Heat theorem in Boltzmann, Clausius and Helmoltz views

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The first paper of Boltzmann on the subject (1866):

Second Law $\longleftrightarrow$ Least Action

Initial: T is the average kinetic energy + second law

New ideas

1) Motion of given energy is periodic

2) Thermodynamic equilibrium state identified with collection of values which are the average values of the observables

3) Use least action principle to compare averages

' Extension of the Least action: comparison btw averages performed by calculus of variations

1) $\Rightarrow$ is essentially the *ergodic hypothesis* and

2) $\Rightarrow$ associates with a therm. state a probability distribution (fraction of time spent on set)

3) $\Rightarrow$ The least action varies, comparing two periodic orb. of periods i and $i+\delta i$, from $\delta(\overline{K}-\overline{V})=0$ for fixed extremes and potentials V and $V+\delta\widetilde{V}$

$$\delta(\overline{K}-\overline{V}) = -2\overline{K}\,\delta\log i + \delta\overline{\widetilde{V}}$$

which implies that $T=\overline{K}$ is the integrating factor of

$$\delta\,(\overline{K}+\overline{V}) + \delta\overline{W} = 2\overline{K}\,\delta\log(i\overline{K})$$

where $\delta\overline{W} = -\delta\overline{\widetilde{V}}$ is interpreted as the work done.

$$\frac{d\overline{U}+d\overline{W}}{\overline{K}} = d\,2\log(i\overline{K})$$

This looks easy: however B.'s argument is difficult to follow: in fact interpreting the formulae is necessary.

The technique is calculus of variation which B. uses freely, "exchanging d's and δ's".

The proof is that Clausius, four years later, derived the result in the above form without knowing B.'s paper.

Obliged to respond to angry B., points out that the works would coincide IF symbols were properly interpreted. For C. comparison not possible due to ambiguities in definitions.

More: B. does not allow variations $\delta\widetilde{V}$ of V; so considers very special transf.: in a gas they would be isovolumic (no change of the volume: and in this case the second law would be trivial). In C.'s approach V can change.
He points that ONCE everything clearly defined the change is trivial. B. did not take advantage of this and promises to take $\delta\widetilde{V}$ into account in future.

Interesting that Boltzmann, Clausius, Maxwell did not hesitate to think motion as periodic. Sheepishly B. says in 1866 "aperiodic motion can be regarded as periodic with infinite period", Clausius tries to argue that periodicity is not necessary and his theorem can be extended to the case in which atoms can be divided into groups each moving periodically even with different periods as long as the number of such groups is very large.

This is natural if one keeps in mind the Ptolemaic conception of motion as composed by periodic motions (deferents and epicycles): chaos was not yet dominant.

Clearly there was a problem, however. Periodic motion going through all possible states could be maintained only if phase space was discrete.

But Boltzmann considered integrals and derivatives as (convenient) approximations of sums and differences (unlike most of us, biased by social pressure).

Manifestly unhappy about his early way out came back to the question repeatedly trying to free his analysis from too detailed assumptions on microscopic motion.

Published what I call the “trilogy” in 1871: still imagining microscopic states as going through all possible states, concentrates on deriving the probability distributions without any assumption other than that the atoms were bound into molecules each of which, if unperturbed, going through all possible states, but occasionally jumping from one state to another due to a binary collision. This led him to the following results:

1) discover the canonical distribution for gases of poliatomic molecules (Maxwell had treated the monoatomic gases)

2) imagine a system of interacting atoms as a giant molecule and derive the canonical distribution of the small subsystems from the microcanonical one for the total system

3) obtain results by only examining the collisions kinematics: arriving essentially to the B. equation, published in 1872

The 2d of the 3 papers is quoted by Gibbs as deduction of canonical and microcanonical ensembles. Curiously Gibbs quotes the paper with the obscure title of its first section: referring to the "*Jakobi principle of the last divisor*".

After some effort it appears that this refers to the fact that several changes of variables are involved in the discussion: and the integrals change correspondngly via the introduction of a factor that we call today the "Jacobian". The latter is often just 1 because the transformations considered by B. are canonical. However B. does not seem familiar with the concept and spends several pages in several papers to check the property.

But the question of the periodicity kept bothering him: it made his derivation still resting on an hypothesis: that there are no other constants of motion besides the energy. Of course this is again related to the ergodic hypothesis.

After the Loschmidt objection to the Boltzmann equation, in 1877, B. answers by stating that it gives the correct evolution because every other is exceedingly improbable (although not impossible). A new breakthrough.

In the same paper of "remarks" B. makes the statement that the probabilistic interpretation leads naturally to an "interesting derivation of the equilibrium properties".

A second remark is an explicit derivation of the second law in a case in which the periodicity assumption holds. This would be a curiosity: but it will become very important a few years later.

It realizes an explicit example of the general theory of the connection between the second law and the variational principles.

Consider a 1-dim. conservative sys., potential $\varphi(x)$

$|\varphi'(x)| > 0$ for $|x| > 0$, $\varphi''(0) > 0$ and $\varphi(x) \xrightarrow[x\to\infty]{} +\infty$.

Suppose $\varphi(x)$ to depend on a parameter V. "*a state*" is a motion with given parameters $E = U$ and V. Let

U = total energy of the system $\equiv K + \varphi$
T = time average of the kinetic energy K
V = the parameter on which φ is supposed to depend
p = $-$ average of $\partial_V \varphi$.

If parameters change by dU, dV let:

$dL = -pdV,\ dQ = dU + pdV$. Then

Theorem: *The differential* $(dU + pdV)/T$ *is exact.*

Proof: let $x_\pm(U,V)$ be the extremes of the oscillations of the motion (given U,V) and define S as:

$$\begin{aligned} S =& 2\log\int_{x_-(U,V)}^{x_+(U,V)} \sqrt{K(x;U,V)}dx \\ \equiv& 2\log\int_{x_-(U,V)}^{x_+(U,V)} \sqrt{U-\varphi(x)}dx \end{aligned}$$

so that

$$dS = \frac{\int \left(dU - \partial_V\varphi(x)dV\right)\frac{dx}{\sqrt{K}}}{\int K\frac{dx}{\sqrt{K}}}$$

since $\frac{dx}{\sqrt{K}} = \sqrt{\frac{2}{m}}dt$ the time averages are given by integrating with respect to $\frac{dx}{\sqrt{K}}$ and dividing by the integral of $\frac{1}{\sqrt{K}}$. $\Rightarrow dS = \frac{dU+pdV}{T}$.

B. comes back immediately, still in 1877, on the statement that the Loschmidt paradox can lead to a new derivation of the equilibrium distributions.

He takes complete advantage of his discrete conceptions of space, time, integrals and derivatives and shows that the equilibrium distribution (in its canonical and microcanonical form) follow from a *simple combinatorial count* of the different possible locations of the molecules into small cells into which space is imagined decomposed.

The method is the same thence used by Planck and in the derivation of the quantu statistics (of course it leads to what we call the Boltzmann-Maxwell distribution). In this paper the formula for the entropy $S = k_B \log W$ appears.

The ergodic hypothesis remains still such: perfectly meaninglul in a context in which the phase space is discrete.

But a new idea emerged: the equilibrium distributions can be characterized without appealing to the detailed dynamics.

It becomes therefore natural to ask whether there exist other distributions which are invariant and which have the property that $dU + pdV = T \cdot (exact\ differential)$.

Little later, 1884, several events conspire to build a new viewpoint. Helmholtz remarks, in four long papers, that one can define “models of Thermodynamics” in systems that are *monocyclic.*

Systems of one or more particles all moving independently with periodic motion of equal period. Helmotltz shows how to define U, p, V, T with U equal to the energy per particle, V a parameter on which the potential φ of the forces acting on the system depend, $p = -\langle\partial_V \varphi\rangle$, $T =$ (average kinetic energy) so that $\frac{dU+pdV}{T}$ is an exact differential.

This is clearly already in B. at least since the first quoted paper of 1877. In 1884 B. had been invited to go to work in Berlin by Helmholtz: this might explain why instead of being angry he writes instead a long paper discussing further properties of monocyclic systems.

Collections of equilibrium states are identified with collections of as twenty years earlier with Clausius as twenty years earlier with Clausius time invariant prob. distrib: called *monodes*.

Then a monode is an *orthode* if there are averages of suitable mechanical quantities to be called U, V, p, T with T equal to the average kin. energy so that by changing the parameters on which the states depend the variations dU, dV of U, V are such that $\frac{dU+pdV}{T}$ is an exact differential.

He then proceeds to show that the collection of

1. the *canonical* distributions μ_c, called *holode*, is orthodic

2. so for the *microcanonical* distr. μ_{mc}, called *ergode*,

if one takes as U, V the average of the energy and the volume, defining the work done by the system by the variation of the average of potential energy V.

This is a general foundation of ensembles theory: it completes the B.'s program to find the mechanical interpretation of the second fundamental theorem.

The program had been essentially completed in the "trilogy" of 1871: the works of Helmholtz have been of stimulus to formalize the theory and cast it in the form in which we use it today.

A thermodynamics model, properly defining U, p, V, T, S, holds for "all mechanical systems": from a pendulum to a gas of 10^{19} molecules. Is it the thermodynamics of the system under consideration?

B. shows that: yes it is if the states are described by the holede or he ergode (and possibly by many other orthodic ensembles) provided the system is ergodic.

The latter property is necessary in order to identify the mathematically defined averages with respect to time evolution with the microcanonical averages and hence with the canonical ones.

The same approach is being attempted in the theory of stationary states out of equilibrium: are there relations valid for "all systems" which might be trivial for simple systems (as is the heat theorem for one dimensional systems) but which become interesting and useful for systems of many molecules?

It led to an extension of the ergodic hypothesis (into the *chaotic hypothesis*) and to the derivation of various identities among which a prominent role is plaid by the *fluctuation theorem.*