Physics. — "*A mechanical theorem of* BOLTZMANN *and its relation to the theory of energy quanta*". By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of November 29, 1913).

When black or also not black radiation is compressed reversibly and adiabatically by compression of a perfectly reflecting enclosure, it is known that the following takes place: The frequency v_p and the energy E_p of each of the principal modes of vibration of the cavity increase during the compression in such a way that we get:

$$\delta\left(\frac{E_p}{v_p}\right) = 0 \qquad (p = 1, 2, \ldots, \infty) \quad \ldots \ldots \quad (1)$$

for each of the infinitely many principal vibrations.

Relation (1) is of fundamental importance for the purely *thermodynamic* derivation of WIEN's law; it is no less so for every statistic theory of radiation, which is to remain in keeping with the second law of thermodynamics [1]. In particular it is also the basis of PLANCK's assumption of differences of energy: [2]

$$\frac{\varepsilon}{v} = 0, h, 2h, \ldots \quad \ldots \ldots \ldots \quad (2)$$

Of late PLANCK's supposition (2) of the original region (Content of energy of systems vibrating sinusoidally) has been applied to a rapidly extending region. Of course tentatively. Two questions arise:

1. Does there continue to exist an adiabatic relation analogous to equation (1) in the transition of systems vibrating sinusoidally (in which the motion is governed by linear differential equations with constant coefficients) to general systems?

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[1] P. EHRENFEST. Welche Züge der Lichtquantenhypothese spielen in der Theorie der Wärmestrahlung eine wesentliche Rolle? Ann. d. Phys. 36 (1911) p. 91; § 5.

[2] By way of elucidation: differences of energy e. g. of the form

$$\frac{\varepsilon}{v^2} = 0, h, 2h, \ldots$$

would lead to a conflict with the second law of thermodynamics. It is known that PLANCK arrived at (2) by first carrying out his combinatory calculation in general on the assumption

$$\varepsilon = 0 \ , \ f(v) \ , \ 2f(v) \ , \ 3f(v) \ , \ldots$$

and by then determining the form of $f(v)$ from the condition that the formula of radiation found by the combinatory way shall satisfy WIEN's law. Thus he brought his energy quanta *implicite* in harmony both with relation (1) and with the second law of thermodynamics.

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2. If so — how can it be applied heuristically, when PLANCK's assumption (2) is extended to systems vibrating not sinusoidally?

The answer to the first question is in the affirmative. In the search for the extension of the adiabatic relation (1) I perceived that such an extension, and indeed a surprisingly far-reaching one, follows immediately from a mechanic theorem found by BOLTZMANN and CLAUSIUS independently of each other (see § 1).

For the present I can only answer the second question by giving an example (§ 3). The difficulties which in general present themselves in this — Prof. EINSTEIN drew my attention to the most troublesome one (§ 4) in a conversation — I have stated in § 2, 3, 4, without being able to remove them.

Another objection may be raised against the whole viz. : there is no sense — it may be argued — in combining a thesis, which is derived on the premise of the mechanical equations with the anti-mechanical hypothesis of energy quanta. Answer : WIEN's law holds out the hope to us that results which may be derived from classical mechanics and electrodynamics by the consideration of macroscopic-adiabatic processes, will continue to be valid in the future mechanics of energy quanta.

§ 1. Let $q_1, \ldots, q_n$ be the coordinates of a mechanic system. The potential energy Φ may depend, besides on the coordinates q, also on some "slowly variable parameters" $r_1, r_2, \ldots$ Let the kinetic energy T of the system be an homogeneous. quadratic function of the velocities q_1, and contain in its coefficients besides the q's, eventually also the r's.

Let further the system possess the following properties : For definite but arbitrarily chosen values of the parameters $r_1, r_2, \ldots$ all the motions of the system are *periodical*, no matter with what initial phase $(q_1, \ldots, q_n, p_1, \ldots, p_n)$ the system begins. The period P will in general not only depend on the values of $r_1, r_2, \ldots$, but also on the phase (q_0, p_0), with which the system begins.

By changing the parameters $r_1, r_2, \ldots$ infinitely slowly we can transform every original motion (A) of the system into another (B). This particular mode of influencing the system is called "adiabatic influencing" of the motion.

If moreover the respective *periods* of the motion are indicated by P_A and P_B, or their reciprocal values (the "*frequencies*") by ν_A and ν_B, and further the *temporal mean of the kinetic energy* by $\overline{T}_A$ and $\overline{T}_B$, then

$$\left(\frac{T}{\nu}\right)_A = \left(\frac{T}{\nu}\right)_B \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

With adiabatic influencing of a periodic system the quotient of the temporal mean of the kinetic energy and of the frequency remains unchanged (adiabatic relation).

If σ' denotes an infinitesimal adiabatic change, P the original period, then:

$$\sigma'\left(\frac{\overline{T}}{\nu}\right) = \sigma' \int_0^P dt \cdot T = 0 \quad . \quad . \quad . \quad . \quad . \quad (II)$$

(The action calculated over a period remains constant on adiabatic influencing). The last assertion is nothing but a *special case* of the thesis of BOLTZMANN, CLAUSIUS and SZILY, the derivation and formulation of which may be found in BOLTZMANN's "Vorlesungen uber Mechanik", Vol. II, § 48. [1])

§ 2. *Remarks.*

a. In the case that there is no potential energy at all in the system, or that the potential energy is in a fixed ratio to the kinetic energy [2]), the relation

$$\sigma'\left(\frac{E}{\nu}\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II')$$

holds at the same time as equation (II) (compare equation (1) for systems vibrating sinusoidally). But it is noteworthy that (II') only holds in such particular cases, and is not of such general application as (II).

b. A practical extension of thesis (I) to *non*-periodical motions would be very desirable. That it is not at once possible, follows immediately from early investigations by BOLTZMANN[3]). I prefer not to follow the way which BOLTZMANN chose to extend his thesis to non-periodical systems [4]), because it essentially rests on the untenable [5]) hypothesis of ergodes.

c. In case the adiabatic influencing leads to some singular motions, in which a periodic motion begins to detach itself into two or more separate motions, assertion (II) must be modified accordingly.

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[1]) Original papers : L. BOLTZMANN, Wissensch. Abh. I. p. 23, p. 229. R. CLAUSIUS, Pogg. Ann. 142 p. 433. SZILY, Pogg. Ann. 145.

[2]) $\overline{\Phi} = \overline{T}$ for systems vibrating sinusoidally, when the potential energy in the state of equilibrium is taken zero.

[3]) L. BOLTZMANN, Ges. Abh. II p. 126 (1877); Vorles. üb. Mechanik II § 41.

[4]) Ges. Abh. III p. 132, 139, 153.

[5]) P. u. T. EHRENFEST Mathem. Encykl. IV. 32 § 10a (ROSENTHAL, Ann. d. Phys. 42 (1913) p. 796; M. PLANCHEREL, Ann. d. Phys. (1913) 42 p. 1061.

E x a m p l e [1]). Let a point move to and fro free from forces in a
tube closed on either side. Let a repulsive field of force arise and
increase infinitely slowly in the middle of the tube. At last a moment
comes when the point with its store of kinetic energy cannot get
any longer through that "wall", and only moves to and fro in one
half of the tube. If this field of force is of infinitely small extension,
the kinetic energy of the motion is the same at the end as at the
beginning ; the frequency on the other hand is twice the value, for
the path has been halved. Accordingly the original motion has split
up into two distinct separated branches during the adiabatic influencing.

§ 3. An example may illustrate the way in which the "adiabatic
relation" I may be applied. This example refers to the extension of
PLANCK's assumption (5) from resonators vibrating sinusoidally to
rotating dipoles.

A fixed dipole may be suspended so that it can revolve freely
round the z-axis. Parallel to the x-axis a very strong directional
field is made to act. We first consider infinitely small oscillations
of the dipole. The angle of rotation may be denoted by q, the cor-
responding moment (moment of inertia $\times$ angular velocity) by p,
the frequency of the oscillation by v_0. According to PLANCK's
assumption (2) the image point (q, p) of such a dipole can lie
nowhere else in the (q, p)-plane than on certain ellipses, which
belong to the quantities of energy $0, hv_0, 2hv_0, \ldots$ and for which
therefore :

$$\left(\frac{T}{v}\right)_0 = 0, \qquad \frac{h}{2}, \qquad 2\frac{h}{2}, \ldots\ldots n\frac{h}{2}, \ldots\ldots \quad \cdot \cdot \cdot \quad (3)$$

We have namely (sinus vibration !):

$$T = \frac{\varepsilon}{2} . \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

The infinite number of points of rest and equilibrium :

$$p = 0 \qquad q = 0, \qquad \pm 2\pi, \qquad \pm 4\pi, \qquad \pm 6\pi, \ldots.$$

belong to the value of the energy $\varepsilon = 0$.

Some congruent ellipses, which have these points (5) as centres,
belong to the value $\varepsilon = nhv_0$.

We now consider an adiabatic influencing of such an initial
motion of the dipole by an infinitely slow change of the orientating
field of force, and eventually also of the moment of inertia. In this
way it is possible to convert the infinitely small oscillations into

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[1]) Mr. K. HERZFELD gave this example on the occasion of a discussion.

oscillations of finite amplitude, till at last the dipole changes its form of motion and begins to rotate to the right or to the left; at first still noticeably irregularly, at last with constant velocity of rotation. When we consult Fig. 1, the continuous change of the motion will become clear, particularly also the transition through the singular motion *GH*. A complete oscillation corresponds in the final state to a *double* rotation of the uniformly rotating dipole
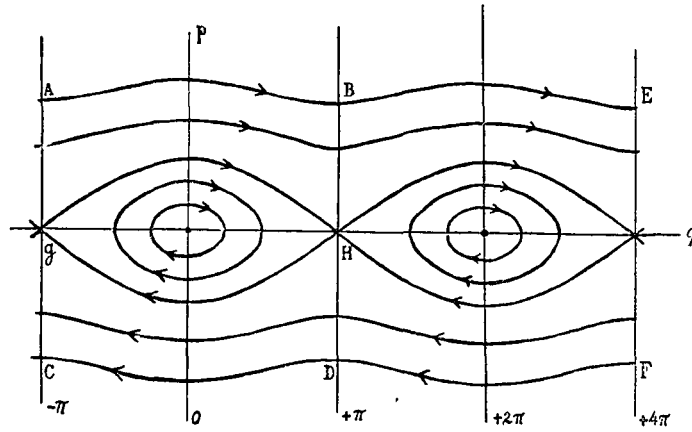

Fig. 1.

$(0 \leq q \leq 4\pi)$: *ABE*. Hence if we wish to derive the kinetic energy T_1 of the uniform rotation by the aid of the "adiabatic relation" from the mean kinetic energy T_0 of the original oscillatory motion, we must take as corresponding period the time

$$P_1 = \frac{4\pi}{\dot{q}_1} \quad \cdots \quad \cdots \quad \cdots \quad (6)$$

where $\dot{q}_1$ is the constant velocity of rotation of the dipole; so as corresponding frequency

$$\nu_1 = \frac{\dot{q}_1}{4\pi} \quad \cdots \quad \cdots \quad \cdots \quad (7)$$

Then according to (7) (I) and (3), we have

$$\left(\frac{T}{\nu}\right)_1 = \frac{4\pi T_1}{\dot{q}_1} = \left(\frac{T}{\nu}\right)_0 = 0 \ , \ \frac{h}{2} \ , \ 2\frac{h}{2} \ , \ \cdots \ n\frac{h}{2} \ , \ \cdots \quad (8)$$

or also, as

$$T_1 = \frac{p_1 \dot{q}_1}{2} \quad \cdots \quad \cdots \quad \cdots \quad (9)$$

$$p_1 = 0 \ , \ \pm \frac{h}{4\pi} \ , \ \pm 2 \frac{h}{4\pi} \ , \ \ldots \ \pm n \frac{h}{4\pi} \ , \ldots \ . \ . \quad (10)')$$

If other values of p were admitted for a uniformly rotating dipole, it would be possible that by reversal of the described adiabatic process sinusoidal vibrations were obtained; with an amount of energy which would come in collision with PLANCK's *assumptions* (3) *and* (2).

If we have N dipoles, and if with given total energy, we wish to calculate the "most probable" distribution of the dipoles over the possible motions (10), it is still to be fixed by definition to what regions in the (q,p)-plane the same probability must be assigned. By the "adiabatic influencing" every separate ellipse of PLANCK's in the (q, p)-plane passes finally into a definite pair of straight lines of the length of 2π, which lie symmetrically on either side of the q-axis. If in the statistic treatment of dipoles vibrating sinusoidally with PLANCK we consider all the separate ellipses as regions of equal probability, we are naturally led to treat the just-mentioned pairs of lines for the uniformly rotating dipoles as regions of equal probability [2]) (Hypothesis A). However natural this may be, yet it is a new hypothesis. Is this hypothesis inevitable?

Seemingly the following course is open. Let us start from N dipoles vibrating sinusoidally (frequency v_0), which are distributed over PLANCK's ellipses in the *most probable* manner. Apply the above-described "adiabatic influencing" to all the poles at the same time. Then an entirely definite distribution of the N-dipoles over the different modes of motion is obtained finally (10). This distribution (distribution B) is, however, *another* than follows as the most "probable" from the hypothesis A (distribution A). Is distribution B to be taken as the distribution which corresponds with the state of equilibruim, and is therefore the distribution A and the hypothesis A to be rejected? The remarks made in the following § try to demonstrate that the distribution B cannot be considered as a distribution of equilibrium.

§ 4. In case of adiabatic compression black radiation is trans-

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[1]) In my monograph: "Bemerk, betreffs der specif. Wärme zweiatomiger Gase", Verh. d. deutsch. phys. Ges. 15 (1913) p. 453, I have erroneously put:

$$v_1 = \frac{q_1}{2\pi} \qquad \text{so} \qquad p_1 = \ldots \pm n \frac{h}{2\pi} \ldots$$

This, however, has no further influence on the derivations given there than that the numerical value of the moment of inertia J of the hydrogen molecule calculated finally must be divided by four.

[2]) P. EHRENFEST. Bemerk. betreffs der specif. Wärme zweiatomiger Gase. Verh. d. deutschen phys. Ges. 15 (1913) p. 453.

formed into black radiation as well when there is a "black grain" in the contracting reflecting enclosure, as in the absence of such a "catalyser". Else we should get into collision with the second law of thermodynamics.[1] If there are N monatomic molecules in a vessel with rough walls, distributed according to MAXWELL's law, and if this ideal gas is compressed by an infinitely slow shifting of the walls of the vessel, the distribution finally follows again MAXWELL's law, both when the molecules during the compression can collide, and when they could penetrate perfectly through each other. Probably more examples might be found in which through an "adiabatic influencing" of the separate degrees of freedom a state of equilibrium arises from a state of equilibrium.[2] But in general this is not the case, e.g. for molecules consisting of more than one atom or for mon-atomic molecules on which an external field of force acts.[3]

Chemistry. — *"Equilibria in ternary systems. XI."* By Prof. F. A. H. SCHREINEMAKERS.

In all our previous communications we have always contemplated the case that the occurring solid substances are ternary compounds. Now we shall assume that a binary compound occurs.

It is evident that we may deduce the saturationcurves under their own vapour-pressure and the boilingpointcurves of a binary compound in the same way as has been done in the previous communications for a ternary compound.

We take a compound composed of B and C, we represent this in fig. 1 by the point F on the side BC of the components-triangle ABC. We now take a definite temperature T and a pressure P in such a way, that no vapour can be formed and the isotherm consists only of the saturationcurve of F. This is represented in fig. 1 by curve pq.

On decrease of P, a gasregion occurs somewhere and also the region $L-G$, which separates gas- and liquidregion from each other.

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[1] M. PLANCK, Wärmtestrahlung II. Aufl. § 71.

[2] The two mentioned cases have this in common that the pressure only depends on the total energy of the system, and not on its distribution over the different degrees of freedom.

[3] In an analogous way we can see that a canonical ensemble of gases generally does *not* remain canonical after an "adiabatic influencing".