Conflating Mechanics and Thermodynamics in the 1880s Max Planck's Thermo-elasticity

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Abstract: In the 1860s and 1870s, the recently emerged Thermodynamics branched out into two different directions: the refinement of the kinetic theory of gases, and the questionable alliance between mechanical laws and statistical procedures, on the one hand, and the attempt at recasting Thermodynamics in accordance with the mathematical structures of Analytical Mechanics, on the other. Different meanings of the adjective mechanical were at stake. The second approach was developed in different countries of Europe and the United States. In 1880 the young German physicist Max Planck lamented that the theory of mechanical processes, in particular mechanical elasticity, had been put forward without any connection with the thermal properties of bodies, and the thermal actions on them. He aimed at filling the gap between thermodynamics and the theory of elasticity. In the dissertation he published in order to be given the *venia legendi*, he outlined a mathematical theory where the mechanics of continuous media merged with thermal processes. He relied on the two principles of "the mechanical theory of heat", and "specific assumptions on the molecular structure of bodies" were "not necessary". In accordance with this theoretical option, he assumed that isotropic bodies consisted of "continuous matter".

Keywords: Thermodynamics, Mechanics, Elasticity.

1. Introduction

In the last decades of the nineteenth century, electromagnetic theories had already been translated into fruitful technologies, which were deeply transforming the occidental way of life. The new age of electromagnetism, whose symbolic device was the electromagnetic machine, seemed to supplant, at least in part, the old age of smoky thermal engines. Meanwhile, in the 1860s and 1870s, the recently emerged thermodynamics branched out into two different directions: the refinement of the kinetic theory of gases as a questionable alliance between mechanical laws and statistical procedures on the one hand, and the attempt at recasting thermodynamics in accordance with the mathematical structures of analytical mechanics on the other. Thanks to Joseph-Louis Lagrange and his *Mécanique analytique* (1788), mechanics had undergone a meaningful generalisation, and an abstract physical space came to replace the ordinary Euclidean space in the tradition of mathematical physics. In the 1830s

William Rowan Hamilton propounded a very abstract mechanics based on a set of variational principles expressed in generalised coordinates. In 1839, an Irish mathematician and natural philosopher, James MacCullagh, developed a mathematical theory of optics by Lagrangian methods. Another Irish physicist, George Francis FitzGerald, formulated a Lagrangian theory of electromagnetic fields in 1880.[1]

Thermodynamics offered not only new technological improvements but also new theoretical horizons: the widespread philosophical and cosmological debate on the second law, the development of thermochemistry, and a new mathematization of an enlarged physics.[2] Physicists took different theoretical pathways, even though we can single out two main traditions. James Clerk Maxwell and Ludwig Boltzmann pursued the integration of thermodynamics with the kinetic theory of gases, whereas other scientists relied on a macroscopic approach in term of continuous variables, setting aside specific mechanical models. One of the essential features of thermodynamics, the irreversibility of its laws regarding the inversion of time, made it very different from mechanics. The kinetic theory of Maxwell and Boltzmann nevertheless bridged the gap between the mechanical and thermal domains. Toward the end of the century, it was successfully applied to other fields including electromagnetism and radiation (Darrigol, Renn 2003, p. 498, p. 505; Boltzmann 1872, 1877; Maxwell 1860, 1867).

The purpose of this paper is to analyse the more abstract approach to thermodynamics, its roots in Rudolf Clausius's and William Macquorn Rankine's researches in the mid-nineteenth century, and some developments that took place in the 1880s.

In 1854, Rudolf Clausius, who was then teaching at the Royal Artillery and Engineering School in Berlin, stated that the equivalence between heat and work, and "Carnot's proposition" did not necessarily clash, provided that the latter was slightly modified. To the above law of equivalence he associated another law of equivalence, in order to maintain a sort of symmetry in the axiomatic structure of thermodynamics: a law of equivalence between "transformations". He specified that two kinds of transformations were at stake in thermal machines: the transformation of heat into work, and the transformation of an amount of heat, which was stored in the boiler at a high temperature, into heat which is received by the cooler at a low temperature. Clausius pointed out that the two kinds of transformation were tightly linked to each other: the former could not take place without the latter (Clausius 1854, p. 133).

In 1855 Clausius became Professor of mathematical physics at the Zurich Polytechnic. In 1862 he tried to deepen his 1854 approach, and in 1865 he put forward a theoretical synthesis, which soon became well known. In the case of reversible transformations, the quantity dQ/T was "the complete differential" of a new physical entity S (Clausius 1865, pp. 31-33),

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[1] For the primary sources, see (Hamilton 1834; MacCullagh 1848; FitzGerald 1880). On Hamilton's equations see (Hankins 1980, pp. XV-XVIII, pp. 61-87, pp. 172-209). On MacCullagh's Lagrangian approach to Optics, and "Fitzgerald's electromagnetic interpretation of MacCullagh's ether", see (Darrigol 2010, pp. 145-154, pp. 157-159).
[2] For the methodological and philosophical debate that stemmed from the second principle of thermodynamics, see (Kragh 2008, chapters 3 and 4).

$$dS = \frac{dQ}{T}$$

In 1865 Clausius reported that he had been looking for a new word for the entity *S*, a word that would encapsulate the conceptual analogy between the "content of transformation" and the energy *U*. He chose the word *Entropie* as a German transliteration of the Greek $\varepsilon\nu\tau\rho o\pi\eta'$, whose semantic field contains the meanings of transformation and conversion (Clausius 1865, pp. 34-35).

Clausius's "theory of heat" was "mechanical" in a structural sense: the analogy between mechanics and the science of heat was an analogy between the corresponding laws. The adjective "mechanical" made reference to formal structures rather than specific mechanical models of heat. However, in the last part of his paper, he put forward a remarkable cosmological synthesis: the formal symmetry between energy and entropy was partially broken, and the two laws became fundamental properties of the world as a whole. The following statements are well known:

1. Die Energie der Welt ist constant,
2. Die Entropie der Welt strebt einem Maximum zu.[3]

The tradition of mechanics also offered structural analogies to the Scottish engineer Rankine. In 1855, when he was appointed to the chair of Engineering at Glasgow University, a position he maintained until his death, he had already made meaningful researches in the field of "pure science," in particular in the emerging thermodynamics. In the same year he published a wide-scope memoir, "Outline of the Science of Energetics" in the *Proceedings of the Philosophical Society of Glasgow* (Rankine 1855). According to Rankine, the whole of physics could be unified by the generalisation of the concepts of *Substance*, *Mass*, *Work*, and energy. He insisted that such terms had to be looked upon as "purely abstract" or as "names" which made reference to "very comprehensive classes of objects and phenomena", rather than associated to "any particular object" or "any particular phenomena". He attained a further generalisation by introducing the terms *Accident* and *Effort*. If the former could be identified with "every variable state of substances", the latter was a generalisation of the concepts of force and pressure (Rankine 1855, pp. 214-216).

The concept of work encompassed *accidents* and *efforts*, and was a key concept in Rankine's theory. The new meaning of the word *work* stemmed from the generalisation of the meaning of the words *force* and *displacement*, which corresponded to the new words *effort* and *accident*. The generalisation of the concept of work entailed the generalisation of the concept of energy, which was the core of Rankine's *Energetics*. The concept of *Actual energy* was a generalisation of the mechanical *living force*: it included "heat, light, electric current", and so on. The concept of *Potential energy* was extended far beyond gravitation, elasticity, electricity and magnetism. It included "chemical affinity of uncombined elements", and "mutual actions of bodies, and parts of bodies". In

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[3] See (Clausius 1867, p. 44): "The energy of the universe is constant. The entropy of the universe tends to a maximum".

general, work was the result of "the variation of any number of independent accident, each by the corresponding effect" (Rankine 1855, pp. 216-217, p. 222):

$$W = X\,dx + Y\,dy + Z\,dz + \ldots\ldots$$

2. Planck's thermo-elasticity

In 1880, the young German physicist Max Planck was pursuing a slightly different aim. He lamented that the theory of mechanical processes, in particular mechanical elasticity, had been put forward without any connection with the thermal properties of bodies, and the thermal actions on them. He aimed at filling the gap between thermodynamics and the theory of elasticity. In the dissertation *Gleichgewichtzustände isotroper Körper in verschiedenen Temperaturen*, which he published in order to be given the *venia legendi*, he outlined a mathematical theory where the mechanics of continuous media merged with thermal processes. Planck became *Privatdozent* at the University of Munich in 1880, and was appointed as extraordinary professor of physics at the University of Kiel in 1885. In 1889, two years after Kirchhoff's death, he became assistant professor at the University of Berlin, and director of the Institute for Theoretical physics: in 1892 he was appointed ordinary professor (Jungnickel, McCormmach 1986, vol. 2, pp. 51-52, p. 152, p. 254; Gillispie, 1970-80, vol. XI, p. 8).

He relied on the two principles of "the mechanical theory of heat", and "specific assumptions on the molecular structure [*Beschaffenheit*] of bodies" were "not necessary". In accordance with this theoretical option, he assumed that isotropic bodies consisted of "*continuous* matter". The body could be subject to "an external pressure", and the condition of equilibrium was assured by the counteraction of "internal elastic forces". Both mechanical work and heat flow could act on the body: under those actions, both the reciprocal of density (*spezifische Volumen*) and temperature could change from $(v; T)$ to $(v'; T')$. In particular the geometrical co-ordinates of a point inside the body underwent a transformation in accordance with the equations

$$x = x_0 + \xi;\ y = y_0 + \eta;\ z = z_0 + \zeta\,,$$

where x_0, y_0, z_0 are the initial values and ξ, η, ζ the infinitesimal variation. The elastic forces acting on the surfaces parallel to the planes YZ, ZX, and XY were labelled by Planck

$$X = (X_x, X_y, X_z),\ Y = (Y_x, Y_y, Y_z),\ Z = (Z_x, Z_y, Z_z),$$

where $X_y = Y_x, Y_z = Z_y, Z_x = X_z$, "as usually assumed in the theory of elasticity" (Planck 1880, pp. 3-4).[4]

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[4] On the developments of the theory of elasticity in the first half of the nineteenth century, see (Darrigol 2002, sections from 2 to 6).

In the internal part of the body, the conditions of equilibrium were

$$\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} = 0,$$

$$\frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} = 0,$$

$$\frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} = 0,$$

whereas on the external surface they were

$$\Xi + \alpha X_x + \beta X_y + \gamma X_z = 0,$$

$$H + \alpha Y_x + \beta Y_y + \gamma Y_z = 0,$$

$$Z + \alpha Z_x + \beta Z_y + \gamma Z_z = 0,$$

where (Ξ, H, Z) were the components of the external force, (α, β, γ) the directive cosines, and $d\Phi = \Xi \cdot d\xi + H \cdot d\eta + Z \cdot d\zeta$ the work done by the external force (Planck 1880, pp. 4-6).[5]

The first principle of thermodynamics allowed a unified account of phenomena, and a unified overview on physical space. If $T' = T + \tau$ was the relationship between initial and final temperature in the course of a transformation, Planck specified that, in the end, energy depended on τ and on the derivative of (ξ, η, ζ) with reference to (x, y, z). In particular it depended on the seven new variables τ and Cauchy's six strain components (Planck 1880, pp. 9-10):

$$x_x = \frac{\partial \xi}{\partial x}, \quad y_y = \frac{\partial \eta}{\partial y}, \quad z_z = \frac{\partial \zeta}{\partial z},$$

$$x_y + y_x = \frac{\partial \xi}{\partial y} + \frac{\partial \eta}{\partial x}, \quad y_z + z_y = \frac{\partial \eta}{\partial z} + \frac{\partial \zeta}{\partial y}, \quad z_x + x_z = \frac{\partial \zeta}{\partial x} + \frac{\partial \xi}{\partial z}.$$

Cauchy had put forward a two-constant relation between stress and deformation, which is "the one now accepted for isotropic elasticity". In brief

$$\sigma_x = kx_x + K\theta, \quad \sigma_y = ky_y + K\theta, \quad \sigma_z = kz_z + K\theta,$$

$$\tau_{xy} = \frac{k}{2}(x_y + y_x), \quad \tau_{yz} = \frac{k}{2}(y_z + z_y), \quad \tau_{xz} = \frac{k}{2}(z_x + x_z)$$

where k and K are the two elastic constants, and $\theta = \varepsilon_x + \varepsilon_y + \varepsilon_z$ is the unit volume change.

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[5] He specified that elastic forces could not rely on "a potential", because "they depended on temperature" (Planck 1880, p. 8).

In 1852 the mathematician and engineer Gabriel Lamé published the first book on the theory of elasticity, *Leçons sur la Théorie Mathématique de l'Élasticité des Corps Solides*. He come to the conclusion that "to determine the elastic properties of an isotropic material, two elastic constants were required." It is worth mentioning that thermo-elastic equations had already been put forward by Duhamel in 1838, and Franz Neumann in 1841, quite before the emergence of thermodynamics (Darrigol 2002, pp. 119-120; Timoshenko 1983,]p. 107, p. 110, pp. 116-117, pp. 242-243; Barus 1905, p. 356).

After having simplified typographically "the dilatation of the unitary volume" by means of a new variable $\Theta = (x_x + y_y + z_z)$, Planck chose an expression for the energy dU of "the element of mass dM" in terms of the new variables:

$$dU = dM\,[const + k \cdot \tau + l \cdot \Theta + \frac{m}{2} \cdot \tau^2 + p \cdot \tau\Theta + \frac{q}{2} \cdot \Theta^2$$
$$+ r \cdot (x_x{}^2 + y_y{}^2 + z_z{}^2) + \frac{r}{2}(x_y{}^2 + y_z{}^2 + z_x{}^2)]\,.$$

The formal structure of entropy was not so different from that of energy:

$$dS = dM\,[const + k' \cdot \tau + l' \cdot \Theta + \frac{m'}{2} \cdot \tau^2 + p' \cdot \tau\Theta + \frac{q'}{2} \cdot \Theta^2$$
$$+ r' \cdot (x_x{}^2 + y_y{}^2 + z_z{}^2) + \frac{r'}{2}(x_y{}^2 + y_z{}^2 + z_x{}^2)]\,.$$

Planck could compare the two expression and the two sets of coefficients by means of the relationship between energy and entropy (Planck 1880, pp. 12-16):

$$dS = \frac{dQ}{T} = \frac{dU - d\Phi}{T}\,.$$

The comparison gave rise to seven relationships between the derivatives of u and s, namely the densities of energy and entropy:

$$\frac{\partial u}{\partial \tau} = T' \frac{\partial s}{\partial \tau}\,,$$

$$\frac{\partial u}{\partial x_x} + v' X_x = T' \frac{\partial s}{\partial x_x}\,,$$

$$\frac{\partial u}{\partial y_y} + v' Y_y = T' \frac{\partial s}{\partial y_y}\,,$$

$$\frac{\partial u}{\partial z_z} + v' Z_z = T' \frac{\partial s}{\partial z_z}\,,$$

$$\frac{\partial u}{\partial x_y} + v' X_y = T' \frac{\partial s}{\partial x_y}\,,$$

$$\frac{\partial u}{\partial y_z} + v' Y_z = T' \frac{\partial s}{\partial y_z}\,,$$

$$\frac{\partial u}{\partial z_x} + v' Z_x = T' \frac{\partial s}{\partial z_x}.$$

The first relationship led to

$$k = Tk', \quad m = Tm' + k', \quad p = Tp'.$$

The second, third and fourth led to

$$X_x = \frac{Tl'-1}{v} + \frac{l'}{v} \cdot \tau - \frac{(q-l) - T(q'-l')}{v} \cdot \Theta - \frac{2(r-Tr')}{v} \cdot x_x, \tag{1}$$

and similar expressions for Y_y and Z_z. The fifth, sixth and seventh led to

$$X_y = -\frac{r-Tr'}{v} \cdot x_y, \tag{2}$$

and other similar expressions for Y_z and Z_x (Planck 1880, pp. 17-18).

   The combinations of coefficients in (1) and (2) could be typographically simplified in accordance with simple physical remarks and the typographical tradition of the theory of elasticity. If the first expression in (1) corresponded to the external pressure, the third expression corresponded to the traditional term λ, whereas the fourth expression in (1) and that in (2) corresponded to the traditional term μ. In brief:

$$P = \frac{Tl'-1}{v},$$
$$\lambda = \frac{(q-l) - T(q'-l')}{v},$$
$$\mu = \frac{r-Tr'}{v},$$

and therefore (Planck 1880, p. 19):[6]

$$X_x = P + \frac{l'}{v} \cdot \tau - \lambda \cdot \Theta - 2\mu \cdot x_x,$$
$$X_y = -\mu \cdot x_y.$$

Internal energy, entropy, and the specific heats could be expressed in terms of k, λ, μ, and the other coefficient α, which represented "the variation of the specific volume with temperature, at constant pressure", namely

$$\alpha = \left(\frac{v'-v}{T'-T}\right)_P = v \left(\frac{\Theta}{\tau}\right)_P.$$

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[6] For the introduction of parameters λ and μ in the theory of elasticity in the first half of the nineteenth century, see (Darrigol 2002, p. 110, p. 113, pp. 122-124).

If $u = k \cdot \tau + \left[\alpha \left(\lambda + \frac{2}{3} \mu \right) T - Pv \right] \cdot \Theta$ and $s = \frac{k}{T} \cdot \tau + \alpha \left(\lambda + \frac{2}{3} \mu \right) \cdot \Theta$, then the constant k could be identified with "the specific heat at constant volume". Planck showed that the specific heat at constant pressure could be expressed by

$$c = k + \alpha^2 \left(\lambda + \frac{2}{3} \mu \right) \frac{T}{v}.$$

In the end (Planck 1880, pp. 21-23),

$$X_x = P + \frac{\alpha(3\lambda + 2\mu)}{3v} \cdot \tau - \lambda \cdot \Theta - 2\mu \cdot x_x.$$

In brief, energy, entropy, and elastic stresses depended on a combination of mechanical and thermal variables, which were multiplied by a combination of mechanical and thermal coefficients In the remaining part of the chapter, Planck showed some applications to specific states of matter: solid bodies, fluid drops, and vapours and gases.

3. Further developments

Two years later, in the paper *Vaporising, melting, and sublimating* (*Verdampfen, Schmelzen und Sublimiren*), he claimed once again that his theoretical approach was based on "the two principles of the mechanical theory of heat", and was "completely independent of any assumption on the internal structure of bodies". In physical-chemical transformations there were "several states corresponding to relative maxima of entropy", but there was only one "stable state of equilibrium", which corresponded to "the absolute maximum of entropy": the others states were nothing more than "unstable states of equilibrium". In the last part of his paper, Planck stressed that his previous statements were pure consequences of a more general law: "in natural processes, the sum of the entropies of the parts of a given body does increase". Only in reversible processes, the entropy would remain unchanged, but those kinds of processes did "not really exist": they could "be looked upon as merely ideal". When a physical system reached the maximum entropy, "no transformation" could "take place any more". The maximum entropy would therefore correspond to "a stable state of equilibrium", and this correspondence between entropy and equilibrium would represent "the best way to base the search for the conditions of equilibrium on rational grounds", both in physics and chemistry (Planck 1882, p. 452, p. 472).[7]

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[7] The distinctive feature of an unstable equilibrium was the establishment of "a finite change of state" as a consequence of "an arbitrary small change in external conditions". According to Planck, a specific instance of unstable equilibrium was offered by "explosions in mixtures of gases", where the addition of "a convenient but arbitrary small amount of energy" could trigger off sudden and dramatic transformations (Planck 1882, p. 474).

Planck published a series of papers and essays on thermodynamics between 1880 and 1892. In 1879, in his doctoral thesis, he had stressed that the increase of entropy dealt with all natural processes: in no way was it confined to thermal phenomena. He held the same position on the foundation of thermodynamics for many years. In 1891, in a paper he read at the annual meeting of German scientists, Planck claimed that Maxwell and Boltzmann's skillful "analysis of molecular motion" was not "adequately rewarded by the fruitfulness of the results gained". In particular, he found that the kinetic theory was not at ease with phenomena placed on the borderline between Physics and Chemistry: he did not expect that it could "contribute to further progress" in that field. Similar remarks can be found in the book on the foundation of Thermochemistry Planck published in 1893. As Darrigol and Renn pointed out some years ago, "Helmholtz and Planck preferred a macroscopic approach in terms of differential equations, which involved really observable entities". Nevertheless they had different attitudes with regard to molecular hypotheses: whereas Helmholtz made minimal use of them without denying molecular reality, Planck rejected any form of atomism (Deltete 2012, pp. 3-4; Darrigol, Renn 2003, p. 503, p. 505; Kuhn 1987, p. 22; Born 1948, p. 163).

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