J.J. Thomson's Lagrangian approach to thermodynamics[*]

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Abstract: In the last decades of the nineteenth century, we find two main theoretical pathways to thermodynamics: abstract, phenomenological mathematizations, on the one hand, and microscopic, molecular motions together with probabilistic hypotheses, on the other. In reality, in the first pathway, different nuances and different attitudes can be found: Helmholtz and Planck relied on the complementarity between mechanical and thermal variables, and Oettingen explored the symmetry between mechanical and thermal capacities. J.J. Thomson explored the two main pathways, and put forward a Lagrangian theory for the unification of physical and chemical processes. He made use of two kinds of Lagrangian coordinates that corresponded to two components of kinetic energy: macroscopic energy stood beside microscopic, molecular energy. Subsequently Duhem was to put forward an even more general design of unification between physics and chemistry, which was based on the two principles of thermodynamics.

Keywords: Thermodynamics, Lagrange's equations, Unification

1. Introduction

From William Thomson and Rudolf Clausius' classical versions of thermodynamics two different traditions of research emerged. If Maxwell and Boltzmann pursued the integration of thermodynamics with the kinetic theory of gases, others relied on a macroscopic and more abstract approach, which rejected specific mechanical models. In 1869, the French engineer François Massieu showed that thermodynamics could be based on two 'characteristic functions' or potentials. In the 1870s and the early 1880s, Josiah W. Gibbs and Hermann von Helmholtz explored the structural analogy between mechanics and thermodynamics: from a mathematical point of view, Helmholtz's 'free energy' corresponded to Gibb's first potential. In the meantime, in 1880, the young Max Planck put forward a theory of elasticity consistent with thermodynamics. In 1885, Arthur von Oettingen put forward an abstract theory wherein a dual mathematical structure was based on mechanical work and fluxes of heat. It led to the mathematical generalization of thermal capacities, and a striking series of symmetries. In the meantime, starting from Joseph-Louis Lagrange's *Mécanique Analitique* (1788), mechanics had experienced a meaningful generalisation, and the more abstract set of generalized coordinates had replaced the Euclidean ones. In the 1830s William Rowan Hamilton had put forward a very abstract mechanics that was based on a set of

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[*] This subject has already been extensively developed in two papers: Bordoni (2014) and Bordoni (2013).

variational Principles. In 1839, an Irish mathematician and natural philosopher, James MacCullagh, had developed a mathematical theory of optics on the track of Lagrange. On the same track, another Irish physicist, George Francis FitzGerald, put forward a Lagrangian theory of electromagnetic fields in 1880.[1]

In 1884, Helmholtz followed an intermediate pathway, which was neither Boltzmann's nor the Massieu-Gibbs pathway. He introduced a microscopic Lagrangian coordinate, corresponding to a fast, hidden motion, and a set of macroscopic coordinates, corresponding to slow, visible motions. The energy associated with the first coordinate corresponded to thermal energy, whereas the energy associated with the others corresponded to thermodynamic work. In 1888, Joseph John Thomson put forward a very general approach to physical and chemical problems. He remarked that physicists had at their disposal two different methods: a detailed mechanical description of the physical system, and a more general description that depended on "the properties of a single function of quantities fixing the state of the system". He acknowledged that the second approach, which was based on "purely dynamical principles", had already been "enunciated by M. Massieu and Prof. Willard Gibbs for thermodynamic phenomena". He found a deep connection between "the extension of the principle of the Conservation of Energy from Mechanics to Physics", and "the belief that all physical phenomena can be explained by dynamical principles", where the expression "dynamical principles" corresponded to "Hamilton's principle of Varying Action and the method of Lagrange's Equations." He also found that the methods of Analytical Mechanics had shown their powerfulness when scientists had realised that "the kinetic energy possessed by bodies in visible motion can be very readily converted into heat". (Darrigol 2002, p. 142; Thomson 1888, pp. V-VI, 1-2, 4)

Starting from 1891, while he was lecturing at Lille university, the French physicist Pierre Duhem began to outline a systematic design of mathematisation and generalisation of thermodynamics. He put forward an even wider mathematical framework where Lagrangian equations also hosted dissipative terms that could account for irreversible processes, and more specifically explosive chemical processes. (Duhem 1891, 1892, 1894a, 1894b, and 1896) In this mathematical and conceptual context, the concept of motion was also generalised: it corresponded to any variation of a Lagrangian coordinate. It seems that Duhem and J.J. Thomson developed their theories unconsciously of each other. Duhem did not mention J.J. Thomson, and this is worth stressing because Duhem was quite attentive to historical developments, and had always acknowledged the contributions of other scientists, Massieu, Gibbs, Helmholtz, and Oettingen included. The fact is that Duhem sharply opposed any microscopic approach, and therefore he did not appreciate J.J. Thomson's 'mixed' approach, where macroscopic and microscopic variables interacted with each other.

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[1] For the primary sources on the two pathways to thermodynamics, see Clausius (1876), Massieu (1869a), Massieu (1869b), Massieu (1876), Boltzmann (1872), Maxwell (1860), Maxwell (1867), Boltzmann (1877), Gibbs (1875-8), Helmholtz (1882), Planck (1880), Oettingen (1885). For a Lagrangian approach to optics and electromagnetism, see Hamilton (1834), MacCullagh (1848) (1839), and FitzGerald (1880). On Hamilton's equations see Hankins (1980, pp. XV-XVIII, 61-87, and 172-209). On MacCullagh's Lagrangian approach to Optics, and "Fitzgerald's electromagnetic interpretation of MacCullagh's ether", see Darrigol (2010, pp. 145-154, and 157-159).

2. J.J. Thomson's mathematical unification between physics and chemistry

In 1888 Joseph John Thomson, then Cavendish Professor of Experimental Physics at Cambridge, published a book, *Applications of Dynamics to Physics and Chemistry*, which collected "the substance of a course of lectures" he had delivered at the Cavendish laboratory in 1886. He studied phenomena where both mechanical stresses and magnetic actions were involved, or elastic and thermal effects interacted with each other, or electromotive forces emerged from a thermal disequilibrium. He noted that the phenomena under investigation were "generally either entirely neglected or but briefly noticed" in contemporary treatises. (Thomson 1888, p. v)

He was to pursue the pathway of "purely dynamical principles", and in particular he was interested in attaining the greatest number of useful results "without using the Second Law of Thermodynamics". In brief he endeavoured to exploit all the advantages of the formal structure of Analytical Mechanics when compared to the method based on "the two laws of Thermodynamics". He saw essentially three main advantages: the greater generality, the possibility of making use of one principle instead of two, and the application to cases where heat fluxes were not explicitly involved. On the other hand, he was aware of a specific shortcoming. The results were expressed in terms of "dynamical quantities, such as energy, momentum, or velocity", and they had to be translated into the physical entities under investigation, "such as intensity of a current, temperature, and so on". The second Law was "based on experience", and therefore it did not involve "any quantity which cannot be measured in the Physical Laboratory". Analytical Mechanics had a pliable and more general structure, but the attempts to deduce the second law from "the principle of Least Action" had been unsuccessful. (Thomson 1888, pp. 4-5)

It is worth remarking that the separation between 'mechanical' and 'dynamical' approaches was also at stake in the context of British theories of elasticity. In 1845 George Gabriel Stokes had introduced two distinct kinds of elasticity, "one for restoration of volume and one for restoration of shape". As Norton Wise pointed out in 1982, "he worked only with observable macroscopic concepts", and distinguished between 'mechanical' and 'dynamical' theories. He reserved the term *mechanical theory* for 'speculations' into the structure of matter or aether, and *dynamical theory* for an approach independent of such hypotheses. (Darrigol 2002, p. 142; Norton 1982, pp. 185-6; Stokes 1883, pp. 244-245)

The structure of Lagrange's equations

$$\frac{d}{dt}\frac{dL}{d\dot{q}_i}-\frac{dL}{dq_i}=Q_i \qquad i=1,......,n,$$

where $L=T-V$, and Q_i were the forces acting on the coordinates q_i, was suitable for dealing with a set of coordinates which were geometrical only in part. Temperature or a distribution of electricity could be interpreted as 'coordinates' in a very general sense. Thomson appreciated the possibility of giving "a more general meaning to the term *coordinates* than that which obtains in ordinary Rigid Dynamics". He insisted on this opportunity: “any variable quantities” could be considered as coordinates if the corresponding Lagrangian functions could be expressed “in terms of them and their first differential coefficients”. Two kinds of ambiguity emerged from that pliable structure: the impossibility of a sharp separation between kinetic and potential energy, and the difficulty of determining whether a given symbol should be associated with a generalised coordinate or velocity. According to Thomson, some “dynamical considerations” could enable physicists to overcome this difficulty. (Thomson 1888, pp. 9, 17, 19)

In the sixth chapter of his book, *Effect of temperature upon the properties of bodies*, he extended the methods to those cases “in which we have to consider the effects of temperature upon the properties of bodies”. A dynamical interpretation or “a dynamical conception of temperature” had already been offered by “the Kinetic Theory of Gases”: temperature was a measure of “the mean energy due to the translatory motion of the molecules of the gas”. In this case Thomson attributed two different meaning to the adjective ‘dynamical’, and it might mislead the reader. He made ‘dynamical methods’ and mechanical models overlap, and let the readers think that the mechanical interpretation of temperature was an essential feature of the general dynamical method. We can remark that the two approaches are independent of each other: in particular the former has a narrower scope than the latter. He made use of the concept of “sensible heat”, namely the amount of heat that was associated to a variation of temperature. Sensible heat was due to “the motion of the molecules”, and it could be looked upon as “part of the kinetic energy of the system”. In reality he extended the mechanical interpretation of temperature to liquid and solids: in the range of temperatures where “specific heat is constant”, the rise in temperature was proportional “to the energy communicated to the system”. He could therefore assume that “the kinetic energy of some particular kind is a linear function of the temperature”. (Thomson 1888, pp. 89-90)

The superposition between dynamical methods and mechanical models led Thomson to divide the kinetic energy of a system into two parts: the first part T_u depended on “the motion of unconstrainable coordinates u”, and was proportional to the absolute temperature ϑ, whereas the second part T_c depended on the motion of “controllable coordinates ϕ”. The component T_c corresponded to what Helmholtz had called *die freie Energie* [‘free energy’]. The generalized velocities $\dot{u}$ and $\dot{\phi}$ could not mix, and in particular

$$\frac{dT_u}{d\dot{\phi}} = 0 .$$

Since T_u might contain ϕ, Lagrange’s equation for the coordinates ϕ was

$$\Phi = \frac{d}{dt}\frac{dL}{d\dot{\phi}} - \frac{dL}{d\phi} = \frac{d}{dt}\frac{d(T_c + T_u - V)}{d\dot{\phi}} - \frac{d(T_c + T_u - V)}{d\phi} =$$

$$=\frac{d}{dt}\frac{dT_c}{d\dot{\phi}}+\frac{d}{dt}\frac{dT_u}{d\dot{\phi}}-\frac{dT_c}{d\phi}\frac{dT_u}{d\phi}+\frac{dV}{d\phi},$$

where Φ was “the external force of this type acting on the system”. Taking into account the above mentioned assumptions, the equation could be written as

$$\Phi=\frac{d}{dt}\frac{dT_c}{d\dot{\phi}}-\frac{dT_c}{d\phi}-\frac{dT_u}{d\phi}+\frac{dV}{d\phi} \qquad (1)$$

(Thomson 1888, pp. 95-96)

The last equation was the starting point of a mathematical derivation which led to a differential relationship between the microscopic kinetic energy T_u and the applied forces Φ, and then between heat fluxes and Φ. In the end, simple relationships between thermal and mechanical effects in elastic bodies could be derived. At first he arrived at the equation

$$-\frac{d\Phi}{dT_u}=\frac{1}{T_u}\frac{dT_u}{d\phi} \quad \text{or} \quad \frac{dT_u}{d\phi}=-T_u\frac{d\Phi}{dT_u} \qquad (2)$$

(Thomson 1888, p. 96)

and then he introduced the flux of heat δQ that had to obey to the conservation of energy:

$$\delta Q+\sum\Phi\cdot\delta\phi=\delta T_c+\delta T_u+\delta V.$$

The term δV depended only on $\delta\phi$, and therefore

$$\delta Q=\sum\left(\frac{d}{dt}\frac{dT_c}{d\dot{\phi}}-\frac{dT_c}{d\phi}\right)\delta\phi-\sum\Phi\cdot\delta\phi+\delta T_u+\sum\frac{dV}{d\phi}\delta\phi.$$

Equation (1) and (2) allowed Thomson to simplify the expression for δQ:

$$\delta Q=\sum\left(-T_u\frac{d\Phi}{dT_u}\right)_{\phi=const}\cdot\delta\phi+\delta T_u\ .$$

(Thomson 1888, pp. 97-98)

At this point he took into account the specific case of isothermal transformations. In particular he assumed that “the quantity of work communicated to the system is just sufficient to prevent T_u from changing", but T_u was "proportional to the absolute temperature θ". As a consequence,

$$\delta Q = \sum \left(-T_u \frac{d\Phi}{dT_u} \right)_{\phi\ const} \cdot \delta\phi \left(\frac{dQ}{d\phi} \right)_{\theta\ const} = \left(-T_u \frac{d\Phi}{dT_u} \right)_{\phi\ const}$$

or

$$\left(\frac{dQ}{d\phi} \right)_{\theta\ const} = -\theta \left(\frac{d\Phi}{d\theta} \right)_{\phi\ const} . \quad (3)$$

The last equation linked the dependence of heat fluxes on mechanical coordinates to the dependence of external forces on temperature. As Thomson pointed out, a deep connection between thermal and mechanical effects was at stake. Thomson reminded readers that both Maxwell and Helmholtz had arrived at the same result although starting from different assumptions. Then he made use of this equation in order to tackle 'the relations between heat and strain', and in particular the "effects produced by the variation of the coefficients of elasticity m and n with temperature". (Thomson 1888, pp. 98-100)

In Thomson's mathematical approach, the Greek letters α, β, γ corresponded to "the components parallel to the axes x, y, z of the displacements of any small portion of the body". Six Latin letters corresponded to longitudinal and transverse strains:

$$e = \frac{d\alpha}{dx}, \quad f = \frac{d\beta}{dy}, \quad g = \frac{d\gamma}{dz},$$
$$a = \frac{d\gamma}{dy} + \frac{d\beta}{dz}, \quad b = \frac{d\alpha}{dz} + \frac{d\gamma}{dx}, \quad c = \frac{d\beta}{dx} + \frac{d\alpha}{dy}.$$

He assumed that Φ corresponded to "a stress of type e", and therefore

$$\Phi = m(e + f + g) + n(e - f - g),$$
$$\frac{d\Phi}{d\theta} = \frac{dm}{d\theta}(e + f + g) + \frac{dn}{d\theta}(e - f - g).$$

Now the coordinate e corresponded to what had been labelled ϕ, δQ corresponded to the amount of heat that had to be supplied to the unit volume of a bar "to keep its temperature from changing when e is increased by δe":

$$\frac{dQ}{de} = -\theta \frac{d\Phi}{d\theta} = -\theta \left[\frac{dm}{d\theta}(e + f + g) + \frac{dn}{d\theta}(e - f - g) \right]$$

or

$$\delta Q =- \left[\frac{dm}{d\theta}(e+f+g)+\frac{dn}{d\theta}(e-f-g)\right]\theta\delta e$$

(Thomson 1888, pp. 20, 47-48, 100-101)[2]

When the coefficients of elasticity decreased as the temperature increased, $dm/d\theta<0$ and $dn/d\theta<0$, and therefore the equation showed that $\delta Q>0$: a given amount of heat had to be supplied in order "to keep the temperature of a bar constant when it is lengthened". In other words, "a bar will cool when it is extended", if no heat is supplied from outside.

In the case of a twist, Φ represented "a couple tending to twist the bar about the axis of x", and a was the corresponding twist. Thomson wrote

$$\Phi = n\,a, \qquad \frac{d\Phi}{d\theta}=\frac{dn}{d\theta}a.$$

He therefore computed the amount of heat that assured the temperature to be preserved:

$$\delta Q = -\frac{dn}{d\theta}\,\theta\,\delta a.$$

The physical interpretation was not different from the previous one: when a rod is twisted, "it will cool if left to itself", provided that "the coefficient of rigidity diminishes as the temperature increases", which is what usually happens.[3]

3. Conclusion

In the abstract pathway to thermodynamics in the late nineteenth-century, Lagrangian theories represented one of the most interesting contributions to theoretical physics. J.J. Thomson put forward a wide mathematical framework, wherein both microscopic motions, macroscopic stresses, and macroscopic heat fluxes could find room. Today J.J. Thomson's contribution is definitely underestimated whereas the importance of Duhem's contribution has been acknowledged since the 1940s. The latter can be looked upon as the creator of modern phenomenological thermodynamics or the theory of continuous media based on thermodynamics. However J.J. Thomson promoted the integration of dynamical methods and mechanical models. His general mathematical-physical framework still deserves to be studied and appreciated.

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[2] Thomson specified that e,f,g represented the dilatations of a bar "parallel to the axes x, y, and z respectively". (Thomson 1888, p. 47)

[3] Even in this case Thomson mentioned previous researches in the same field: he reminded readers that William Thomson had first obtained those results "by means of the Second Law of Thermodynamics". (Thomson 1888, p. 101)

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