DUHEM'S CONTRIBUTION TO THE DEVELOPMENT OF MODERN THERMODYNAMICS

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Pierre DUHEM was a great French scientist who lived at the end of the nineteeth century and at the beginning of the twentieth. Generally, people know his works in history of science, in particular history of physical theories but they never know his contribution to thermodynamical development. The French scientific community did not recognize his work for a long time and yet it contained the seeds of further development of thermodynamics of irreversible processes such as

- De Donder's work on chemical affinity
- Onsager's work
- Glansdorff and Prigogine's discoveries which led to the attribution of the Nobel Prize in Chemistry in ninety seventy nine to Prigogine.

The major works of Pierre Duhem who is also the author of many other articles in papers and letters to various academies are the following:

La Théorie Physique, son objet, sa structure (1906)
La Systéme du Monde (premiers tome) (1913)
Le Potentiel thermodynamique (1886)
Lecons de Mécanique Chimique (1902)
Traité d'Energétique ou de Thermodynamique Générale (1911)

[redacted]

The two first publications are known. The three others, specially scientific are often unknown and represent the essential part of this contribution to understand more comprehensively Duhem's role.

Some informations about the life and the career of Pierre Duhem are of interest:

Pierre Duhem was born in 1861. He died in 1916.

1872: Pierre Duhem studied at Stanislaw College (Catholic school)

1882: He is admitted at E.N.S. (Ecole Normale Supérieure); he passed the exam with the best results

1884: (october 20th): The presentation of his first thesis on thermodynamical potential is refused by the jury (Lippmann chairman)

1885: Duhem passes "agrégation" in physical sciences (first)

1887: "Maitre de conférences" at Lille University

1888: Presents a second thesis in mathematics (Poincaré chairman).
Introduces historical approach in his thesis

1898: From Bordeaux, where he teaches since 1894, takes position against Dreifus, the "third Republic" and its education policy ("Ecole laique")

1906: Pierre Duhem published "La Théorie Physique"

1911: Published the "Traité d'Energétique"

1913: Elected as a member of "Académie des Sciences"
Published the first books of "Le Systéme du Monde"

1916: Died at Cabrespine (near Carcassonne). He was 55.

The life and the carreer of Pierre Duhem illustrate the influence of his social and family environment characterised by

- its conservative ideas
- its strict catholic and monarchist ideas
- its links with tradition and order meanwhile the French political environment is characterized by

- republican (although conservative) choices

- the struggle for the "Ecole Publique", "laique et obligatoire" (Scool for everybody, lay and compulsory) a opposed to clerical, catholic and monarchist forces.

Between 1894 and 1906, republicans on one side and monarchists on the other side were violently opposed on "Affaire Dreyfus". Duhem took position against Dreyfus, favor of the Army and the order against the republican power.

The first thesis was refused in 1884. Such a refusa is unknown in French University. Here begins the scentii opposition between Duhem and Berthelot who was at the to of his carreer. Member of the "Académie des Sciences" (h will be its "Secrétaire perpétuel" in 1889), Marcelin Berthelot was powerful and refused any criticism about h scientific works. In the thesis presented to the jury wi Lippmann (who was a friend of Berthelot) as a chairmann, Duhem, young student of second year at the E.N.S., critcized and questioned the "Principe du Travail maximu (Principle of maximum work), one of the three laws of "Thermochimie" purposed by Berthelot. And yet, on that point, Duhem was right. Here are the reasons of the hostility of chemists. Duhem who hopes to obtain a posit of professor in Paris will be appointed in Bordeaux wher he stayed during 22 years. He said that Bordeaux and its university were for him an "honorable Sepulture".

So Duhem was isolated from the French chemists community. Moreover his assessment about relativity and research on matter constitution, which he condemned, isolated him too from the physicists community. Jean Pe for instance who stood on his side during Berthelot's quarrel could not accept his points of view on physics.

Recognition came from some French mathematicians su as Hadamard and, above all, from foreign countries (Gib Ostwald, Helmholtz recognized Duhem's works in chemical physics).

The main contibutions of Pierre Duhem concern

1. The relation of Gibbs-Duhem

$$SdT - Vdp + \sum n_i d\mu_i = 0$$

where S represents entropy

T temperature

V volume

p pressure

n_i number of moles of constituant i

$_i$ chemical potential of the constituant i

(Duhem gave an elegant demonstration of this relation formulated by Gibbs, using the theorem of Euler.)

2. First calculation of production of entropy

Duhem has calculated in two cases of irreversibility (caused by non uniform repartition of temperature in the first case, and by viscosity in the second) the production of entropy in the "Traité d'Energétique" published in 1911. He was the first.

It seems necessary to review briefly the approach:

Isolated system - Reversible transformation

$$dS = \frac{dQ_r}{T} = 0$$

Isolated system - Irreversible transformation

$$dS = \frac{dQ_i}{T} > 0 \quad \text{(Carnot's or Clausius's Principle)}$$

System exchanging energy with outside environment - Reversible transformation

$$d_eS = \frac{dQ_r}{T}$$

System exchanging energy with outside environment - Irreversible transformation

$$dS = \frac{dQ_i}{T} \quad \text{et} \quad \frac{dQ_i}{T} > \frac{dQ_r}{T} \text{ (Second principle).}$$

It is possible to write

$$\frac{dQ_i}{T} = \frac{dQ_r}{T} + \frac{dQ'}{T} \; .$$

Clausius (and Duhem) called dQ', no compensated heat. Today, we present this last expression in the folloving way:

$$dS = d_eS + d_iS$$

where d_eS represents entropy caused by exchanges and d_iS entropy created inside the system, caused by irreversibility.

Second principle of thermodynamics is expressed in the following way:

$$d_iS \geqslant 0 \; .$$

equality ($d_iS = 0$) concernes equilibrium.

In the isolated systems $d_eS = 0$ and $d_iS = 0$ maximum value of entropy.

So, dQ' (no compensated heat) = Td_iS.

Calculation of dQ' is directly linked with value of entro created by irreversibility (friction, viscosity, non-uniform repartition of temperature...).

That is the most important contribution of Pierre Duhem. was unknown in France but scientists of other European countries have read the treaty of 1911 and have pursued i the same way. It was the case of de Donder in his work on chemical affinity. It is the beginning of the development of thermodynamics of irreversible processes and we know what it happens after with the contributions of Onsager a

others.
3. A presentation of the laws, theories and results in a clear and coherent set based on Energetism Duhem thought that it was necessary to organize physical knowledge in an organised way around the laws of thermodynamics.

In my research work, I found a manuscript which has not yet been published entitled

Leçons sur les théories de la capillarité .

It is a model of an intelligent use of energetic method and of history which could still be used today in teaching. This work is being published with comments. The unexpected discovery of this document gives interesting informations on the conditions of the scientific work at the time of Duhem.

Duhem was one of the scientists of the Energetic School and the only one to be French. Some lines taken in his writings define perfectly his ideas on science.
In his "Théoric Physique", he wrote:

"Une théorie physique n'est pas une explication. C'est un système de propositions mathématiques, déduites d'un petit nombre de principes, qui ont pour but de représenter aussi simplement, aussi complètement et aussi exactement que possible, un ensemble de lois expérimentales."
(A physical theory is not an explanation. It is a system of mathematical proposals, deduced from a small number of principles which aim at representing as simply and as exhaustively and accurately as possible, a set of experimental laws.)

"Il faut avoir grand soin de distinguer d'une part les corps réels et concrets dont nous nous proposons de représenter les propriétés, mais non point d'expliquer la

nature, et, d'autre part, le schéma abstrait, composé de notions mathématiques, qui nous doit fournir une image d propriétés de ces corps concrets".
(We must carefully distinguish, on one hand, concrete an real bodies, the properties of which we want to represen but we must not explain the nature and, on the other han the abstract schema composed of mathematical notions, wh has to give an image of the properties of these concrete bodies.)

"...Nous en avons assez dit pour prouver que l'on peut construire une Optique rationelle, sans faire aucune hypothèse sur la constitution intime des milieux transparents ni sur la nature de la lumière."
(We have said enough to prove that a rational Optics can built without doing any hypothesis on the intimate constitution of transparent media or on the nature of light.)

These opinions had sometimes strange spins off and consequences such as

- to present in a curious way his lessons in Optics
- to refuse atomism
- to condemn theory of relativity.

These attitudes similar to Ostwald and, to some extent, Mach's conceptions were violently condemned by French physicists, in particular by Paul Langevin, who about Duhem's approach said, in a conference presented, in 190 at the Musée Pédagogique of Paris:

"N'y-a-t-il pas là une tendance fâcheuse à limiter les champ des investigations, à déclarer suffisante et définitive une connaissance générale et définitive des choses, à s'interdire un examen plus approfondi parce qu premier succès nous a livré quelques unes des lois les p

générales?"
(Is not there in this case a regretful trend to limit the field of investigations, to declare as sufficient and definitive a general and definitive knowledge of things, to forbid oneself a more through examination because a first success has delivered some of the most general laws.)

As a conclusion, the choices of Duhem, his refusal of atomism and relativity explain that the French scientist does not stand in the forefront of the history of physics. Nevertheless, in the history of thermodynamics, Duhem remains a strong link in the chain relating Carnot to Prigogine and Glansdorff via Clausius, Gibbs, Helmholtz, Ostwald, de Donder and Onsager in particular.

Then, Duhem's works in the scientific domain are a remarkable example of coherence between philosophical choices and scientific approach. They determine at the same time the value and the limits of the contributions of Pierre Duhem.

Finally, time and thus history will have permitted to correct the errors and mistakes that institutions made at the time of Duhem.

It's also one of the interests of history of science.

Bibliography

BROUZENG Paul

- L'oeuvre scientifique de Pierre Duhem et sa contribution au développement de la thermodynamique des phénomènes irreversibles; thèse d'état. Université de Bordeaux. 1981.
- Duhem, science et providence, Belin. 1987. PARIS.

DONDER Théophile (de)

- L'Affinité; Gauthier-Villars. 1927. PARIS.

MANVILLE Octave

- La Physique de Pierre Duhem in Mémoires de la Socie des Sciences physiques et naturelles de Bordeaux. 7-ème Série, tome 1, 2-ème cahier, 1928.

MILLER Donaldi G.

- Duhem and the Gibbs-Duhem Equation, in Journal of Physical Education, vol 40, décembre 1963.

OSTWALD Wilhelm

- L'énergie; traduction française E. Philippi. Felix Alcan 1910. PARIS

PICARD Emile

- La vie er l'oeuvre de Pierre Duhem; Discours à l'Académie des Sciences, 12 décembre 1921.

PRIGOGINE Ilia

- Introduction à la thermodynamique des processus irréversibles; J. Chanu. Dunod 1967. Paris.

and the works of Pierre Duhem

- Le Potentiel thermodynamique et ses applications à la mécanique chimique et la théorie des phénomènes électriques. Hermann 1886 PARIS
- La Théorie physique, son objet, sa structure
  Chevalier et Rivière 1906. PARIS
  Rivière 1914. PARIS (2-eme édition augmentée)
  Vrin 1981 PARIS (reproduction de la 2-eme édition revue, argumentée et commentée).
- Traité d'Energétique ou de Thermodynamique générale
  2 Volumes GAUTHIER-VILLARS 1911 PARIS
- Le Système du Monde, histoire des doctrines cosmologiques de Platon à Copernic. 10 tomes
  A. Hermann et fils. Paris (1913...1959).
- La Science allemande
  A. Hermann et fils. Paris 1915.