HOW KÁLMÁN SZILY DEDUCED THE SECOND LAW FROM THE FIRST LAW OF THERMODYNAMICS*

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A landmark in the development of phenomenological thermodynamics around the sixties of the nineteenth century was the introduction of the entropy concept by RUDOLF CLAUSIUS. [1] This great achievement prompted a new wave of investigation on the molecular dynamical theory of heat. Theoreticians who regarded heat as a "kind of motion" tried to find a mechanical analogy to the Second Law. "Viele Schrifsteller haben durch dynamische Überlegungen Gleichungen abgeleitet, welche der thermodynamischen Gleichung dQ = TdS ähneln." (A number of authors made use of dynamical considerations in order to deduce equations similar to the thermodynamic equation dQ = TdS.) That was how a theoretician of the following generation, BRYAN [2], characterized these early ventures.

Kálmán SZILY,** was fortunate enough to become a sort of what we would nowadays call postgraduate student to Clausius, Magnus and Kirchhoff between 1863 and 1865, i.e. in the years when Clausius was in one of his most active periods working on phenomenological thermodynamics. Szily, an engineer by training, was evidently greatly influenced by this study trip. There is no doubt that a two-year trip to Zürich, Berlin and Heidelberg must have made a considerable impact on a young man — and not only from the purely formal point of view.

Szily's first contribution to the mechanical understanding of the Second Law [3] closely followed the work of CLAUSIUS [4]. Both of them, similarly

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** Born in 1938 in Izsák (Hungary), Kálmán (Colman) Szily was a secondary school pupil of the Piarist Fathers in Pest, an undergraduate of the Joseph School of Technology, Buda, and of the Vienna Polytechnic. After a two-year study trip in Switzerland and Germany he became a professor of physics in Buda. A well-informed lecturer and active researcher in mathematics and mathematical physics he was also renowned as a remarkable organizer of science and, particularly in his later years, as an excellent linguist and a noted editor of dictionaries. Among other duties he served as a secretary of the Scientific Association (the Hungarian equivalent of British Association), founder and editor of its journal, Secretary General and later Chief Librarian of the Hungarian Academy of Sciences. He died in 1924.

also to young BOLTZMAN [5], made use of a basic law of mechanics, respectively following Hamilton's or d'Alembert's Principle in order to deduce the expression

$$\frac{dQ}{T} = d\log(iT)^2$$

called the Clausius—Szily equation [2]. Here dQ denotes the heat exchanged between the system and its surroundings, T the kinetic energy of the system and i a period of time whose meaning will be given a little later.

This equation holds if no dissipative process takes place, i.e. the change of state is reversible. Integrating eq. (1) over a thermodynamic cycle the right hand side equals zero and one finds

$$\oint \frac{dQ}{T} = 0 . \tag{2}$$

i.e. an expression analogous to the Second Law. (But T denotes here kinetic energy!) Szily could even show that with dissipative processes present the integral in eq. (2) becomes negative in complete analogy to the Second Law.

The main shortcoming of eq. (1) lies with a severe restriction regarding particle motion. This amounts to the statement that eq. (1) is true only if the particles of the system perform periodic motion along closed trajectories. The quantity i is the period of this motion. There is nothing that could support such an assumption.

Very much aware of that, Szily tried to rid his theory of this limitation. In a subsequent paper, which bore the proud title "The Second Proposition of the Mechanical Heat Theory deduced from the First [6]," he made an attempt to understand the Second Law in terms of mechanical first principles only. Indeed, no particular assumption on particle motion was made in his article. This did not mean, of course, that Szily was able to fulfil his ambitious aim. However, a very important step forward was the idea that the limitations inevitably imposed referred to the whole ensemble and not to individual particles. Szily assumed that both kinetic energy and potential energy are individually constant in equilibrium.

Apart from these explicit assumptions great use was made of a statement on the rate of heat exchange. The author asserted that the period of heat transfer could be arbitrarily chosen, this would not influence the amount of heat transferred. Exploiting this assertion the Clausius—Szily equation, eq. (1), was deduced again leading to the final conclusion, "the absolute temperature is nothing other than the kinetic energy of unit mass of the body".

It is striking how unsettled the notion of irreversibility seems to be in this reasoning. Although aware of dissipative processes Szily did not realize hat the rate of change influences the extent of dissipation. Here, however,

Szily must not be blamed. Even Clausius was unable to make clear the inter-relation between rate and irreversibility. [1] Pointing out the idea of reversible work to imply infinitesimally small differences between force and counter-force he failed to draw the conclusion that this condition meant also infinitely slow execution of any reversible process.

Even NICHOLS [7] who criticized Szily because of his arbitrariness regarding rate of heat exchange was not fully aware of the kinetic meaning of reversibility. Szily, acknowledging the validity of Nichols' comments, tackled the problem once again [8].

First he clearly realized that the density of a particle system is a time average only. Short-lived density fluctuations cannot be observed only because "there is just as much probability that . . . the partial rarefactions will predominate as that the reverse will be the case". Making the basic assumption that density fluctuations are strictly periodic in time he succeeded in deducing eq. (1). Whereas we know that fluctuation is not a periodic process it cannot be denied that the idea of fluctuation is completely new. Boltzmann himself did not really refer to this notion before the end of the century.

There are two important features in Szily's work I would like to draw to the reader's attention. The first one is the gradual development of the treatment from single particle mechanics to ensemble laws. At the outset he abandoned Clausius' assumption on periodic particle motion and introduced the individual constancy of both kinetic and potential energy of the ensemble, later he even realized the existence of fluctuations.

The second feature is a negative one. Working under the influence of the German school, being spellbound by Clausius, Szily paid no heed to the statistical work of Boltzmann nor to the relevant papers of Maxwell.

Apparently he himself did not realize how close a kinship existed be-tween his own ideas and the slowly emerging statistical method.

Summary

In keeping with the general trends of mechanical heat theory in the mid-nineteenth century K. Szily attempted to rationalize the Second Law in terms of a mechanical model. Although falling short of its original aim the contribution seems to be important because of the use of ensemble properties instead of single particle mechanics and because of the introduction of the notion of fluctuation.

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