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HEAT AS MANUFACTURING POWER OR THE SOURCE OF DISORDER?

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Abstract

The notion of heat is thoroughly analyzed and historical links are discussed particularly with accentuation on its interdependence to contemporary thermal physics. Thermodynamics is discussed in relation to both the traditional development of equilibrium and the modern description of disequilibrium (related to real-open systems) as well as to the affiliated aspects of information. Dissipation is shown to provide a new kind of self-organized structure. Impact of mathematics is also displayed (fractal structures, bifurcations, vibration, topology, etc.). Exploitation of fire as an analytical tool and manufacturing power is analyzed. Generalized engines are shown in the sense of information transducers. The text gives a congruous view to various historical and modern concepts and gradual development of ideas that emerged during the continual understanding of order and disorder.

Keywords: dissipation, entropy, heat, history, non-equilibrium, philosophy, self-organization, thermodynamics

Historical roots and links to present thermal science

The Universe, including our planet, has been shaped by the impact of heat, with its destructive (disordering) and manufacturing (ordering) power. Mankind has experienced this world in its dependence on fire, in the integrative meaning of light, heat, caloric, power or energy, recognized as a rudimentary element in the pathway of ordering matter and society [1–4]. A key feature of human consciousness enables the understanding of fire from its visible wholeness down to its imaginary composition of internal vibrations and capacity to sustain life. The early Greeks [5, 6] believed that the single unifying thing (the One) was some material, like water, stone or fire. They were concerned with finding the unchanging principle of substances that lay behind all changes within a stable component of the Universe (‘arche’) and living nature (‘physis’) [1, 6]. Fire was held as the most rare, sacred and powerful, a kind of a chief,

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assuming the souls of all sentience and intellectuals are issue from a central fire, or the soul of the world.

People gradually realized that for obtaining useful work one needs to apply not only heat but also cognition (i.e., attached know-how understood as today's information [7, 8]). In accordance with electro-magnetism understanding of heat had to be encapsulated into an auxiliary field of thermal science, the development of which became distant from traditional method adopted in more fundamental mechanics. The difference between thermal science and mechanics arises largely out of tradition. Mechanics has long ago reached the status of rational science while thermal science has reached a similar status only recently. It is customarily related to the notion thermal equilibrium [9] where all processes came to a halt and any organism would die. We actually reside in an obvious disequilibrium [10] – in a series of self-organized processes lying evidently outside the traditional concept of equilibrium. It associates with a delicate interplay between chance and necessity, between fluctuations and deterministic laws, under subtle interactions between mass and heat flows. It was also reflected by our gradual development of the understanding of our Universe, from the static view up to the present complex world of novelty and diversity.

Mankind would like to live in thermostable environments, but Earth's ecosystem (sometimes simplified as a sort of a Carnot super-engine) is not everywhere stable [9, 11]. Mankind uses to obtain what it wants in a dissipative way by heating and cooling with machines when manipulating this disequilibria of our ecosystem. Disequilibrium is a source of work and a thermostabilizing power. It is also a global datum of Nature as it derives from the cosmological history of the present Universe. For instance, on a larger scale we know that the 2.8 K thermal (cosmic microwave background) radiation that fills the universe is not in a thermal equilibrium with the matter in the galaxies. On a smaller scale, the Earth (atmosphere, biosphere, life, etc.) is in non-equilibrium due to the constant influx of heat delivered from the Sun. Even on a smaller scale we use to experience everyday variety of non-equilibrium processes visualized. However, all dissipative processes take place with a time arrow, they belong to a world in which there is past and future, memories, culture and discoveries, including the recent discovery of the laws of irreversibility themselves.

Adopting fire for use as a manufacturing power, three principles of early thermal treatments are known, (i) amount of fire (temperature) can be level, (ii) fire affects different materials in different ways and (iii) materials compatible at ordinary temperatures can react to give new products on firing. The notions of heat and temperature (temper-temperament, first used by Avicena in the 11th century) were not distinguished until the middle of the seventies ([1, 12]). It took another 150 years until thermal science was introduced on the basis of Maxwell's works [13] and named by Thompson as 'thermodynamics' according to the Greek terms 'thermos' – heat and 'dynamis' – force. The contradiction of its 'dynamic' notion against its 'static' applicability (thermostatics) is described here. Only the statistical thermodynamics (Boltzmann) interconnected microcosmos of matter with actual observations. In the evaluation of heat capacity, Einstein and Debye associated temperature with the distinguishable micro-particles (atoms) oscillating around their lattice sites where all degrees of freedom correspond to the vibrational modes [14]. Vibrational nature, as that of heat, has been an inspiration related to an old Pythagorean idea of chord harmony tuned in rational ratios. This became reflected in a modern cosmological approach called superstring theory [15], mathematically based on the structure of vibrating strings.

Through a better understanding the heat it was recognized that although energy is conserved in physical processes, it is degraded into less ordered forms as observed in a closed system that tends to become more and more disordered. This is not a kind of law like gravity but a principle having statistical nature and is very important for considering what is technologically possible. Yet the succession was found in the interconnection between the newly introduced notions of entropy and information (gain or loss). Information can be seen as a commodity and it takes effort to acquire it [7, 16]. So that it is possible to classify all technological enterprises in terms of the amount of information needed to specify the structure completely and the rate at which the information needs to be changed in order for the system to change.

Fire as an industrial tool

Fire has always played a significant role as a destroying and creating power: the profitable industrialized power in the process of manufacturing goods. It also has a novel application as an instrumental reagent for modern analysis of the properties of materials. Understanding heat led to the formulation of a consistent science of thermal physics, thus developed the related domain of thermal analysis touching on any adjacent field of science where changes in temperature are responsible for changes in the observed properties of the material. In fact, erroneous premises of a non-material notion ‘thermogen’ or ‘caloric’ were early suggested. The caloric theory supplied a plain solution to thermal expansion and contraction. If the only known force of gravitational attraction would not be compensated for every particle of matter they would be attracted towards each other, resulting in a single solid homogeneous mass. To prevent this collision a repulsive force was postulated which was considered to be this self-repulsive caloric. Such an early fluid hypotheses became important in the formulation of modern laws of elementary forces. It was common to the way of thinking of Archimedes, Epicureans [1, 5, 6] and later used in the Carnot and Clausius’ [22] concept of thermodynamics. Heat flow equations applied in thermal analysis bear the approach of caloric-like philosophy.

The concept of heat [23, 24] became complicated by the introduction of an artificial quantity called entropy (after the Greek ‘trepo’ – turn and ‘en’ – internal). Dislodging traditional heat out of its mathematical framework, see Fig. 1, citing ‘actually the first law gives the quotation of energy conservation law but only under specific conditions for heat that is not fully equivalent with other kinds of energies’ [23]. Heat cannot be converted back to mechanical energy without changes affiliating heat with entropy via the second law of thermodynamics, which intuitively states that heat cannot be annihilated in any real physical process. It may be said that Hamiltonian physics [18, 25] kept alive in the halls of Academies while entropy lived in the workshops of the smiths where it was actually born.

Fig. 1 Discourse on thermodynamics

By the end of the nineteenth century, there were available two different mathematical tools to model natural phenomena – exact, deterministic equations of motion and the equations used in thermal physics, based on statistical analysis of average quantities. Whenever any non-linearity appeared, it was put in linear regimes, i.e., those whereby double cause produces double effect and the solution is linear in the known term (classical thermodynamic laws). In these linear system small changes produced small effects and large effects were due either to large changes or to a sum of many small changes. In non-linear systems small changes may have dramatic effects because they may be amplified repeatedly by self-reinforcing feedback being thus basis of both instabilities and the sudden emergence of new forms of order, characteristic for self-organization [26–28]. Such a drastic move away from a standard configuration can lead to states displaying spatial or temporal order. These regimes, called dissipative structures [29, 30] can only exist in conjunction with their environment (non-equilibrium thermodynamic laws). If constraints are relaxed the systems return to standard equilibrium and, the entire long-range molecular organization collapses.

With the concept of entropy and the formulation of the second law, modern thermodynamics introduced the idea of irreversible processes, including the arrow of time. It says that some (mechanical) energy is always dissipated into heat which cannot be recovered. During 1960s, when Prigogine [26–28] developed of non-linear thermodynamics, a concept of local equilibrium was introduced, where traditional relations remain valid for the thermodynamic variables assigned to elementary and finite small volumes. The new idea became a vehicle to help to describe the curiosity of self-organization phenomena making possible for supplementary formation of the self-possession structures [27–30]. This enabled inclusion of typical dissipation energies of heat transfer or friction that granted a quite different nature of structures (turbulence, vortices), showing that dissipation can be a source of order [28].

Let us imagine two horizontal plates heated from below. No convection occurs if the hot plate is above the cold one but it occurs in the reverse situation. Whether it does so or not depends on the magnitude of the temperature difference represented by the dimensionless Rayleigh number. When a certain value is exceeded, a pattern of convective rolls, known as Bernard cells, is established between the plates. Such asymmetrical heat flows can happen even within a thin layer of a solid body (e.g., micro-discs used in DSC). It merges when a critical point of instability is achieved (bifurcations). A constant flow of energy and matter through the system is a necessary condition for this instability to self-organize.

Physically, a non-linear pattern results in a mutually co-coordinated process because molecules are not in random motions but are interlined through multiple feedback loops, mathematically described in terms of non-linear equations. Further away from equilibrium, the fluxes become stronger, entropy production increases, and the system no longer tends towards equilibrium. This does not contradict the second law of thermodynamics because the total entropy of the open system keeps increasing, but this increase is not uniform throughout disorder. In fact, the dissipative structures are fluctuations of order in the background of disorder, maintaining or increasing their order at the expense of greater disorder in their environment [31–33]. This may occur at a reaction interface under the cooperative action of thermal and concentration gradients, within yet unreacted layer of reactants Other examples are the Belousov–Zhabotinsky reactions [34, 35] or the biophysical signals emitted by living cells to control a number of key processes [28, 36]. Particularly in this living world, order and disorder are always created simultaneously when the transfer of heat plays a crucial role.

Exploitation of fire

A most conscious exploitation of fire [1], proposed by Newcomen, Watt and Stephenson at the turn of nineteenth century (while constructing a steam heat engine and later a functional locomotive) gave a practical dimension to thermodynamics. It interconnected the three forms of the basic elements: heating water by fire to get a thick air (steam) capable of performing useful work (moving piston and turning a wheel). Later, Lenoir's gas-engine and particularly Ott and Diesel's combustion engines imprisoned fire into the cylinder, forming thus the shaped earth. Such a four-stroke engine is fully restricted by the laws of thermodynamics and controlled by the four-cycle sequence essential to starting and ending in the same originating point. The encircled loop for the given pair of associated intensive (e.g. temperature, pressure) and extensive parameters (entropy, volume) provides then a convenient estimate (Carnot) of the net gain [37] with a general applicability, (Fig. 2).

For unidirectional (ordered) motion of a piston, the notion of internal energy, U, equals $P.\ V$ defines the state variables pressure, P, and volume, V. For multi-directional (disordered) heat motion one can analogously write $U=TS$ which leads to the definition of entropy, S, and complete the pair with the already known temperature, T. Any thermal engine can work only between two heat reservoirs, at different temperatures T_1 and T_2 and the transformation between these two states is less than ideal and needs some non-equilibrium encouragement. Thermal discontinuity $T_1>T_2$ is needed to push a heat flow through the $T_1 \rightarrow T_2$ interface. Such a disequilibrium coincides with the irreversibility of the reverse heat flux dQ. Equilibrium thermodynamics has only one way to describe such a disequilibrium, that is splitting the system into subsystems, each one being mutually in equilibrium, providing the efficiency, ξ, does not exceed $(T_1 - T_2)/T_2$. If entropy is assumed reversibly proportional to order a ratio between the actual, I, and initial, I_o , information (where $I \rightarrow I_o$ when $S \rightarrow 0$) can be used to account for an information gain by employing the relation: $I_{gain}=\log(1-\xi_{actual}/\xi_{maximum})$ [7].

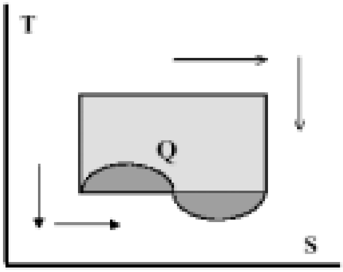

Fig 2 Textbook Carnot thermodynamic cycle [7, 9, 37, 39] on the equilibrium temperature, T, *vs.* entropy, S, diagram. Solid arrows show the power cycle while the opposite cycle shows the reverse heat pump (refrigeration process). Applied to the economy [39], a similarly assumed business cycle (replacing conditions of minimum Gibbs energy by maximum economic prosperity), can be imagined by using a non-conventional depiction of T as the mean property of a society while entropy (understood as society order or disorder) remains the same. Products are manufactured in a cheap (lower T) market and sold in a more affluent market (higher T). The shaded area represents useful work Q (either as heat or money) and the dotted line illustrates the more natural, non-equilibrium processing due to delays caused by, e.g., thermal conductivity (Cruzon–Ahlborn diagram) or business transport obstacles. Similar non-linear backgrounds are known in various thermophysical measurements where, for example, an s-shaped zero line is obtained by the instrumental method of differential thermal analysis – DTA [39] (cf. the last paragraph ‘Heat as a thermoanalytical tool’).

Moving from equilibrium to the situation of two or more subsystems in a mutual disequilibrium one has to operate from the outside at the expense of some energy. This way of reasoning appealed to Gibbs who, a century ago, defined the concept of minimum work necessary to take a thermodynamic state out of equilibrium. In other words it is saying that the arrow of thermodynamics goes in the direction of increased entropy [38] or dissipated energy. If the system is driven away from equilibrium, it occurs only at the expense of displacement of another system towards equilibrium. If such a system proceeds in a given direction while opposed continuously by a force field tending to reverse it, the system can produce useful work at the expense of entropy [7, 8, 39]. Although these changes can be measured, entropy itself appears as an abstract mathematical quantity whose reality is difficult to visualize because entropy is somehow outside the range of our common sense and experience. Entropy should be understood, as a function of internal make up of the system, its organization and disorganization, rather than merely a phenomenological function of the heat content and temperature (Q/T) of the system.

This idea developed to a wide variety of engines, turbines, pulse-jets and other power cycles all governed by the same principles of thermodynamic efficiency for the external and/or internal utilization of heat/fire. We should remind that a combustion engine is an open system – it consumes fuel, often together with oxygen, at a higher potential energy and is exhausting excess heat and combustion products at a lower potential energy. Such a pattern of activity produces, however, disorder and becomes fully compliant with the second law of thermodynamics.

The earth's based and assembled machine (engine, clockwork) can thus be regarded as an information transducer [7, 8], that actually does not change itself during this work-producing thermodynamic process (except its wearing out). It implies that for producing useful work, it is necessary to apply not only energy but also cognition (information derived from the Greek 'in-formare' in the sense of ether as internal shape joining the four early elements of earth, water, air and fire).

Theoretical progress became possible through a more extensively developed field of rational thermodynamics [41, 42] making possible the generalization of laws for all 'open' systems. These 'true flow' features helped to open an insight for a better understanding of chaos as an entire source of order necessary for systems to undergo evolution. It was necessary to introduce differential equations describing the local flows as small linear parts laying on a non-Euclidean surface. Every particle is subjected to a random Brownian motion [43, 44], possessing a characteristic diffusion coefficient and acting under an external field according to Newton's law. It may lead to the formula equivalent to the quantum-mechanical form of the Schrödinger equation [25, 29, 44] with a Hamiltonian structure as a charged particle in an electromagnetic field. Elementary physics has already gone a stage beyond complex numbers in order to describe weak and strong interactions. Temperature can be seen to play the role of concentration of the diffusing substance. Complex numbers can be avoided by applying a more general diffusion coefficient based on hyper-complex (multivector) mathematics capable of describing life processes taking place within solid matter.

Any heat production is a source of heat flows, accomplishing a function of non-equilibrium passkey. Thus for any reaction, at some distance from a reacting zone the neighboring matter (often fluid) undergoes irregular turbulent motion caused by intimate heat and mass transfers. It naturally creates a mushy zone consisting of a cascade of branches and side branches of dendrites [45, 46] (from the Greek 'dendros' – tree) of products (often crystals). Their resulting microstructure is of highly heterogeneous morphology. Increased sensitivity to small input changes results in localized and non-steady mass and heat diffusion, effected by temperature fluctuations, surface tension, interface curvature, etc. These circumstances determine whether the growing solid looks like a snowflake or like seaweed (seen in terms of fractal geometry [47]) and never follows simple integral geometry, closely associated with the theory of chaos [48–51].

Complex structures seem to display threshold of complexity. Just assume a group of people. Gradually increasing the collection the number of complex interrelations expand enormously, and a very high level of complexity is achieved within a connected logical network [52]. It may become as common a property as 'fire' [1] and it may develop a systematic framework such as was the case of early theory of thermal physics (thermodynamics). We just need to look for some basic links between mathematical description of particles (strictly controlled by laws of thermodynamics in reaching lowest energy) and human beings (affected by their feelings in achieving for example maximum happiness [7, 8, 37]).

Heat as a thermoanalytical tool

Thermal behavior has been mostly studied by thermal analysis [8, 39, 45, 53] when roots extend back to the eighteenth century where temperature became an observable, experimentally decisive and monitorable parameter. It implied control of heat flux and heat itself was understood to be a kind of physico-chemical reagent [39]. Heat, however, could not be directly measured but calculated on the basis of the measurable temperature gradients. Heat flow is intermediated by massless phonons so that the inherent flux does not exhibit inertia as is the case for the flow of electrons. The apparent thermal inertia (observed, e.g., in DTA experiments [39, 54]) is caused by heating a real body and is determined by the properties of the materials which form the body [55].

Rudberg (1829) who monitored inverse cooling-rate data for various alloys, did the earliest recorded thermal analysis experiment. Fifty years later this method was found useful as a standard metallurgical research procedure (Osmond). Differential mode (ΔT between the sample and inert reference known as DTA) was used by Roberts–Austen and Kurnakov at the turn of twentieth century and the inherent heat flows and temperature gradients became the center of investigations. Later White showed the effects of different experimental variables on the resulting heating/cooling curves. Factor, Hanks, Gray, Šesták [39] completed these premises by consistent theory of non-stationary (heat flow) type of calorimeter (DTA, DSC [54]). It was embedded within a 'caloric-like' framework as based on macroscopic heat flows between large bodies (cells, thermostats). The need of a more quantitative calibration brought about the use of pulse heating [55] by defined rectangular and triangular electric strokes showing again the importance of heat–capacity inertia. It also helped to realize inward heat flows originally proposed in 1974 [56]. For a high-resolution temperature derivative there was found a straightforward match to the 'noise' in the heat flow signal. Instead of the standard way of eliminating such 'noise/fluctuations' by more appropriate tuning of an instrument, or by intermediary measurements of the signal in distinct windows, the fluctuations were incorporated in a controlled and regular way. The temperature oscillations (often sinusoidal) were superimposed on the heating curve and thus incorporated in the entire experimentation. The response is to be evaluated through deconvolutions and the determination of heat capacities is carried out via a pseudo-isothermal analysis where the effect of modulation is suitably separated. It provides so called reversible and non-reversible heat capacities, with the latter connected with irreversible processes that cannot be reversibly modulated. Such a relevant separation became unavoidable in the determination of true (non-equilibrium or 'kinetic') phase diagrams [45]. The method known as temperature-modulated DSC (Reading) [57, 58] was preceded by the method of so called periodic TA proposed in the late sixties [59]. It was aimed at removing the kinetic problem of undercooling by cycling temperature (over its narrow range for the sample investigated placed directly into the thermocouple junction) until the equilibrium temperature for the coexistence of two phases was attained. Oscillatory mode of heating was also put to use to ease the early derivation of kinetic parameters [60].

Important perception of a more generalized knowledge of disequilibria allied with thermal analysis can be seen when analyzing internal flows linked not only with the external heating of a sample [39, 61] but also, and chiefly, with internal release of localized reaction heats. It affects the reaction kinetics traditionally treated on the basis of an oversimplified (and customary isothermal-like) modeling [39]. All industrially significant processing, however, put emphasis on turbulent motion caused by interplay of heat and mass flows across and along the entire reaction interface Conceptual underpinning for much of the advanced perception of phase transformations (showing local depletion of reactants due to actual temperature, stress, concentration and/or curvature gradients) made it necessary to use a more complicated mathematics [62]. It became gradually accessible by modern image processing and stereology of imagines obtained by analyzing entire interfaces by EDAX, ESM, STM, AFM, etc. Naturally it is associated with the novel idea of fractal dimension [47, 63] that corresponds in a unique fashion to the geometrical shape, which is not entirely integer (Euclidean). Fractals can also be built by simple geometrical interactive segregation to obey a certain growth rule similarly to the formulation of traditional models in thermal kinetics. Any such an aggregation process can be defined by the density, $\rho(L)$, which equals $M(L)/L^2$ (where M and L are the mass and edge length of the object under construction). Density decreases with L not only monotonically (so that we can achieve an object of limitless porosity) but also in a predictable fashion (according to a simple power law, $y=ax^n$, fractal $n\neq1, 2, 3$). Regardless of the definition of the characteristic length, the same scaling exponent describes its asymptotic behavior and is defined by $\sqrt{t}$ (analogous to parabolic law of diffusion limited aggregations known from electro-deposition, dendrite solidification, thermal growth, viscous fingers in porous media, etc.). This concept would provide a more solid basis to contemporary kinetic evaluations whose models are often too simple to match with visual observations. Altogether it may well exemplify the complexity of future addresses [10, 64–69] necessary to open and enrich the foresight access of modern thermal analysis.

There should follow a concluding inquiry: is there any prospect for our everyday thermoanalytical business to trouble ourselves with a deeper reflection about the historic imagination and future aspects of the concept of heat [1, 23, 24, 39, 53, 63].

First, it shows natural continuation of Greek philosophy [5, 6] to the contemporary modern science [1]. It also appreciates the work of our dear colleagues, particularly late Robert Mackenzie [1, 10, 59]. Finally we should note that some of our goals are like those of the past – encouraged by human curiosity and interest in exploitation of heat. We have to realize in even more details its ordering and disordering power. The second law of thermodynamics tells us that we need to do work to acquire information. This way of thinking allows us to quantify the cost of any labor. We also need to know the cost of its implantation, either in terms of time, money, energy or computation power. Increase in human abilities to manipulate heat and other energetic resources of our universe presents us with increasingly big decisions that will necessarily be based partly on the extent of learning and partly on other, yet unknown things. In ecological and environmental areas we must decide how much to compromise the immediate use of such resources in order to protect ourselves. Beside deeper knowledge of the character of flows we have to deal with carefulness, appreciation, understanding and affliction of intimidated heat on micro- and macro-scopic levels. Our Sun has another few billion years of much the same benevolent heat support for us providing thereby free energy sources to make possible our survival. This leaves much space to think about it most seriously taking into account the certain prophecy.

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This article is a condensed part of my newly composed book ‘Heat, Thermal Science and Society’, which is in the course of preparation for the year 2003. The text was written in a compressed form and its objective is also based on my recent experience with teaching university courses on the order and disorder in the scientific world (organized within the novel program of our cross-disciplinary education). The theme is the extension of our recent research directed to the study of non-equilibrium processes and practice of trans-disciplinary understanding of consequences of heat (projects No 522/01/1399 and 401/02/0679 of GA CR; A 4010101 of GA AV CR and 23000009 MSM). Most of the involved (but in this article purposefully omitted) mathematics (as well as detailed literature references) can be found in the related articles, such as current ‘Irreversible thermodynamics and true thermal dynamics in view of generalized solid-state reactions’ by Šesták and Chvoj, and ‘1111On the mechanism and mutual linking of some self-organized chemical reactions’ by Stavek, Sipek and Šesták, both recently submitted for the publication in Thermochimica Acta (to the Michael E. Brown and Andrew E. Galwey’s special honorary issue edited by Takeo Ozawa and Sergey Vyazovkin) to appear early in the year 2002.

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