Amsterdam,1990).
30 L. de la Peña and A. M. Cetto, The Quantum Dice – An Introduction to Stochastic Electrodynamics (Kluwer Academic Publishers, Dordrecht, 1996).
31 P. W. Milloni, The Quantum Vacuum – An Introduction to Quantum Electrodynamics (Academic Press Inc., Boston, 1994).
32 J. Palacios, Dimensional Analysis (MacMillan and Comp., Ltd., London, 1964).
33 J. D. Bernal and R. H. Fowller, J. Chem. Phys., 1 (1933) 515.
34 L. Pauling, J. Am. Chem. Soc., 57 (1935) 268.

DOI: 10.1007/s10973-005-6886-2