Physics. — *"On adiabatic changes of a system in connection with the quantum theory."* By Prof. Dr. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 24, 1916).

Introduction. In an increasing number of physical problems the foundations of classical mechanics (and electrodynamics) are used together with the quantum hypothesis, which is in contradiction with them. It remains of course desirable to come here to some general point of view from which each time the limit between the "classic" and the "quantum" region may be drawn.

WIEN's law has been found by an application of classic principles: the changes of the distribution of the energy over the spectrum and the work done by a reversible adiabatic compression are calculated quite according to classic electrodynamics. This law derived without the use of quanta stands unshaken amid the quantum theory. This fact now is worth our attention.

Perhaps something similar holds in more general cases, when no longer harmonic vibrations take place, but more general motions:

the *reversible-adiabatic* changes for such more general motions might e.g. be calculated by the classic method, while in the calculation of *other changes* (e.g. of the isothermal addition of heat) the quanta already play a role.

This was the starting-point in some papers in which partly PLANCK's hypothesis of the energy steps ($\varepsilon = nh\nu$) was investigated in details[1]) and partly its generalization from harmonic to more general motions was treated[2]). Especially the following hypothesis was used, to which EINSTEIN gave the name of adiabatic hypothesis[3]).

"*Adiabatic hypothesis*"[4]) If a system is exposed to adiabatic influences the "admissible" motions are transformed into "admissible" ones.

Let us suppose for some class of motions the quantum hypothesis to be introduced for the first time. In some cases the adiabatic hypothesis quite determines which special motions are "admissible": namely in the case that the new motion can be derived from a former class of motions by a reversible adiabatic process, for which has been fixed already, which special motions are "admissible" (especially therefore if the new motions can be obtained from harmonic motions with one degree of liberty").[5])

In other cases the adiabatic hypothesis puts at least limits to the arbitrary way in which otherwise the quantum hypothesis might be applied.

In each such application of the adiabatic law a great part is played by the "*adiabatic invariants*", viz. those quantities which before and after the adiabatic process have the same value. Formerly there has been shown especially that for arbitrary periodic motions (of one or more degrees of liberty) there exists the adiabatic invariant:

$$\frac{2\overline{T}}{\nu} \quad \ldots\ldots\ldots\ldots \quad (1)$$

1) P. EHRENFEST. Welche Züge der Lichtquantenhypothese spielen in der Theorie d. Wärmestrahlung eine wesentliche Rolle? Ann. d. Phys. **36** (1911) p. 91—118. [Further cited as communication *A*].

2) P. EHRENFEST, Bemerk. betr. d. Spezif. Wärme zweiatomiger Gase. Verh. d. deutsch. phys. Ges. **15** (1913) p. 451. [Comm. **B**]. — P. EHRENFEST. Een mechan. theorema van BOLTZMANN en zijne betrekking tot de quanten-theorie. Versl. Amsterdam. XXII (1913) p. 586. [Comm. **C**].

3) A. EINSTEIN. Beiträge z. Quantentheorie. Verh. d. deutsch. phys. Ges. **16** (1914) p. 826.

4) For the definition of the expressions used here comp. § 1, 2.

5) Comp. the transformation used in *C* § 3 of infinitesimal vibrations in uniform rotation, for other examples see §§ 7, 8 of this paper.

6) Comm. B § 1.

(ν is the frequency, T the mean value of the kinetic energy with respect to the time), which in the special case of harmonic vibrations of one degree of liberty coincides with [1]:

$$\frac{\varepsilon}{\nu} \quad \ldots\ldots\ldots\ldots \quad (2)$$

The purpose of the considerations in this paper is:

1. To formulate the adiabatic law as sharply as possible, at the same time indicating where this sharpness is failing especially with respect to non-periodic motions.

2. To indicate what great significance must be ascribed to the "adiabatic invariants" in the quantum theory. The discussion of the above mentioned invariant $\frac{2\overline{T}}{\nu}$ especially will show how it forms a link between the adiabatic hypothesis on the one hand and the quantum hypothesis of PLANCK, DEBIJE, BOHR, SOMMERFELD on the other hand.

3. To point out difficulties, which rise at the application of the adiabatic hypothesis, as soon as the adiabatic reversible changes lead through singular motions.

4. To show at least how the adiabatic problems are connected with the statistical mechanical bases of the second law of thermodynamics. The statistical mechanical explanation BOLTZMANN gave of it rests on statistical foundations which are destroyed by the introduction of the quanta.

Since then a statistical deduction has been given of the second law for some special systems (e.g. for those with harmonic vibrations) but not for more general systems [2]).

Hoping that others may succeed in removing the difficulties I was not able to surmount, I will publish my considerations.

Perhaps a close investigation will show that the adiabatic law may not be maintained in general. At all events W. WIEN's law seems to show that in the quantum theory a special place is taken by the reversible, adiabatic processes; that for them the classic foundations can be of most use.

§ 1. *Definition of the reversible adiabatic influence on a system. Adiabatic related motions: $\beta(a)$ and $\beta(a')$.*

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[1]) See A § 2, C § 2. The existence of this adiabatic invariant may be considered as the root of WIEN's law.

[2]) Comp. P. EHRENFEST. Zum BOLTZMANN'schen Entropie-Wahrsch. Theorem. Phys. Zschr. **15** (1914) p. 657 and § 8 of this paper.

Let $q_1 \dots q_n$ be the coordinates of a system, while the potential energy depends not only on the coordinates q, but also on certain "slowly changing parameters" $a_1, a_2 \dots$ Suppose the kinetic energy T to be a homogeneous quadratic function of the velocities $\dot{q}_1, \dots \dot{q}_n$, while in its coefficients there occur besides the $q_1, q_2 \dots$ eventually also the $a_1, a_2 \dots$ Some original motion $\beta(a)$ can be transformed into a definite other motion $\beta(a')$ by an infinitesimal slow change of the parameters from the values $a_1, a_2 \dots$ to the values $a_1', a_2' \dots$ This special way of influencing the system may be termed "reversible adiabatic", the motions $\beta(a)$ and $\beta(a')$ "*adiabatically related*".

Remarks: *A*. The addition "reversible" needs no further justification, if all motions that are considered are periodic. It becomes different if under the considered motions there are aperiodic ones as e.g. the motion in a hyperbola under the attraction according to NEWTON's law. Here the addition loses its original meaning. By the introduction of well-chosen coordinates, quasi-periodic motions as e.g. the oscillations of a conical pendulum or irrational motions of LISSAJOUS may be treated as periodic ones.

B. The definition given above needs generalization if the influence of a magnetic field has to be considered (ZEEMAN-effect) or if we have to do with an electro-magnetic system (reversible, adiabatic compression of radiation by a mirror).

§ 2. *Formulation of the adiabatic hypothesis for systems with periodic or quasi-periodic motions.*

Let the values $a_{10}, a_{20} \dots$ of the parameters if the system be determined in any way. The quantum theory will not allow every motion $\beta(a_0)$, which can exist with these parameter values according to the fundamental equations of mechanics, but only some of them [1]. Therefore we speak of the motions $B\{a_0\}$ as "admissible" for the parameter values $a_{10}, a_{20} \dots$ To another set of values of the parameters $a_1, a_2 \dots$ there belong then "admissible" motions $B\{a\}$.

Now the adiabatic hypothesis may be formulated as follows;

For a general set of parameter values $a_1, a_2, \dots$ only those motions are possible that are adiabatically related with motions possible for the special values $a_{10}, a_{20} \dots$ (that is which can pass into these by a reversible change).

Remarks: *A*. Because of some difficulties rising in that question,

[1]) In order to avoid too many details, we leave aside that in PLANCK's recent treatment of the theory of radiation only "critical" motions are considered, besides which also the other motions are "admissible". It is obvious how our discussion might be adapted to this new treatment.

(comp. § 9) I am not able to say whether the adiabatic law might be generalized to the real aperiodic motions and how this would have to be done.

B. Some forms of adiabatic influence may be realized without difficulties, e.g. the increase of an electric or magnetic field in the neighbourhood of an atom (STARK and ZEEMAN effect). Some others are more fictitious e.g. the change of a central force, (comp. § 7).

At all events from the example of WIEN's law it is evident, that such a fiction may show the right way. Only further investigation and the control by experiment can teach where the "natural" adiabatic influencing becomes "unnatural". At any rate the adiabatic law gives a statement that is the more positive the more multiple influencing we allow.

§ 3. *The adiabatic invariants and their application.*

Every use of the adiabatic proposition induces us to seek for "adiabatic invariants", viz. quantities which remain constant at the change of a motion $\beta(a)$ into an adiabatically related motion $\beta(a')$. From the adiabatic proposition namely the following conclusion may be immediately drawn.

If we assume that for the admissible motions $B(a_0)$ a definite adiabatic invariant Ω has the discrete numerical values Ω', Ω'' for the special values $a_{10}, a_{20} \ldots$, then it has exactly the same values for the admissible motions belonging to the arbitrary values of the parameters a_1, a_2.

§ 4. *The adiabatic invariant* $\frac{\overline{2T}}{\nu}$ *for periodic motions and* $\frac{\varepsilon}{\nu}$ *especially for harmonic motions.* [1])

Let us suppose that the considered system has the following properties: For fixed but arbitrarily chosen values of the parameters $a_1, a_2, \ldots$ all motions of the systems that have to be considered, are *periodic*, for any phase $(q_{10}, \ldots q_{n0}, \dot{q}_{10}, \ldots \dot{q}_{n0})$ the motion

[1]) Comp. communication C §§ 1. 2. *Other examples of adiabatic invariants* are the cyclic moments, if the system has cyclic coordinates. If the rotation of a ring of electrons is influenced by an increasing magnetic field, this is the sum of its moment of momentum and its electro kinetic moment (ZEEMAN-effect, magnetization). If an increasing electric field acts on a hydrogen atom of BOHR, then it is the moment of momentum with respect to the direction of the lines of force. At the change of the field of a central force (comp. § 7) it is the moment of momentum.

may begin with. Here the period P may still depend in any way on $a_1, a_2, \ldots$ and on the beginning phase of the motion.

Then the time integral of the (double) kinetic energy taken over the period is an adiabatic invariant:

$$\delta' \int_0^P dt\, 2T = 0 \quad \ldots \ldots \ldots \ldots \quad (3)$$

δ' will denote: the difference in the values for two infinitely near, adiabatically related motions of the system. [For the proof of (3) see appendix I]. If the reciprocal value of the period P is called the frequency ν and the mean with respect to the time of T $\overline{T}$, then (3) says:

$$\frac{2\overline{T}}{\nu} \text{ is an adiabatic invariant} \quad \ldots \ldots \quad (4)$$

In the case of a harmonic vibration of one degree of liberty the means with respect to the time of kinetic and potential energy are known to be equal to each other and therefore also to half the total energy, so that:

$$\frac{\varepsilon}{\nu} \text{ is an adiabatic invariant.} \quad \ldots \ldots \quad (5)$$

§ 5. *A geometrical interpretation of the adiabatic* $\frac{\overline{2T}}{\nu}$ *in the* (q,p) *space. Connection with a theorem of* P. HERTZ.

In order to find a connection with the quantum hypotheses of PLANCK, DEBIJE, BOHR and others we shall use a deduction of the integral of action to which SOMMERFELD has drawn the attention.[1])

$$\int_0^P dt\, 2T = \int_0^P dt \sum_1^n{}^h p_h \dot{q}_h = \sum_1^n{}^h \int dq_h \cdot p_h = \sum_1^n{}^h \iint dq_h\, dp_h. \quad . \quad (6)$$

therefore

$$\frac{\overline{2T}}{\nu} = \sum_1^n{}^h \iint dq_h\, dp_h. \quad \ldots \ldots \ldots \quad (7)$$

where the double integrals on the right hand side have the following meaning: If the system executes its periodic motion, its phase point

[1]) A. SOMMERFELD: Zur Theorie d. Balmerschen Serie. Sitzber. d. Bayr. Akad. 1916 p. 425 (§ 7).

describes a closed [1]) curve in the $2n$ dimensional (q,p) space and its n projections on the 2 dimensional planes (q_1,p_1), (q_2, p_2), ... (q_n, p_n) describe n closed curves.

$\iint dq_h\, dp_h$ is the area enclosed by the h^{th} projection curve.

Remarks: *A*. The numerical value of $\frac{2T}{\nu}$ does not change if in the description of the motion we pass from one system of coordinates $q_1 \ldots q_n$ and the corresponding $p_1 \ldots p_n$ to another one $q'_1 \ldots q'_n$ and the corresponding $p'_1 \ldots p'_n$. Therefore the right hand side of (7) can neither change its numerical value.

B. There are systems, for which if the system of coordinates has been chosen rightly, not only the total sum on the right hand side of (7) is an adiabatic invariant, but also the single terms $\iint dq_h dp_h$ (comp. the example in § 7). In this case we obtain thus at once more invariants.

C. For a system of one degree of liberty:

$$\frac{2T}{\nu} = \iint dq\,dp \text{ is an adiabatic invarant} \quad (8)$$

according to (7) viz.: for a system of one degree of liberty the area enclosed by the phase curve in the (q,p) plane is an invariant (in this case there are no other invariants independent of this one).

D. A theorem of P. HERTZ (1910) [2]). Give definite values $a_{10}, \ldots a_{n0}$ to the parameters and consider some motion compatible with these. The corresponding path of phase in the (q, p) space lies on a definite hypersurface of constant energy $\varepsilon(q, p, a_0) = \varepsilon_0$. This hypersurface encloses a definite $2n$ dimensional volume:

$$\int \ldots \int dq_1 \ldots dp_n = V_0 . \quad (9)$$

In the first place an adiabatically reversible influencing $a_0 \rightarrow a$ works on the system. Secondly the hypersurfaces have now another position in the (q, p) space than before. We may now consider the volume V of that energy surface on which the phase path of the system lies *after* the adiabatic influencing. The theorem of P. HERTZ teaches now:

1) This expression needs further interpretation, if e. g. one of the coordinates is an angle and this angle increases each period with 2π.

2) P. HERTZ: Mechanische Grundlag. d. Thermod. Ann. d. Ph. **33** (1910) p. 225—274; p. 537—552. [§ 11. Adiabat. Vorgänge. Comp. 173]. P. HERTZ in "Repert. d. Physik" (TEUBNER 1916) p. 535 (Comp. (7).

$$V = V_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

For a system with *one* degree of liberty (10) and (8) are evidently identical; for a system with more degrees of liberty this is however not the case [1]).

§ 6. *Connection between the adiabatic hypothesis and the quantum-hypotheses of* PLANCK, DEBIJE, and others *for systems with one degree of liberty.* PLANCK's hypothesis of the energy steps (1901) says, that a harmonically vibrating resonator of the frequency ν_0 can only have one of the following energies ε: [2])

$$\varepsilon = 0, \; h\nu_0, \; 2h\nu_0, \ldots \quad . \quad , \quad . \quad . \quad . \quad . \quad (11)$$

Therefore the adiabatic invariant of the resonator can only have the values

$$\frac{\varepsilon}{\nu_0} = \frac{2\bar{T}}{\nu_0} = \iint dq dp = 0, h, 2h, \ldots \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Let us now consider a resonator with the non-linear equation of motion

$$\ddot{q} = -(\nu_0{}^2 q + a_1 q^2 + a_2{}^2 q^3 + \ldots) \ldots \quad . \quad . \quad . \quad (13)$$

This does not execute harmonic vibrations: the frequency $\nu \neq \nu^0$ of its oscillations depends not only on $a_1, a_2 \ldots$ but also on the intensity with which they are excited.

For the special parameter values $a_1 = a_2 \ldots = 0$ it becomes the resonator of PLANCK. Therefore the adiabatic hypothesis (comp. the formulation in § 3) becomes: For these non-harmonic resonators too only those motions are possible for which

$$\frac{2\bar{T}}{\nu} = \iint dq dp = 0, h, 2h, \ldots \quad . \quad . \quad . \quad . \quad . \quad (14)$$

From the hypothesis of PLANCK's energy-steps we have thus

1) In the deduction of his theorem P. HERTZ has to calculate the mean with respect to the time of the force acting on the parameter a. He replaces this mean with respect to the time by a corresponding numerical mean in a microcanonical ensemble. It is known that BOLTZMANN and MAXWELL have only been able to justify this way of proceeding by the assumption that the considered system is ergodic. A resonator with *one* degree of liberty is really ergodic. This is however not the case for molecules with two or more degrees of liberty. Therefore a special investigation is needed here whether the above defined quantity V_0 is adiabatically invariant. *If for all degrees of liberty of a molecule only harmonic vibrations* can occur, V_0 is really an adiabatic invariant:

$$V_0 = \frac{\varepsilon_1}{\nu_1} \cdot \frac{\varepsilon_2}{\nu_2} \cdot \frac{\varepsilon_3}{\nu_3} \ldots\ldots$$

2) Comp the note in § 2.

deduced by means of the adiabatic hypothesis the quantum hypothesis DEBYE gives for the values of $\iint dq\,dp$ for non-harmonic vibrations. [1])

Let us suppose that an electric dipole with the electric moment a_1 and the moment of inertia a_2 can rotate about the Z-axis. [2]) An orientating field of the intensity a_3 may act parallel to the x-axis. As coordinate may be chosen the angle over which the dipole has turned.

If we begin with very great values of a_1, a_3 and also of a_2, then we may regard the vibrations as *infinitesimal* also for considerable values of the energy with which they are excited: a resonator of PLANCK. By letting a_2 and a_3 decrease infinitely slowly we can pass reversibly adiabatically to vibrations of finite amplitude, finally reversing the pendulum. If then the moment of inertia is kept constant, while the orientating field decreases to zero, we finally obtain *molecules on which no force is acting and which therefore are rotating uniformly.* For all these adiabatically related motions the adiabatic invariant

$$\frac{\overline{2T}}{\nu} = \iint dq dp$$

is thus necessarily confined to the original values o, h, $2h$, . . . If for the uniform rotation with frequency ν this is identified with the number of complete rotations of the dipole per second:

$$\nu = \pm \frac{\dot q}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

while it is taken into consideration that

$$\overline{2T} = 2T = p\dot q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

it is therefore required that p can have no other values than

$$p = 0, \pm \frac{h}{2\pi}, \pm 2\frac{h}{2\pi}, \ldots \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Remark: The considerations given above must still be completed, especially with a view to the difficulty, that during the adiabatic change the singular, *non-periodic* motion is passed, which forms the

[1]) P. DEBIJE. Zustandsgleich. u. Quantenhyp. ("Wolfskehlwoche" TEUBNER 1914) § 3.

S. BOGUSLAWSKY. Pyroelektricität auf Grund der Quantentheorie. Phys. Z schr. **15** (1914) p 569 gl. 3.

[2]) Comp. the treatment and application of this example in communication B § 2 and C § 3, and especially see the figure in C § 3.

limit between the pendulum motions and the rotations. It must therefore be investigated, how the invariants of both kinds of motion are connected. [1])

§ 7. *Connexion with* SOMMERFELD's *quantum hypothesis for systems with more than one degree of liberty.*

We want to show, that the adiabatic law is satisfied by the quantum hypothesis recently given by SOMMERFELD for the plane motion of a point about a centre of attraction according to NEWTON's law.

Let $\chi(r, a_1, a_2, \ldots)$ be the potential of a central attracting force. Then the differential equations of the plane motion of a point are in polar coordinates: $r = q_1$, $\varphi = q_2$

$$m\ddot{r} - mr\dot{\varphi}^2 + \frac{d\chi}{dr} = 0 \quad \ldots\ldots\ldots \quad (18a)$$

$$\frac{d}{dt}(mr^2\dot{\varphi}) = 0 \quad \ldots\ldots\ldots \quad (18b)$$

(18*b*) expresses directly — which is very plausible — that the moment is invariant with respect to a change of the parameters $a_1, a_2, \ldots$

$$mr^2\dot{\varphi} = p_2 \quad \text{adiabatically invariant} \quad \ldots \quad (19)$$

By eliminating $\dot{\varphi}$ by means of (19) from (18*a*) we obtain

$$m\ddot{r} = \frac{mr^3}{p_2^{\,2}} - \frac{d\chi}{dr} \quad \ldots\ldots\ldots \quad (20)$$

This differential equation has the same structure as if it described the motion of a point oscillating under the influence of a force with the potential:

$$\Phi = -\frac{p_2^{\,2}}{2mr^2} + \chi(r, a_1, a_2) \quad \ldots\ldots \quad (21)$$

over a fixed straight line between two extreme values of r ($r_A > r_B > 0$). For this periodic motion (of one degree of liberty) however we have according to §§ 4 and 5 the adiabatic invariant:

$$\frac{2\overline{T_1}}{\nu_1} = \iint dq_1\,dp_1 = \text{adiabatically invariant} \quad \ldots \quad (22)$$

Equation (19) may be formulated in an analogous way:

$$\frac{2\overline{T_2}}{\nu_2} = \iint dq_2\,dp_2 = \text{adiabatically invariant} \quad \ldots \quad (23)$$

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[1]) Perhaps this will be possible by considering the *conical* pendulum or a system acted upon by a magnetic force. As to this uncertainty comp. § 9 of this communication and § 3 of communication C.

As

$$\frac{\overline{2T_2}}{\nu_2} = \frac{p_2 q_2}{\left(\frac{q_2}{2\,\tau}\right)} = 2\,\pi p_2 = \int\limits_0^\pi dq_2 \cdot p_2 = \iint dq_2\, dp_2$$

SOMMERFELD introduces the quanta by the equations:

$$\iint dq_1\, dp_1 = 0, h, \ldots, nh, \ldots \qquad (24)$$

$$\iint dq_2\, dp_2 = 0, h, \ldots, n'h, \ldots \qquad (25)$$

These hypotheses are thus actually in harmony with the adiabatic hypothesis (comp. the formulation in § 3).

Remarks. A: We see that the adiabatic invariants (22) and (23) do not only exist for the periodic motions about a centre of force which attracts either according to the law of NEWTON-COULOMB or elastically ($\chi = \frac{a}{r}$ or $\chi = \frac{ar^2}{2}$), but also for the quasi-periodic motion (in a rosette) about a centre of force with general $\chi\,(r, a)$. But in the first case are $\nu_1 = \nu_2 = \nu$, so that the invariants can be taken together to:

$$\frac{2(\overline{T_1 + T_2})}{\nu} = \frac{\overline{2T}}{\nu} = \text{adiabatically invariant}$$

(comp. here remark *B* of the appendix).

B. Now it would be interesting to find the adiabatic invariants for more general quasi-periodic motions, (in the first place for anisotropic instead of isotropic fields of force). This would at the same time furnish an answer to the question to which system of coordinates SOMMERFELD's quantum hypotheses have to be applied).

C. If the attracting force obeys COULOMB's law, the hypothesis (23) is equivalent with PLANCK's [2]) new method of introducing the quanta, as has been remarked by SOMMERFELD (p. 455). This is also the case, when we have to do with an elastic attraction [3]).

I have not yet succeeded in finding a more general connexion between the adiabatic hypothesis and PLANCK's new assumptions.

D. In the refinement of his theory SOMMERFELD has still taken into consideration the dependency of the mass of the electron on

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[1]) A. SOMMERFELD. Zur Theorie d. Balmerschen Serie. Sitzber. Bayr. Ak. 1916 p. 425—500; See p. 455 at the bottom.

[2]) M. PLANCK. We again leave aside, that PLANCK only speaks of "critical" motions, beside which also the other motions are "stable".

[3]) Comp Appendix II.

its velocity. This causes the motion to take place no longer in a closed curve, the path becoming a rosette and an uncertainty arising as to the limits between which the integrals in (23) have to be taken [1]). In order that we might make a conclusion from the viewpoint of the adiabatic hypothesis, it would first have to be investigated, which quantities are adiabatically invariant in this case.

§ 8. *Connexion of the adiabatic hypothesis with the statistic basis of the second law* [2]).

BOLTZMANN's statistical mechanical deduction of the second law and especially of the equation

$$\frac{E + A_1 \Delta a_1 + A_2 \Delta a_2 + \ldots}{\Theta} = k \, \Delta \log W \quad . \quad . \quad . \quad . \quad (26)$$

has been based upon a definite agreement as to what regions in the (q,p) space for the molecules ("μ-space") will have to be considered as "a priori equally probable". As such regions were taken to which in the μ-space equal volumina $\int \ldots \int dq_1 \ldots dp_n$ viz. correspond. BOLTZMANN ascribes the same weight to each part of the μ-space

$$G(q, p) = constant$$

By the hypothesis of PLANCK's energy-steps and its generalizations this no longer holds, for here a weight

$$G(q, p, a)$$

dependent on q, p, and a we may say to be introduced. In other words to all regions of the μ-space the weight zero is ascribed, except to the discontinuously spread "admissible" regions, the situation of which is defined by the value of the parameters a. Here especially this last circumstance is of importance.

The problem may be formulated in the following way: How must we confine the choice of the weight function $G(q,p,a)$—how that of the "admissible" regions especially with regard to their dependency on the a's—in order that BOLTZMANN's equation (26) remains valid?

This question has been treated by the author, first in a special case [3]), afterwards generally [4]).

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[1]) A. SOMMERFELD l. c. p. 499

[2]) Comp P. EHRENFEST. Zum BOLTZMANN'schen Entropie-Wahrsch. Theorem. Phys. Zschr. **15** 1914 p. 657.

[3]) Comm. A (1911) § 5.

[4]) Comm. D (1914).

For molecules with one degree of liberty (harmonically and non-harmonically vibrating resonators) the question could be treated completely. The result[1]) that was found can be formulated in the terminology of this paper as follows:

For an ensemble of such molecules (resonators) BOLTZMANN's *relation between entropy and probability will exist then and only then when the steady motions are characterised by the condition*:

$$\frac{\overline{2T}}{\nu} = \iint dq\,dp = \text{constant numerical values } \Omega_1, \Omega_2, \ldots \quad (29)$$

which condition is invariant with respect to adiabatic changes[2]).

PLANCK's hypothesis of the energy-steps and DEBIJE's quantum hypothesis for resonators which do not vibrate harmonically fulfil this condition $\Omega_1, \Omega_2, \ldots$ being here equal to $0, h, 2h, \ldots$

It is however still doubtful whether for molecules with *more than one* degree of liberty the above given necessary and sufficient connexion remains valid between the adiabatic hypothesis on one hand and BOLTZMANN's relation between entropy and probability on the other hand.

Remarks A. Of late it has become usage to introduce the relation between probability and entropy (or free energy).

$$S = k \log W \quad \ldots \ldots \ldots \quad (30)$$

$$F = E - Tk \log W \quad \ldots \ldots \ldots \quad (31)$$

simply as a *postulate*.

The problem discussed in this paragraph might seem to be rendered superfluous by this. The author has proved however that the question is only removed to another point[3]).

B.[4]) By a reversible adiabatic compression black radiation is converted into black radiation whether within the reflecting envelope a black grain is present as a katalysator or not. Analogously in a gas with molecules without dimensions and on which no forces are acting a distribution of velocities according to MAXWELL becomes one of MAXWELL whether during the reversible adiabatic compression

[1]) Comm. D § 7.

[2]) In this theory of radiation PLANCK first leaves the energy quanta undetermined. At a certain moment in order to *bring the obtained radiation formula in harmony with* WIEN's *law* he ascribes to them the value $h\nu$ (see PLANCK, Vorlesungen über Wärmestrahlung I, Aufl. 1906, p. 153, Gl. 226. Comp, also the other quanta hypotheses, l.c. § 6). This is the reason why the hypothesis of the energy steps is in harmony with the second law and with the adiabatic hypothesis).

[3]) l. c. Introduction.

[4]) See Communication C § 4

in a vessel with rough walls impacts between the molecules occur or not [1]).

Generalizing the question might be put as follows: Is in an ensemble of molecules one *most probable* state converted into an other *most probable* one, if the molecules are subjected to a reversible adiabatic change also when no mutual action exists between the molecules? In general this question must be *denied*. This is evident for the case that can be treated completely viz for that of molecules with *one* degree of liberty. The above mentioned supposition is only true, (but then always) when between the invariant for adiabatic processes and ε and a there exists a relation of the special form

$$\varepsilon = A(a)\frac{\overline{2T}}{\nu} + B(a) \qquad (32)$$

§ 9. *Difficulties which occur, if the adiabatic reversible change gives rise to a singular motion. Non-periodic motions.*

These difficulties are already met with at the adiabatic change of an oscillation into a uniform rotation (remark § 6). In somewhat different form they occur, when the vibrations in an *anisotropic* field of force are changed in an adiabatic reversible way into those of an *isotropic* field [2]). Let the mass of the moving point be *one*, the potential energy of the field of force

$$\Phi = \tfrac{1}{2}(\nu_1^2\xi_1^2 + \nu_2^2\xi_2^2)$$

For the case of isotropy

$$\nu_1 = \nu_2 = \nu \qquad (33)$$

SOMMERFELD's way of introducing the quanta may be characterized as follows [3]):

Only those motions are admissible, for which the moment of momentum $mr^2\dot{\varphi}$ and the total energy satisfy the equations:

$$2\pi mr^2\dot{\varphi} = nh \qquad (33a)$$

$$\frac{\varepsilon}{\nu} = (n+n')h \qquad (34)$$

(n and n' are arbitrary whole numbers).

---

1) The two mentioned cases have this in common, that the pressure depends only on the total energy of the system and not on the distribution over the different principal vibrations (molecules).

2) Already in 1912 in a paper "On energy elements" (Versl. Kon. Akad. 1912, Dl. XX p. 1103), H. A. LORENTZ drew the attention to the fact that in the quantum theory difficulties arise for isotropic resonators with two or three degreesof liberty.

3) Comp Appendix. II.

In the case of *anisotropy* on the other hand PLANCK's hypothesis of the energy steps is usually applied to each of the principal vibrations separately:

Only those motions are steady for which the energy belonging to the two principal vibrations (ε_1 and ε_2) satisfies the equations:

$$\frac{\varepsilon_1}{\nu_1} = n_1 h \quad , \quad \frac{\varepsilon_2}{\nu_2} = n_2 h \quad . \quad . \quad \quad . \quad . \quad . \quad (35)$$

Let ν_1 and ν_2 approach infinitely slowly to the common value ν, then the quotients (35), being adiabatic invariants, remain constant and the total energy ε of the system satisfies finally the equation:

$$\frac{\varepsilon}{\nu} = (n_1 + n_2) h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

which is in good agreement with (34). [1])

On the other hand it is not evident, why in this way only one of the discrete values (33) for the moment of momentum would be obtained.

When ν_2 and ν_1 have already become nearly equal to each other the motion takes place in a figure of LISSAJOUS, which "densely" covers a rectangle, (with sides parallel to the axes ξ_3 and ξ_4 proportional to $\sqrt{\varepsilon_2}$ and $\sqrt{\varepsilon_1}$).

During this motion the moment of momentum does not remain constant but oscillates slowly to and fro between zero (at the moments when the motion takes place nearly exactly along the diagonals of the rectangle) and certain maximal positive and negative limits [2]) (at those moments in which the motion takes place on the largest ellipse described in the rectangle).

The more ν_1 and ν_2 approach to each other, the slower these oscillations of the moment of momentum are. Which value of the moment of momentum is reached after an infinitely slow adiabatic change in the case of *isotropy* depends therefore on a double boundary passage.

It is thus evident, that the adiabatic hypothesis needs a special completion to render the result in this case (and in analogous cases of the passage of singular motions) quite definite. It is to be hoped that a plausible completion will be found, which leads us to SOMMERFELD's values (33) of the moment of momentum.

As we can pass adiabatically from the elastic central force to each arbitrary central force (comp. § 7), the quanta might be

[1]) [Remark at the correction]. P. EPSTEIN drew my attention to the fact, that there is no good agreement between (36) and (34), for the circular motion n' must be equal to 0, n arbitrary; in (36) however $n_1 = n_2$, therefore $n_1 + n_2$ even.

[2]) $\pm\ 2 \sqrt{n_1 n_2}\ h$.

introduced for arbitrary central forces, starting from the hypothesis of the energy steps for harmonic vibrations.

Here we must also mention the difficulties which we meet when we want to apply the notion: reversible adiabatic change, adiabatic invariant etc. to an ensemble of non-periodic motions, as e.g. the *hyperbolic* motions of a point under the influence of a force of NEWTON or COULOMB: here too the change of the energy and the moment of momentum depend on a double boundary passage on the course of the complete motion from $t = -\infty$ to $t = +\infty$ and on the infinitely slow adiabatic change.

§ 10. *Conclusion.* The purpose of this paper was to show, that the adiabatic hypothesis and the notion of the adiabatic invariants are important for the generalization of the quantum theory to an always increasing number of classes of motion (§§ 6, 7); further they throw some new light on the question, for which conditions BOLTZMANN's relation between entropy and probability remains valid (§ 8). The analyzation of the difficulties occurring at the passage of singular motions will perhaps lead to a completion of the adiabatic hypothesis. But at any rate I believe that in view of WIEN's law it must be given in the quantum theory a special place to the reversible adiabatic processes.

APPENDIX I.

Proof, that $\frac{2\bar{T}}{\nu}$ is an adiabatic invariant for a system with periodic motions.

Let

$$L = T(q, \dot{q}, a) - \Phi(q, a)$$

be the function of LAGRANGE of the system (the motions of which are for the moment not yet supposed to be periodic). And let us consider two infinitely near systems, for which the parameters have the values: $a_1, a_2, \ldots$ and $a_1 + \Delta a_1, a_2 + \Delta a_2, \ldots$ [1]), further the moments t_A, t_B and $t_A + \Delta t_A$, $t_B + \Delta t_B$. We shall consider:

I a continuous passage of the system from the configuration $q_{1A} \ldots q_{nA}$ at the time t_A to the configuration $q_{1B} \ldots q_{nB}$ at the time t_B with the values of the parameters a (change I).

II a continuous passage of the system from the configuration $q_{1A} + \Delta q_{1A} \ldots$ at the time $t_A + \Delta t_A$ into the configuration $q_{1B} +$

[1]) For the sake of implicity we shall further use only one parameter. It is easily seen that at each point of the discussion we can return to the case of more parameters.

$+ \Delta q_{1B} \ldots$ at the time $t_B + \Delta t_A$ with the values of the parameters $a + \Delta a$ (change II).

For both changes we take the integral $\int_A^B dtL$ and calculate the difference between the two values. By taking apart what remains at the beginning and at the end of the integration period we first obtain

$$\Delta \int_{t_A}^{t_B} dtL = L_B \Delta t_B - L_A \, \Delta t_A + \int_{t_A}^{t_B} dt \, \delta L \quad . \quad . \quad . \quad . \qquad (a)$$

where δL is the difference between the values of L for two simultaneous phases of the motions viz.

$$\delta L = \sum_1^n \frac{\partial L}{\partial q_h} \delta q_h + \sum_1^n \frac{\partial L}{\partial \dot{q}_h} \delta \dot{q}_h + \frac{\partial L}{\partial a} \Delta a \quad . \quad . \quad . \quad . \qquad (b)$$

where δq_h, $\delta \dot{q}_h$ are again differences for simultaneous phases. Therefore

$$\delta \dot{q} = \frac{d}{dt} (\delta q) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (c)$$

By partial integration of the integral in (a) we obtain therefore:

$$\Delta \int_{t_A}^{t_B} dtL = (L_B \, \Delta t_B - L_A \, \Delta t_A) +$$

$$+ \sum_1^n \left(\frac{\partial L}{\partial \dot{q}_h}\right)_B \delta q_{Bh} - \sum_1^n \left(\frac{\partial L}{\partial \dot{q}_h}\right)_A \delta q_{hA} +$$

$$+ \int_{t_A}^{t_B} dt \sum_1^n \delta q_h \left\{ \frac{\partial L}{\partial q_h} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_h}\right) \right\} +$$

$$+ \Delta \, a \int_{t_A}^{t_B} dt \frac{\partial L}{\partial a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (d)$$

As however δ refers to simultaneous, Δ to non-simultaneous phases we have:

$$\left. \begin{aligned} \delta q_{hA} &= \Delta q_{hA} - \dot{q}_{hA} \, \Delta t_A \\ \delta q_{hB} &= \Delta q_{hB} - \dot{q}_{hB} \, \Delta t_B \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (e)$$

Further:

$$\frac{\partial L}{\partial \dot{q}_h} = \frac{\partial T}{\partial \dot{q}_h} = p_h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (f)$$

So that we obtain:

$$\Delta \int_{t_A}^{t_B} dt\, L = \left(\Delta t \left\{ L - \sum_1^n p_h \dot{q}_h \right\}\right)_A^B +$$

$$+ \left(\sum_1^n p_h \Delta q_h\right)_A^B +$$

$$+ \int_{t_A}^{t_B} dt \sum^n \delta q_h \left\{ \frac{\partial L}{\partial q_h} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_h}\right) \right\} +$$

$$+ \Delta a \int_{t_A}^{t_B} dt \frac{\partial L}{\partial a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (g)$$

Supposition A. The change I is a mechanical motion belonging to the values of the parameters (a). Therefore:

$$\frac{\partial L}{\partial q_h} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_h}\right) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (h)$$

so that

$$+ \frac{\partial L}{\partial a} = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

where $(-A)$ is the external force, which at every moment must act on the system according to the parameter a, in order that a remains constant. Then also the total energy of the system

$$L - \Sigma p_h \dot{q}_h = T - \Phi - 2T = -E. \quad . \quad . \quad . \quad . \quad (j)$$

remains constant during the motion (a is kept constant, so that during the motion no work is done on the system!) We thus obtain

$$\left.\begin{aligned} \Delta \int_{t_A}^{t_B} dt\, (T - \Phi) = - E\,.\,\Delta(t_B - t_A) + (t_B - t_A)\,\bar{A}\,\Delta a \\ + \sum_1^n p_{hB}\, \Delta q_B - \sum_1^n p_{hA}\, \Delta q_{hA}, \end{aligned}\right\} \quad . \quad (k)$$

where $\bar{A}$ is the mean with respect to the time of the force A for the interval t_A, t_B.

Supposition B. The change II is also a mechanical motion and belongs to the parameter values $a + \Delta a$. Then $T + \Phi = E$ has also for this second motion a value $E + \Delta E$, which does not change with the time. Therefore

$$\Delta \int_{t_A}^{t_B} dt\,(T + \Phi) = \Delta\{E\,(t_B - t_A)\} = (t_B - t_A)\,\Delta E + E\Delta\,(t_B - t_A) \quad (l)$$

Adding (l) to (k) we obtain

$$\Delta \int_{t_A}^{t_B} dt \,.\, 2T = (t_B - t_A)\,[\Delta E + \overline{A}\Delta a] + \Sigma p_{hB} \Delta q_{hB} - \Sigma p_{hA} \Delta q_{hA} \quad . \; (m)$$

Supposition C. Let both motions be periodic (periods P and $P + \Delta P$). Let us now take for both motions the time integral over their period. Now

$$p_{hB} = p_{hA}, \quad \text{further} \quad q_{hB} = q_{hA}$$

and

$$q_{hB} + \Delta q_{hP} = q_{hA} + \Delta q_{hA}$$

so that the two last terms of the right hand side of (m) neutralize each other. We thus find:

$$\Delta \int_{t_A}^{t_B} dt\, 2T = P\,[\Delta E + \overline{A}\,\Delta a\,], \quad . \; . \; . \; . \; . \quad (n)$$

Supposition D. The motions I and II can be adiabatically changed into each other. The adiabatic change {I, II} lasts a time rather long compared with P and $P + \Delta P$. Only during this time the parameter a changes (from a to $a + \Delta a$). At the same time the system does the work

$$\overline{A}\,\Delta a$$

on the outer force. This is just the difference between the energies of the motions II and I, the latter being the larger of the two.

$$\Delta E = -\overline{A}\,\Delta a \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (p)$$

Therefore

$$\Delta' \int_0^P dt \,.\, 2T = 0 \quad . \; . \; . \; . \; . \; . \; . \quad (q)$$

The symbol Δ' will remind us, that we have not to do with an arbitrary variation, but that just two adiabatically related motions are compared. This is the proof of equation (3) in § 5.

Remarks: A: Equation (n) has been deduced already by BOLTZMANN and CLAUSIUS, when they tried to deduce the entropy law purely mechanically without using statistical methods [1]).

They do not confine themselves to adiabatic influences and consider therefore the quantity:

$$\Delta E + \overline{A}\Delta a = \Delta Q \quad . \; . \; . \; . \; . \; . \; . \; . \quad (r)$$

[1]) L. BOLTZMANN. Wien. Ak. **53** (1866) p. 195 [= Abh. Bd. I N⁰. 2]; Pogg. Ann. **143** (1871) p 211 [= Abh. I N⁰. 17]; Vorles. Princ. d.Mech. Bd. II. p. 181. R. CLAUSIUS Pogg. Ann. **142** (1870) p. 433.

as the added heat. Then equation (n) becomes:

$$P\Delta Q = 2\Delta(P\overline{T}) \quad \ldots \ldots \ldots \quad (s)$$

or

$$\frac{\Delta Q}{T} = \Delta \log (P\overline{T})^2 \quad \ldots \ldots \ldots \quad (t)$$

This equation is then compared with the entropy law.

B. BOLTZMANN has further investigated, whether it is possible to alter the above considerations, referring to systems with periodic motions, in such a way that they may be applied to systems with quasi-periodic motions e.g. to the motion of a point in a rosette under the influence of a centre of force [1]).

Now the terms $\Sigma p_h \Delta q_h$ in equation (n) give rise to difficulties. These terms do not vanish now, neither by an integration from one perihelium to another, nor for one on a complete rotation ($\varphi = 0$ to $\varphi = 2\pi$). Therefore BOLTZMANN has still tried the following: On both paths he chooses such stretches that these terms vanish and speaks then of "orthogonal" variations of the end configurations A and B. If however we pass from a motion I through different intermediate motions to a finitely different motion (N), going back again to (I) through other intermediate motions, then the succeeding "orthogonal" variations finally give other end configurations A and B for the motion than those from which we started (BOLTZMANN has illustrated this with examples).

From this BOLTZMANN concluded that the second law would have to be derived not by means of pure mechanics, but only by statistic mechanics. Proceeding as in § 7 it is however possible to indicate adiabatic invariants also for such a case.

APPENDIX II.

Motions in an isotropic elastic field of force according to the quantum hypothesis of SOMMERFELD. *Comparison with* PLANCK'S *formulae.*

Let us put:

$$\left.\begin{array}{ll} \varphi = q\,, & r = q' \\ mr^2\dot{q} = p\,, & m\dot{r} = p' \end{array}\right\} \quad \ldots \ldots \quad (a)$$

Then according to SOMMERFELD:

$$\iint dq\, dp = nh \quad \ldots \quad (b) \qquad\qquad \iint dq'\, dp' = n'h \quad \ldots \quad (c)$$

Now we have however:

[1]) L. BOLTZMANN. Bemerk. über einige Probleme der mechan. Wärmetheorie Cap. III. (Wien. Ak. **75** (1877) p. 62—100 = Abh. II. p. 122); Vorles über Princ. d. Mech. Bd II. p. 156.

"separation of the variables" for the quantization of the motions of more degrees of liberty. Therefore the question may be put: In how far are the additional parts, with which P. EPSTEIN and also P. DEBIJE [Gött. Nachr. 1916] form the action integral adiabatic invariants? In SOMMERFELD's case they are still invariant, as shown in § 7.