Excerpted from: L. Brillouin, *La théorie des quanta et l'atome de Bohr*, Blanchard, Paris, 1922.

CHAPTER VII

BOLTZMANN'S FORMULA AND ADIABATIC INVARIANTS

1. Thermodynamics of periodic systems. – I already had occasion to appeal to an important formula that is due to Boltzmann at the end of the second chapter. It was concerned with the thermodynamical properties of periodic systems. The arguments on that subject are very old, since they go back to Clausius and Szily (1871-1872) ([1]) and the first theoretical discussions of Carnot's principle. Those remarks are often not very well known. One finds that quantum theory has returned those already-old ideas to the forefront. The proof was given in a very general form by Boltzmann ([2]). One also knows of numerous works by Helmholtz on that subject, which are works that Poincaré summarized remarkably and discussed in the last chapter of his course on thermodynamics.

It was Ehrenfest who recalled the importance of those ideas from the quantum viewpoint. He showed that Wien's law is attached to the general ideas that were developed by Boltzmann and Helmholtz. He then showed that the quantization conditions for orbits according to the Bohr-Sommerfeld rules (Chap. III) satisfy some important properties of adiabatic invariance. That question then became the object of numerous works, such as those of Burgers, Bohr, Kramers, etc. ([3]).

I cannot summarize the general proofs here, which are very delicate and appeal directly to the fundamental principles of classical mechanics. Boltzmann established his argument on the principle of least action, which I intend to discuss in detail in a different place. Here, I will content myself to presenting the general ideas, and above all, to

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([1]) CLAUSIUS, Ann. Phys. (Leipzig) **142-144** (1871); **146** (1872); **150** (1873); analysis in J. de Phys. **1** (1872), pp. 72; **2** (1873), pp. 108.
SZILY, Ann. Phys. (Leipzig) **145** (1872), analysis in J. de Phys. **1** (1872), pp. 339.

([2]) BOLTZMANN, *Prinzipe der Mechanik*, J.-A. Barth, Leipzig, 1897.
P. EHRENFEST, Ann. Phys. (Leipzig) **36** (1911), pp. 91; **51** (1916), pp. 346; Proc. Amst. **19** (1917), pp. 576.
L. BRILLOUIN, *Thesis*, Ann. Ec. Norm. Sup., Sec. III, **37** (1920), pp. 364.

([3]) N. BOHR, *Abhandlungen über Atombau*, Vieweg, Braunschweig, 1921; Zeit. Phys. **2** (1920), pp. 423; Fysisk. Tideskrift **19** (1922), fasc. 4-6; Zeit. Phys. **9** (1922), 1-67.
J. H. BURGERS, Proc. Amst. **20**(1918), pp. 149, 158, and 163; Ann. Phys. (Leipzig) **52** (1917), pp. 195.
G. KRUTKOW, Proc. Amst. **21** (1919), pp. 1112; **23** (1921), pp. 826.
H. A. KRAMERS, *Thesis*, Comptes rendus Acad. Sc. Copenhagen, *loc. cit.*; Zeit. Phys. **3** (1920), pp. 199.
A. SOMMERFELD, *Atombau und Spektrallinien*, 3rd ed., Vieweg, Braunschweig, 1922, pp. 374 and pp. 718.

presenting a large number of examples. That will permit us to specify the hypotheses that are made in a useful way, along with the conventions that one must assume. We shall also see that Boltzmann's formula is rich in consequences, and the important role that it plays in the study of a multitude of problems in mechanics or electromagnetism.

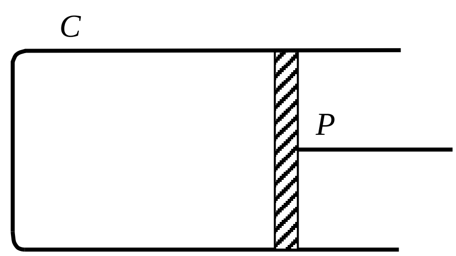

Figure 33.

2. Conventions. Heat and work. – On the basis of Boltzmann's arguments, one will find a convention that plays an important role. It is the distinction between the quantities of heat and mechanical work. That distinction is introduced here in a form that is very close to the one that we have specified already in the preceding chapter in the context of the statistical interpretation of thermodynamics. The guiding idea is the same in the two cases: One represents heat as the disorganized energy, which our methods do not permit us to summarize directly in the form of useful work. A classical example will make the distinct more precise: Consider a gas that is contained in a cylinder that is closed by a piston. We think of that gas as being composed of a very large number of molecules that are animated with large velocities of agitation. Those molecules collide with each other and can strike the walls of the cylinder or piston. We do not seek to pursue the laws of motion in detail, but to deduce certain mean properties that are of interest to us. What means of action do we have to modify the state of the gas?

We can heat the wall, which will transmit energy to the molecules at the moment of impact, and the agitation will increase little-by-little. In truth, only the usual mechanical forces enter here: Heating the wall will communicate a supplementary vibratory energy to it. When the gas molecules collide with the wall in a state of vibration, they will, in the mean, rebound with an accrued kinetic energy, and that is the mechanism of the heating of the gas.

However, even though that process is entirely mechanical, one must nonetheless appeal to very rapid vibrations or oscillations, which are distinguished by their *high frequency*. The changes in energy of the type that we just described are classified by the name of *heat*.

That character will be recovered in the various examples that we shall give later on. One can further note that the forces of heat define an extremely complex system of forces that is specially adapted to the mechanical system in question. In addition, they are forces that are not derived from a potential.

The *mechanical work* that is done under a thermodynamic transformation presents a completely different character: First of all, one must include only continuous forces, and even constant forces that are independent of time, very often. In the preceding example, one considers the mechanical work to be the work that is done by the slow displacement of the piston. The molecules that strike the piston exert a certain *mean force*. If the displacement of the piston is performed at constant velocity then only that mean pressure will be significant and it will provide a certain mechanical work. The work done will have a different value if the displacement of the piston is subject to rapid variations, with a frequency that has the same order as the interval of molecular collisions. One must also specify that *the velocity of the piston is constant and very small*.

These remarks suggest a precise definition: Consider an arbitrary mechanical model. It is subject to a certain number of *constraints* that signify that certain parameters ξ_1, ξ_2, …, ξ_n remain constant during all of the motion of the system.

From the physical viewpoint, we must suppose that a system of exterior forces:

$$\Xi_1, \Xi_2, \ldots, \Xi_n$$

is applied to the system and that it equilibrates the reactions that our system exerts on the constraints at each instant.

This mechanical model of motion represents a certain *thermodynamic state* for us. The motion concerns all of the microscopic coordinates of the system, but they are inaccessible to our means of observation. The only quantities that we can measure are the macroscopic variables, which correspond to the constraints $\xi_1, \xi_2, \ldots, \xi_n$.

Recall the example of a gas that is enclosed in a cylinder, so the microscopic variables will be the coordinates of all the molecules. Those molecules are constrained to remain insider the cylinder; that constitutes the mechanical constraint that is imposed. The motion of the molecules in the cylinder defines the initial thermodynamic state.

I then make one of the constraints $\xi_1, \ldots, \xi_n$ vary slowly, while allowing the motion to continue. It no other modification is made to the system then I will say that I have performed an *adiabatic transformation*. That is what I do when I slowly displace the piston in the cylinder, while being careful that no foreign force (viz., heat) acts on the gas through the wall.

During the variation of the constraints, I will do a certain amount of work:

$$d\mathcal{T} = -\Xi_1\, d\xi_1 - \Xi_2\, d\xi_2 \ldots - \Xi_n\, d\xi_n . \tag{1}$$

That represents the *mechanical work* that was done on the system during the adiabatic transformation.

That convention is fundamental for the comprehension of Boltzmann's formula. It will suffice to give the proof that the author gave.

It is quite obvious that when that distinction between work and heat is applied to ordinary mechanical systems, it will seem very artificial. For the mechanical models that present themselves in thermodynamics, the classification of forces into one category or the other can be done with no hesitation.

In all cases, the definition of an adiabatic invariant is very clear: It is the infinitely-slow variation at constant (or very slowly-varying) velocity of the parameters that define the constraints. The *slowness* of the modification must be such that the phenomenon is reversible. That signifies that in the varied equations of motion, one must neglect the velocities $\dot{\xi}_1$, $\dot{\xi}_2$, … , $\dot{\xi}_n$, which one supposes to be constant or slowly-variable and infinitely-small in comparison to the velocities of the microscopic coordinates of the system.

Under a non-adiabatic modification, there will be a simultaneous variation of the constraints and an action of the forces of heat. If the variation of the constraints is slow then one can write that the variation of the internal energy of the system is:

$$dE = dQ - d\mathcal{T}. \tag{2}$$

3. Boltzmann's formula. – *For a periodic system that obeys classical mechanics,* if the preceding conventions have been specified clearly then Boltzmann's formula will give the heat provided dQ under the transformation of a periodic system:

$$dQ = \frac{2}{\tau} d\,(\tau \bar{E}_{kin}). \tag{3}$$

In that formula, τ represents the period of the system and $\bar{E}_{kin}$ represents its mean kinetic energy, which is defined by the relation:

$$\tau \bar{E}_{kin} = \int E_{kin}\,dt\,, \tag{4}$$

where the integral on the right-hand side is taken over a duration of τ.

We write that the heat provided under an adiabatic transformation is zero, which immediately gives us the condition:

$$\tau \bar{E}_{kin} = \text{const.} \tag{5}$$

The expression $\tau \bar{E}_{kin}$ then represents an *adiabatic invariant.*

The preceding formulas are valid for a holonomic system that obeys the laws of *classical mechanics* and executes a perfectly arbitrary periodic motion. One must further specify that the mechanical system considered must be subject to only *constraints that are independent of time* in its normal state.

For systems that include constraints that are functions of time or the ones that obey relativistic mechanics, the statements will take on a slightly more complicated aspect, which we shall point out a bit later.

Among the mechanical systems of that type, there exists an important category for which the formula simplifies. They are the *purely-sinusoidal oscillatory motions,* for which one has:

$$\bar{E}_{kin} = \bar{E}_{pot} = \tfrac{1}{2} E\,. \tag{6}$$

The mean kinetic energy and the mean potential are equal to each other and to one-half the total energy E. Boltzmann's formula will then reduce to:

(7)
$$dQ = \frac{d(\tau E)}{\tau}.$$

In order to modify the motion of the system without changing the period, one must provide a quantity of heat:

$$dQ = dE.$$

When an adiabatic transformation does not modify the period τ, the system will exert no force on the corresponding constraint. However, if the adiabatic deformation varies the period τ then it will be easy to calculate the mean force that is exerted by the vibrating system on the corresponding constraint parameter.

Indeed, in that case, the adiabatic invariant is written:

(8)
$$2\tau \bar{E}_{kin} = \tau E = \text{const.}$$

At the time of the modification, one will then have:

(9)
$$\frac{d\,\tau E}{\tau E} = 0, \qquad \frac{d\tau}{\tau} + \frac{dE}{E} = 0.$$

However, the variation dE of the internal energy of the system is due to only the mechanical work that is done on the constraint forces, which will give us:

(9 *cont.*)
$$d\,\mathcal{T} = -\,dE = E\,\frac{d\tau}{\tau}.$$

That expression will permit one to easily calculate all of the mean forces that are exerted by vibrating systems on their constraints. For example, one has the radiation pressures of elastic or electromagnetic waves.

We shall see how these various formulas are verified in some examples.

4. Variable-length pendulum. – In the usual mechanical models that I will take for my first examples, the distinction between "heat energy" and "mechanical work" can seem a bit arbitrary. Those terms are not directly suitable to those examples. The study of those simple problems will nonetheless permit us to make the ideas more precise and to know clearly the meaning of adiabatic transformations.

Consider a pendulum that consists of a string that goes through a fixed ring O and carries a mass of m.

The position of the ring constitutes a constraint. We shall vary it by slowly displacing that ring up and down, which will modify the length l of the pendulum. The period of the pendulum is:

(10)
$$\tau = 2\pi\sqrt{\frac{l}{g}}.$$

The force that acts upon the ring can be easily calculated here. Indeed, the tension in the string is:

$$T = mg \cos \theta.$$

Upon composing the two equal tensions T that nonetheless have different directions and act on the ring, one will see that what remains is a vertical component:

$$Z = T (1 - \cos \theta)$$

and a lateral component:

$$X = T \sin \theta.$$

We shall suppose that the ring is kept in a vertical slide whose reactions will equilibrate the force X. The latter is zero in the mean, moreover. On the contrary, for small angles θ, the vertical force will have the mean value:

$$Z = \overline{T(1-\cos\theta)} = T\,\overline{\frac{\theta^2}{2}} = mg\;\overline{\cos\theta}\;\overline{\frac{\theta^2}{2}}.$$

Our oscillations are supposed to have small amplitudes, so we take the value 1 for $\cos \theta$, and the value $\alpha^2 / 4$ for $\theta^2 / 2$, in which α represents the maximum angle between the pendulum and the vertical.

However, one gets, on the one hand, the energy of vibration from the expression:

$$E = mgl\,\frac{\alpha^2}{4},$$

which will permit us to write:

$$\bar{Z} = \frac{1}{2}\frac{E}{l}. \tag{11}$$

When we slowly displace the ring up and down, we will do an amount of work:

$$d\mathcal{T} = \bar{Z}\,dl = \frac{1}{2}\frac{E}{l}dl.$$

That work $d\mathcal{T}$ will be borrowed from the energy of vibration of the pendulum, and one will have:

$$-\frac{dE}{E} = \frac{d\mathcal{T}}{E} = \frac{1}{2}\frac{dl}{l}.$$

The simultaneous variation of the period of oscillation is:

$$\frac{d\tau}{\tau} = \frac{1}{2}\frac{dl}{l},$$

and one will immediately verify the relation:

$$\frac{dE}{E} + \frac{d\tau}{\tau} = 0, \tag{12}$$

$$\tau E = \text{const.}$$

We then recover the invariance of the quantity τE under an adiabatic transformation directly in this particular case. In fact, that is what made us predict Boltzmann's formulas [viz., formulas (8) and (9)].

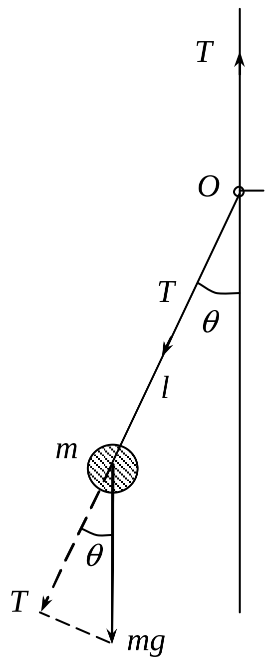

Figure 34.

The variation of the constraint was supposed to be infinitely slow, which signifies that during a period of oscillation τ, the ring will displace only by an infinitely-small quantity. A rapid displacement of the ring will lead to some completely different laws. For example, if I displace the ring briefly by a finite quantity then at the moment when the pendulum passes through the vertical, I will realize the passage from a pendulum length of l_1 to another length l_2 without doing any work.

It is no less important for one to perform the displacement with a constant or slowly-varying velocity. A displacement by fits and starts with period that is close to two times the period τ of oscillation will give entirely anomalous results ([1]).

Any force that acts on the pendulum and is capable of modifying the amplitude of the oscillations (while the ring is fixed) will be called a "force of heat." They will be forces that alternate with the same period as the pendulum, the impacts, etc.

([1]) That anomaly amounts to the fact that the component Z submits to variations of frequency 2τ around its mean value. One will see this easily in the formulas of the preceding page.

We can account for part of the oscillatory energy of the pendulum in the form of mechanical work under an adiabatic transformation. Upon slowly withdrawing the ring out to a infinite distance, we can then extract all of the energy in the system, while the mass *m* finally remains at rest. That is completely analogous to the adiabatic dilatation of a gas. Upon withdrawing the piston indefinitely, we will account all of the caloric energy of the gas. Its temperature will go down progressively and it will conclude by attaining a state of complete rest (viz., absolute zero) after having given up all of its energy of agitation in the form of work.

5. Vibrating string. – The tensed string that executes transverse vibration provides us with a model that is quite analogous to the preceding one.

The string is attached to a fixed point *P* and passes through a ring *O*. We suppose that the ring is capable of displacing in the longitudinal sense. Let l be the length of the vibrating string and let V be the speed of propagation of transverse waves along the string. One possible vibratory mode will consist of, for example, n extrema and $n - 1$ nodes between the extreme points *P* and *O*. The period τ of the vibrations will then be given by the relations:

$$l = n\frac{\lambda}{2}, \qquad \lambda = V\,\tau, \qquad \tau = \frac{2}{V}\frac{l}{n}. \tag{13}$$

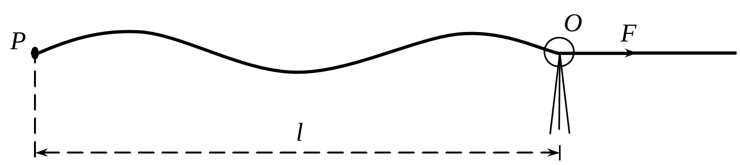

Figure 35.

Lord Rayleigh has calculated ([1]) the mean force F that is exerted by the vibration on the ring directly, and he found:

$$F = \frac{E}{l},$$

in which E represents the vibratory energy of the system. When we displace the ring *O* very slowly, we will produce an adiabatic deformation of the system. The work done $d\mathcal{T}$ is equal to the reduction $-dE$ in the internal energy and is written:

$$d\mathcal{T} = -dE = \frac{E}{l}\,dl,$$

and one will immediately verify the relations:

([1]) Lord Rayleigh, *Scientific Papers*, vol. **5**, pp. 41; pp. 262.

(14) $$-\frac{dE}{E} = \frac{d\tau}{\tau} = \frac{dl}{l},$$

$$E\ \tau = \text{const.}$$

The adiabatic invariance of the expression $\tau\ E$ is then verified effortlessly. The remarks that we made in regard to the pendulum apply immediately here.

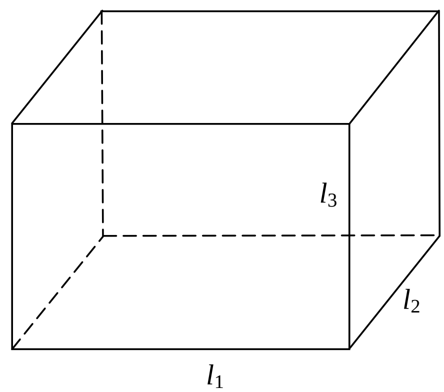

Figure 36.

6. Box that defines a resonant parallelepiped. – In Chapter II, we studied the modes of vibration of a box that is a rectangular parallelepiped with sides l_1, l_2, l_3 . We suppose that one wall is perfectly reflecting, while the side $x = l_1$ can slide like a piston. Since the equations are completely analogous to those of the preceding problem, I shall recall them briefly here. A mode of proper vibration that corresponds to:

n_1	extrema along the edge			l_1,
n_2	″	″	″	l_2,
n_3	″	″	″	l_3

will have a period of vibration:

$$\tau = \frac{2}{V}\sqrt{\left(\frac{l_1}{n_1}\right)^2 + \left(\frac{l_2}{n_2}\right)^2 + \left(\frac{l_3}{n_3}\right)^2}\ .$$

For an elongation dl_1 of the length l_1, the period will vary by $d\tau$:

(15) $$\frac{d\tau}{\tau} = \frac{1}{2}\frac{d\left[\left(\frac{l_1}{n_1}\right)^2 + \left(\frac{l_2}{n_2}\right)^2 + \left(\frac{l_3}{n_3}\right)^2\right]}{\left(\frac{l_1}{n_1}\right)^2 + \left(\frac{l_2}{n_2}\right)^2 + \left(\frac{l_3}{n_3}\right)^2} = \frac{\left(\frac{l_1}{n_1}\right)^2}{\left(\frac{l_1}{n_1}\right)^2 + \left(\frac{l_2}{n_2}\right)^2 + \left(\frac{l_3}{n_3}\right)^2}\frac{dl_1}{l_1}.$$

Lord Rayleigh calculated the radiation pressure that is exerted upon the reflecting piston by stationary waves. His calculations supposed implicitly that the speed V of the waves in the medium that fills up the enclosure is independent of the volume of the enclosure. That is what will be produced if we consider an empty enclosure with electromagnetic waves that propagate inside of it. The pressure on the piston will then be given by the formula:

$$p = \frac{E}{l_1 l_2 l_3}\cos^2\theta = \frac{E}{l_1 l_2 l_3}\frac{\left(\frac{l_1}{n_1}\right)^2}{\left(\frac{l_1}{n_1}\right)^2+\left(\frac{l_2}{n_2}\right)^2+\left(\frac{l_3}{n_3}\right)^2}.$$

θ is the angle of reflection of the wave from the mirror considered, so $\cos^2\theta$ will be expressed as a function of the direction parameters of the light ray ([1]).

If I now produce an adiabatic dilatation of the radiation while slowly displacing the piston whose surface is $l_2\, l_3$ then I will exert a certain amount of work $d\,\mathcal{T}$:

$$-\,dE = d\,\mathcal{T} = p\, l_2\, l_3\, dl_1 = E\,\frac{\left(\frac{l_1}{n_1}\right)^2}{\left(\frac{l_1}{n_1}\right)^2+\left(\frac{l_2}{n_2}\right)^2+\left(\frac{l_3}{n_3}\right)^2}\frac{dl_1}{l_1}. \tag{16}$$

If we compare this with formulas (15) and (16) then we will immediately deduce the adiabatic invariance of the expression τE :

$$\frac{d\tau}{\tau}\mp\frac{dE}{E} = 0, \quad \tau E = \text{const.}$$

Here, as in the preceding case, we appeal to Lord Rayleigh's formulas for radiation pressure. Furthermore, I shall point out the restriction one agrees to make in order to apply those results to the case of radiation. We can take the opposite route for other problems. We know that formulas (9) and (9 *cont.*) are valid for arbitrary sinusoidal vibratory systems, since they are attached directly to formula (3), for which Boltzmann gave an absolutely general proof.

For complex problems in which Lord Rayleigh's procedures lead to the evaluation of the radiation pressure quite laboriously, one will arrive at the result very quickly upon appealing to formulas (9) and (9 *cont.*).

That case will present itself when one supposes that the parallelepiped enclosure is filled with an arbitrary material medium. One must then take into account the variation of the density of the body when one produces a dilatation. On the other hand, the medium can be dispersive – i.e., waves propagate with different speeds for different

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([1]) For all of the details of the calculation, I shall refer to Chapter II and to Note II, in which this problem is treated more thoroughly.

frequencies. Since the dilatation modifies the frequency, one must take that effect into account in the calculations. On the other hand, I have shown (1) that one will thus arrive at the following formula:

$$p = \mathcal{E}\frac{U}{V}\left(\cos^2\theta + \frac{\partial \log V}{\partial \log d}\right), \tag{17}$$

in which:

$\mathcal{E}$	total energy density of the two incident and reflecting waves
θ	angle of incidence
V	phase velocity
U	group velocity
d	density of the medium

That formula applies with no modifications to arbitrary waves, such as longitudinal or transverse elastic waves, as well as electromagnetic waves.

Boltzmann's method then has value for the calculation of the mean forces that are exerted by vibrating systems and analogous calculations of radiation pressures.

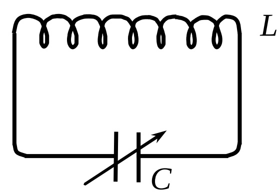

Figure 37.

7. Oscillating electric circuit. – The same results will be recovered effortlessly in an electric example. One knows, moreover, that electromagnetism satisfies the principle of least action, provided that one considers the electric energy to be "potential" and the magnetic energy to be "kinetic."

Consider an electric circuit that includes a self-induction L and a capacitor C. The resistance is assumed to be zero. The circuit is then capable of oscillating continually with a frequency of:

$$\tau = 2\pi\sqrt{LC}\,, \qquad \omega = \frac{2\pi}{\tau}. \tag{18}$$

If one calls the current I and the charge in the capacitor Q then I will have expressions of the form:

$$I = I_0 \cos \omega t, \quad Q = \frac{I_0}{\omega}\sin \omega t$$

for those two quantities.

The energy of the oscillations is:

(1) L. BRILLOUIN, *Thesis*, pp. 420, formula (27).

(19) $$E = \tfrac{1}{2} L I_0^2 = \frac{1}{2}\frac{I_0^2}{C\omega^2}.$$

I shall now impose an adiabatic transformation on the oscillating system. For example, I will slowly vary the value of the capacitance. I must then take into account the forces of attraction that are exerted on the two armatures of the condensor. Upon calling the coordinate that measures the displacement of the electrodes x, the force will have the expression:

(20) $$f = -\tfrac{1}{2} Q^2 \frac{d\left(\frac{1}{C}\right)}{dx}.$$

Indeed, one is dealing with *displacement with given charge*, and formula (20) will represent a classical result in that case ([1]). The mean value of the force can be written:

$$\overline{f} = -\tfrac{1}{2}\overline{Q^2}\frac{d\left(\frac{1}{C}\right)}{dx} = \frac{I_0^2}{4C^2\omega^2}\frac{dC}{dx} = \frac{E}{2C}\frac{dC}{dx}.$$

We will get the work done $d\mathcal{T}$ by that force or the corresponding variation dE of the oscillatory energy in the form:

$$-dE = d\mathcal{T} = \overline{f}\,dx = \frac{E}{2}\frac{dC}{C}.$$

If one takes into account the simultaneous variation of the period τ of oscillation:

$$\frac{d\tau}{\tau} = \frac{1}{2}\frac{dC}{C}$$

then one will see that one has the relation:

(21) $$\frac{d\tau}{\tau} + \frac{dE}{E} = 0, \qquad \tau E = \text{const.}$$

Here again, we recover the adiabatic invariance of the expression τE. I have supposed that the circuit is composed of a variable capacitance and a fixed self-inductance. One will recover exactly the same result if one fixes the capacitance and varies the self-inductance. In the latter case, the force will have the value:

$$\overline{f} = -\frac{1}{2}\overline{I^2}\frac{dL}{dx} = \frac{\overline{I_0^2}}{4}\frac{dL}{dx} = \frac{E}{2L}\frac{dL}{dx}.$$

([1]) Cf., e.g., BOUASSE, *Physique*, t. **3**, *Électricité et Magnétisme*, Chap. I, § **97**, pp. 95.

Under an adiabatic transformation that increases the period (viz., increases the capacitance or the self-inductance), one can assimilate all of the oscillatory energy of the circuit in the form of mechanical work.

8. Systems in rotation. – All of the examples that we just summarized refer to models that are capable of oscillating in accord with a purely-sinusoidal law. We have seen that Boltzmann's formula then yields the expression τE as an adiabatic invariant, and we could verify that property in our various problems. In the general case, the adiabatic invariant is $I = 2\tau \bar{E}_{kin}$; a new example might permit us to verify that point.

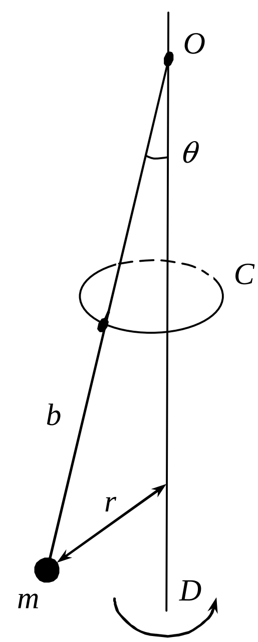

Figure 38

Consider a mass m that is carried by a rod of length l that articulates at the point O. That rod (without the mass) is constrained to slide without friction on a circle C that is normal to the line OD. I will suppose, first of all, that no external force field acts upon the mass m. It will turn around the axis OD with a rotational velocity of ω.

The potential energy is zero, and the kinetic energy is:

$$E_{kin} = \tfrac{1}{2} m r^2 \omega^2, \qquad r = l \sin \theta. \tag{22}$$

I can subject the system to an adiabatic transformation upon slowly displacing the circle C along the axis OD, which will make θ vary progressively. Since my rod is supported without friction on the circle C, I shall exert only central forces, and the area constant:

$$A = \tfrac{1}{2} r^2 \omega$$

will remain unchanged. However, the adiabatic invariant I that I indicated in Boltzmann's formula is nothing but:

$$I = 2\tau E_{kin} = 2\pi\, mr^2\, \omega = 4\tau\, m\, A, \qquad t = \frac{2\tau}{\omega}, \tag{23}$$

and I can indeed verify its constancy in the course of the transformation.

If I have a force field that acts upon the mass m then I must introduce the corresponding potential energy E_{pot} . The total energy $E_{kin} + E_{pot}$ will vary in an arbitrary manner under the adiabatic transformation, but the adiabatic invariant will be obtained, as always, from formula (23), in which only the kinetic energy appears, but not the total energy.

We can push the argument further in this simple example and verify Boltzmann's formula itself:

$$dQ = \frac{2}{\tau} d(\tau \bar{E}_{kin}) = \frac{2}{\tau} dI = \frac{\omega}{2\pi} dI. \tag{24}$$

What forces can be grouped under the term "heat"? They are periodic forces of the same period τ as our system. The central components of those forces (components along the radius) will have no effect here, since they are equilibrated by the reaction of the circle C. Only the components that are perpendicular to the radius will play any role. They will communicate an acceleration φ_θ to the mass m such that:

$$f = m\varphi_\theta = mr \frac{d\omega}{dt}.$$

The work done by the force f during a time dt is written:

$$f\, r\, \omega\, dt = mr^2\, \omega\, d\omega = \frac{\omega}{2\pi} dI. \tag{25}$$

The expressions (24) and (25) are indeed identical.

The work that is done by these particular forces, when specially adapted to our mechanical model, will then be predicted precisely by Boltzmann's formula, which we have been able to verify completely in this simple example.

These special cases have clearly permitted us to make the distinction between mechanical work and heat very precise and to show what an adiabatic transformation that is applied to a mechanical system would signify.

9. Extension of Boltzmann's formula. – Formula (3) can be put into a somewhat different form, which will permit us to extend its field of application considerably. One knows that in classical mechanics, the kinetic energy is a homogeneous function of second degree in the velocities. If $q_1, \ldots, q_m$ are the coordinates that serve to define the state of the system then the kinetic energy will have the form:

(26) $$E_{kin} = a_{11}\,\dot{q}_1^2 + a_{22}\,\dot{q}_2^2 + \cdots + a_{mm}\,\dot{q}_m^2 + 2a_{12}\,\dot{q}_1\,\dot{q}_2 + \cdots + 2a_{rm}\,\dot{q}_r\,\dot{q}_m\,.$$

The moments p are defined by the relations:

(27) $$p_1 = \frac{\partial E_{kin}}{\partial \dot{q}_1},\ \ldots,\ p_m = \frac{\partial E_{kin}}{\partial \dot{q}_m}.$$

The homogeneity of the expression (26) then permits one to easily verify the relation:

(28) $$2E_{kin} = p_1\,\dot{q}_1 + p_2\,\dot{q}_2 + \cdots + p_m\,\dot{q}_m\,.$$

That relation plays a fundamental role in the proof of some general theorems in mechanics.

Boltzmann's formula involves the kinetic energy by way of its mean over time. Upon making that precise, we will get:

(29) $$I = 2\tau\,\bar{E}_{kin} = 2\int_\tau E_{kin}\,dt = \int_\tau \sum_i p_i\,dq_i\,.$$

I is our adiabatic invariant, which is then found to be expressed as something that is equal to the sum of the integrals $\int p\,dq$, when each of them is taken over a duration that it equal to the period τ.

Boltzmann's formula is then written:

(30) $$dQ = \frac{1}{\tau}\,dI.$$

These expressions represent most precise form of our general results.

I will point out their interest forthwith. Formula (3) will cease to be true in problems that are more complex than the ones that we have envisioned. That situation will arise, for example, when we introduce relativistic mechanics and the variation of mass with the velocity. The kinetic energy will no longer be a quadratic form in the velocities (26), while at the same time formulas (27) will cease to be applicable. The moments p will be given by the partial derivatives of a new function, which will no longer be the kinetic energy. The relation (28) will also disappear. If we then repeat Boltzmann's proof step-by-step then we will find that one will arrive at the expressions (29) and (30) ([1]).

We shall then prefer to take the results in that form from now on.

([1]) The details of that proof, which I shall not give here, will be published moreover. That result has been assumed by various authors (Sommerfeld, Ehrenfest, Burgers), but it is not found explicitly in their work.

10. Quasi-periodic systems. – A new extension will give a statement that is valid for the most general mechanical systems with separable variables. We have already recalled some properties of those systems in Chapter III, and in particular, the following one: let $q_1, q_2, \ldots, q_m$ be the coordinates that permit the separation of variables to take place, each of which will correspond to a particular period $\tau_1, \tau_2, \ldots, \tau_m$. The global motion is not periodic, but one can (in an infinitude of ways) find *approximate periods t* such that one will have:

$$t = n_1\,\tau_1 + \varepsilon_1 = n_2\,\tau_2 + \varepsilon_2 = \ldots = n_m\,\tau_m + \varepsilon_m, \tag{31}$$

in which the $n_1, n_2, \ldots, n_m$ are integers, and the absolute values of the ε are less than an arbitrary quantity η that is given in advance. After a time τ, the mechanical system will return as close as one desires to its initial state, but it will never pass through that state again, rigorously speaking ([1]).

The existence of those approximate periods will suffice to prove Boltzmann. Suppose that we then introduce such a period τ into formula (30), along with the notations:

$$I_1 = \int_{\tau_1} p_1\,dq_1, \quad \ldots, \quad I_m = \int_{\tau_m} p_m\,dq_m. \tag{32}$$

The integral I of the formula (29) will take on the appearance of:

$$I = n_1\,I_1 + n_2\,I_2 + \ldots + n_m\,I_m + \zeta, \tag{33}$$

in which the quantity ζ is very small. Upon neglecting all correcting terms that were introduced by our approximate period, we will then find that:

$$\begin{aligned} dQ &= \frac{1}{n_1\,\tau_1}\,d\,(n_1\,I_1) + \ldots + \frac{1}{n_m\,\tau_m}\,d\,(n_m\,I_m) \\ &= \frac{1}{\tau_1}\,dI_1 + \ldots + \frac{1}{\tau_m}\,dI_m. \end{aligned} \tag{34}$$

This represents the most general form that we can give to our results ([2]).

([1]) ESCLANGON, *Thesis*, Paris, 1904.

BOHL, *Thesis*, Dorpat, 1893.

BOHL, "On certain differential equations of a general character…," Dorpat, 1900 (Russian); French transl. Soc. Math. (1913).

KRONECKER, "Näherungsweise ganzzahlige Auflösung linearer Gleichungen," *Werke*, v. 3, pp. 49.

H. POINCARÉ, "Les Méthodes nouvelle de la Mécanique céleste," Bulletin astronomique (1893).

I have J. Hadamard to thank for these references, since he presented this subject in his course at the Collège de France in 1912 (unpublished lecture notes). In regard to that, we cite the following papers:

J. HADAMARD, Bull. Sc. Math. **34** (1906); *ibid.*, **25**, pp. 7, and C. R. (8 January 1906).

([2]) For a variation $dI_1, \ldots, dI_m$ of the integral I, the variation of the internal energy dW is given by the relation (34):

$$dW = dQ = \frac{1}{\tau_1}\,dI_1 + \ldots + \frac{1}{\tau_m}\,dI_m.$$

But what does our adiabatic invariant become here? It seems that we can no longer give a precise definition. If we write $dQ = 0$ then that will give us a relation:

$$\frac{1}{\tau_1} dI_1 + \ldots + \frac{1}{\tau_m} dI_m = 0,$$

but nothing tells us *a priori* that the $dI_1, \ldots, dI_m$ must be separately zero.

However, we can guess what that case will be. From the invariance property of the I, a detailed study will permit us to give a rigorous proof. I shall not recall it here, and I will content myself to only explaining the result. From the physical viewpoint, we must establish a distinction between a transformation for which the total heat provided is zero and a truly adiabatic transformation, under which no quantity of heat is transmitted to any part of the system. The different variables $q_1, q_2, \ldots, q_m$ that define our motion are distinct and obey laws of evolution that are separate from each other. No constraint exists between them in our equations. To write $dQ = 0$ is to write that the sum of the quantities of heat that are provided to each degree of freedom is zero. However, an energy of $(1 / \tau_1)\, dI_1$ will be provided to the first coordinates q_1, and similarly for the other coordinates. That does not correspond to the very clear definition that we have given for an "adiabatic transformation." We shall reserve that name for a modification under which one is content to vary one of the constraints very slowly, and the system is assumed to be *completely isolated*. If the system is completely isolated then one must suppose that no quantity of heat is provided nor borrowed from any degree of freedom, and one can write:

$$dI_1 = 0, \quad \ldots, \quad dI_m = 0,$$
$$I_1 = \text{const.}, \quad \ldots, \quad I_m = \text{const.}$$

The $I_1, \ldots, I_m$ are then adiabatic invariants. They remain constant under any modification that does not involve the forces of "heat."

Our justification cannot take the form of a precise proof. However, it can be established without too much difficulty, and we will arrive at the result that we just pointed out precisely.

11. Adiabatic invariants and quantum conditions. – We have already seen some applications of adiabatic invariants and Boltzmann's formula. The proof of Wien's formula (Chap. II) is directly linked with those general ideas. The most important point, upon which I must insist, is that the quantum conditions are applied to quantities I that are adiabatic invariants. We have only to recall the various examples that we discussed

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This represents precisely the result that we utilized in Chapter V, § **5**, formula (11), in the context of Bohr's correspondence principle. We deduce the relations:

$$\frac{1}{\tau_i} = \frac{\partial W}{\partial I_i}$$

from it.

above one after the other in order to traverse the stages of development in quantum theory.

We have shown that for all systems that are capable of oscillating in accord with a purely-sinusoidal law, the quantity τE will be an adiabatic invariant, where E represents the total energy. That was the case for our examples in §§ **4** to **7**. Now, it was to such systems that Planck first applied the idea of quanta by writing that:

$$\tau E = \frac{E}{\nu} = nh, \qquad n \text{ integer.} \tag{35}$$

For these pure oscillators, the total energy will then be equal to an integer number times $h\nu$. (I pointed that out at the end of Chapter II.) It is important to know that this condition is invariant under an adiabatic transformation. Slowly modifying one of the parameters that define the oscillator will have the effect of changing its frequency ν, but if the energy has the value $nh\nu$ before the transformation then it will constantly keep that expression throughout all of the successive state of adiabatic evolution.

The example in paragraph **8** pertained to a system in rotation. We remarked that one no longer needed to introduce the total energy in order to get the adiabatic invariant, but only to take the kinetic energy. Furthermore, our invariant I will then be linked directly with the area constant A by:

$$I = 2\tau \bar{E}_{kin} = 4\pi mA. \tag{23}$$

After numerous attempts, it was exactly that expression that Bohr chose in order to apply the quantum conditions to it. In his first papers, which arrived at a remarkable interpretation of the Balmer series, Bohr supposed that the electrons gravitated around the central nucleus along circular orbits. After having tried to appeal to a relation $E = nh\nu$ that is analogous to that of Planck for the vibrator, he finally arrived at the condition:

$$4\tau mA = nh. \tag{36}$$

That is therefore yet another adiabatic invariant that one must set equal to n times the quantum h. If one can slowly vary the mass m, or rather the coefficient of the attractive force between the nucleus and the electron then one will provoke an adiabatic transformation that will modify the frequency of rotation and leave our quantum relation (36) invariant.

Finally, the last stage (§§ **9** and **10**) will permit us to find the adiabatic invariants for the very general problems that are solved by separation of variables. Those invariants are nothing but the integrals:

$$I_i = \int_{\tau_i} p_i \, dq_i = n_i h, \tag{37}$$

which are integrals to which Sommerfeld successfully applied the quantum conditions in the form (37). There is then a complete parallelism between the development of our arguments concerning adiabatic invariants and the natural evolution that quantum theory followed while its creators were guided by very different preoccupations.

That coincidence is not fortuitous. As Ehrenfest remarked, it seems indispensible that the quantum conditions must bear upon only adiabatic invariants. Indeed, what are our "quantized" motions? We have been led to attribute a very special property to them, namely, that they must persist indefinitely with neither emission not absorption of radiation. However, the radiation comes from heat, and we have insisted on several occasions upon the role of isothermal radiation as a fundamental thermostat. If perhaps by basing that upon the laws of thermal radiation (viz., black-body) that the notion of absolute temperature will become most accessible to us.

The quantized motion is then characterized by the fact that it will persist with no exchange of heat with the outside. Such a property has meaning only if it stays valid in the case where the motion is perturbed slightly by an arbitrary external force. We are then naturally led to consider all adiabatic transformations that are applicable to our mechanical model and to choose the expressions that remain invariant under all of those modification for the quantum conditions.

If our conditions do not pertain to invariants of that kind then any external action, however, miniscule, will suffice to perturb any motion and to require the system to radiate or absorb energy. We will then be led to utter nonsense.

12. Examples of adiabatic transformations that apply to the Bohr atom. – We can go back to the various types of quantized motions that we envisioned above from this viewpoint. In the absence of any perturbing cause, the electron that gravitates around the hydrogen nucleus will follow a Keplerian ellipse. If I progressively introduce a *magnetic field* then I will deform the orbit. The trajectory will cease to be a closed curve, but it will take the complex form that we have described; the quantum conditions will remain unchanged. If the motion was previously quantized then we will get the very complex manifestations of the Zeeman effect, which can be deduced directly from the various initial elliptic motions.

If we establish an *electric field*, instead of a magnetic field, then the deformations will be different; that is the case of the Stark effect. The introduction of *relativistic* terms will represent a third deformation that one can suppose to be truly adiabatic, and which will translate into a rotation of the perihelia of our ellipses.

In each of these three cases, we know how to solve the problem by separation of variables. That method will fail when two of those effects act simultaneously. One cannot presently solve the case of superimposed electric and magnetic fields, much less the effect of an electric field when one takes relativity into account ([1]). The method that one should employ in that case would be to take a well-defined Keplerian orbit and to follow its modifications when one progressively makes perturbing causes act upon it. Experiments show that one will always obtain a spectrum of sharp lines. There must then always exist well-defined energy levels; i.e., motions that are defined entirely by the quantum conditions.

([1]) Kramers attempted to treat these various problems in his recent works. However, he neglected to point out the details in his calculations, which does not seem to me to be safe from all criticism. The process of adiabatic invariants will certainly be a very reliable guide for attempts of that kind. [Zeit. Phys. **3** (1920), pp. 199]

That notion of adiabatic transformation plays a very important role in Bohr's recent work. That author sought to represent the logical structure of atoms and to comment on the continuity of the evolution of the atomic structure when it follows Mendele'ev's table. He then represented a (fictitious) nucleus whose electric charge one can change in a continuous manner. Whenever that charge increased by one unit, a new electron could be added to the ones that were found around the nucleus already ([1]).

That hypothesis for continuous formation seems to provide a precious guide for that study. In any case, it permits one to eliminate certain structures that are unrealizable by the progressive process that we just supposed. For example, they are the atomic models in which a certain number of electrons gravitate around the same circle while remaining at the summits of a regular polygon. Such a symmetric geometric figure must be formed all at once, but one cannot reasonably suppose that it comes about by the progressive addition of electrons.

One must distinguish the case of *degeneracy* in the adiabatic modifications. They are the motions for which several partial periods must be equal, so the trajectory will reduce to a closed curve. That is the case for the unperturbed Keplerian motion in the hydrogen atom. These degenerate cases are important in that they permit one go from one problem to another.

Therefore, in order to follow the deformation of a trajectory from the case of a magnetic field to the one in which an electric field exists, it will be convenient for us to observe the evolution of the motion by passing though the degenerate intermediate state for which neither of two perturbing fields exists.

Another consideration is often introduced for which a precise mathematical definition would be very desirable: It is the idea of "classes" of motions. Such a mechanical system can often take on very different motions according to the initial conditions. A weight that is suspended from a point O and defines a pendulum can turn indefinitely either by oscillating from one side of its rest position to the other or if it is launched with great vigor and describes a circle around its attachment point. One will find a limiting motion between these two classes of motion in which the weight is launched in such a manner that it will just attain the highest point of the circle, but that motion will last for an infinite time.

Similarly, for planetary motions, the elliptic or hyperbolic trajectories form two distinct classes with the parabolic motion as the limiting case. There again, an infinite duration will be necessary if one is to execute that limiting motion.

An adiabatic transformation will permit one to pass from a motion in one well-defined class to a series of other motions in the same class, but one can never reach a motion in a different class. At least, that is the hypothesis that one recovers very often in those subjects (Ehrenfest-Bohr). In order to make that point more precise, one will need a mathematically-precise definition of the "classes" of motion, but it does not seem that we do not presently possess anything satisfactory.

([1]) However, Bohr's argument is the following: The atom must be capable of being formed by taking only the nucleus, and he then replaced its various electrons one-by-one. The system would then pass through all of the successive stages. Once we have taken n electrons, our atom will have a structure that is very similar to that of the neutral atom of atomic number $N = n$. In particular, the once-ionized atom, which lacks only one electron, will be composed in a manner that is completely analogous to that of the neutral atom that precedes in it Mendele'ev's table, and includes just that number of electrons. One will then arrive at the continuity of the atomic structure all along the Mendele'ev series.

13. Attempts to generalize. – It will be very important to find how one can apply the quantum conditions to mechanical problems that are more complex than the ones that we have treated up to now. The method to follow is clearly derived from the preceding results. One must begin by looking for the adiabatic invariants and choosing the ones that reduce to the forms that we have indicated above in the simple cases. They are the invariants that one will set equal to an integer time the quantum h. That generalization is, without a doubt, very arduous, and we do not presently have the solution to it. Just the same, it seems that a large part of the results that relate to the quasi-periodic problems are capable of being extended to even more general cases, and that one can find adiabatic invariants in them, as well ([1]). Furthermore, these questions are closely related to Poincaré's integral invariants, which might permit one to find the right path to pursue.

From the physical viewpoint, it seems entirely certain that this generalization is possible. In spectroscopy, we see no difference between the problems that we have been able to treat completely and the ones that still elude us. In all cases, even the most complex ones, we observe sharp lines whose frequencies are defined very exactly. The classification of those lines always follows easily from Bohr's second rule. There again, we will find very well-determined discontinuous values for the total energy of the system. That mode of classification will always impose itself when one is dealing with the extremely-numerous lines of band spectra (viz., the Deslandres formulas) or the lines of X-rays and light for arbitrary atoms.

If there are energy levels then there will be preferred motions that must be determined from the quantum conditions. The methods of rational mechanics that we have applied already break down for the three-body problem; i.e., for the helium atom (N = 2). Now, we find sharp lines and energy levels in all atomic spectra up to the uranium atom (N = 92), which is nothing less than a 93-body problem!

One sees that some very difficult questions remain to be resolved. The considerable importance of the results that were obtained already shows that the path followed is extremely interesting. We have attempted to summarize the principal points and the collection of new doctrines in this presentation, and we have not hidden the very numerous imperfections in their present form.

One must find the general form of the link between electromagnetic phenomena and matter (viz., positive nuclei and electrons) from an angle that joins up with classical electromagnetism once more in the problems with numerous quanta and provides the necessary discontinuities in the atomic domain.

Many obscure points remain in the question of the structure of atoms. The distribution of electrons into successive layers and the laws of their quantized motions are yet to be specified.

Finally, the structure of the atomic nucleus itself and the laws of radioactive decomposition have not been given any interpretation up to now. We think that the nuclei are formed from hydrogen nuclei and electrons that are assembled according to the

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([1]) P. S. EPSTEIN, Zeit. Phys. **8** (1922), pp. 211 and 305.
This author followed a very different path from the one that we suggested. He utilized the calculus of variations and Delaunay's method. He proceeded by successive approximation by means of quasi-periodic motions. For each stage of approximation, he then wrote down the quantum conditions and arrived at a precise determination of the quantized motions for a general case whose scope was even more extensive than that of the problems of separated variables.

quantum laws. The primordial elements of matter would then reduce to the positive electron (i.e., the hydrogen nucleus) and the negative electron. That is presently a very reasonable hypothesis, but one whose physical bases are much less numerous. We hope that in the near future we might shed some new light on those problems that would permit us to penetrate even deeper into the mystery of atoms.